Review

Star-Shaped Conjugated Systems

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Abstract: The present review deals with the preparation and the properties of star-shaped conjugated compounds. Three, four or six conjugated arms are attached to cross-conjugated cores, which consist of single atoms (B, C+, N), benzene or azine rings or polycyclic ring systems, as for example triphenylene or tristriazolotriazine. Many of these shape-persistent [n]star compounds tend to π-stacking and self-organization, and exhibit interesting properties in materials science: Linear and non-linear optics, electrical conductivity, electroluminescence, formation of liquid crystalline phases, etc.

Keywords: [n]stars; conjugation; CC coupling; optoelectronics

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1. Introduction

Because of their interesting electrical, optical and optoelectronic properties, conjugated oligomers represent target compounds for many applications in materials science [1-18]. Moreover, they are model compounds for the corresponding polymers.

The conjugated oligomers can have linear, cyclic, star-shaped or dendritic structures (Figure 1). Apart from the repeat(ing) unit $R$, they can contain a core unit $C$ and end groups $E$.

The present article is focused on characteristic star-shaped systems $CA_m$, so-called [m]stars, in which $m$ identical arms $A=R,E$ ($m=3,4,6$) are attached to the central core $C$. Each arm $A$ has the same number $n$ of repeat units $R$, which can be assigned as generation $n$. Figure 2 summarizes the most important cores $C$ and arms $A$. Less regular structures, which do not have identical arms, are normally not considered here.

The cores guarantee a cross-conjugation. Even single atoms, such as sp$^2$-C, B or N (C-1 – C-3), can fulfill this precondition. More important are cores, which consist of benzene (C-4 – C-6), azine (C-7 – C-10) or borazine rings (C-11). The special arrangement of four conjugated arms on C-5 or C-10 is called a cruciform. Moreover, condensed ring systems, as for example triphenylenes (C-12),
hexaazatriphenylenes (C-13), triazatru xenes (C-14) or tristriazolotriazines (C-15) have to be considered. The arms A are constructed by simple (A-1 – A-3) or composed (A-4 – A-9) repeat units, which convey a linear conjugation. The selected building blocks C-1 – C-15 and A-1 – A-9 would lead to $15 \times 9 = 135$ star-shaped oligomer series $\text{C}_{\text{A}m}$. Many of them are still unknown – despite of intense efforts in this field in the previous two decades.

**Figure 1.** Structure types of conjugated oligomers.

- **Linear**: $E - R_n - E$
- **Cyclic**: $R_n$
- **Star-shaped**: $C - \left( R_n - E \right)_m$
- **Dendritic**: for example

$$\text{C}_{\text{A}m} \ (m = 3, 4, 6)$$

**Figure 2.** Selected building blocks of star-shaped conjugated oligomers $\text{C}_{\text{A}m}$ (cores C, arms A).

The synthetic approach to the star-shaped conjugated oligomers $\text{C}_{\text{A}m}$ comprises convergent and divergent strategies, protecting group techniques and orthogonal techniques-like in the other classes of conjugated oligomers [1-18]. Most important are catalyzed CC coupling reactions, such as Heck,
Sonogashira or Suzuki reactions. Condensation reactions for the generation of CC double bonds and oxidative couplings of terminal alkynes play also an important role in this context.

2. Molecular Architecture and Conjugation

An efficient π-conjugation requires a planar or almost planar geometry of the molecules. Figure 3 illustrates the planarity of carbenium centers C-1 and boranes C-2 in contrast to the pyramidal structure of tertiary amine centers C-3. The benzene rings of the arms A, which are attached to the cores C-1–C-3, are twisted by steric reasons. The corresponding dihedral angle φ is defined as the average angle between the planes of the three benzene rings and the plane, which is determined by the three marked (●) ipso-C atoms.

Triphenylborane can be taken as a model compound. According to its crystal structure analysis, the coplanar B-C bonds have an average length of 1.577 Å, their trigonal arrangement is characterized by bond angles of 120 ± 0.4° and the average torsion angle φ amounts to 30° [19]. This geometry guarantees the cross-conjugation by overlap of the pₓ (B) orbital and the π and π* orbitals of the three arms.

Triphenylmethylium cores C-1 have a corresponding molecular architecture, which was established for various triphenylmethane dyes [20].

The situation seems to be different for the amine cores C-3. However, the pyramidal structure of triarylamines differs only very slightly from the totally planar conformation, which represents the transition state of the N-inversion. Triphenylyamine as model compound has in the crystalline state a very small height h = 0.08 Å of the pyramide (Figure 3) [21]. A histogram of the h values of all triarylamine structures, listed in the Cambridge data file, reveals 0.00 ≤ h ≤ 0.18 Å with a mean value of 0.053 Å and median of 0.040 Å. The dihedral angles range from φ = 13 to 70° with a mean value of 40.8° and a median of 40.9° [22]. Thus, the cross-conjugation of oligomers with C-3 cores and A-3, A-7 or A-9 arms (Figure 2) seems to be guaranteed, which is particularly important for push-pull systems.

Figure 3. Molecular architecture of oligomers having C-1–C-3 cores and A-3, A-7 or A-9 arms. The numbers in the tertiary amine structure are related to the crystal structure analysis of tri-phenylyamine.

All other cores C-4–C-12 are planar rings or ring systems. Three, four or six attached benzene rings lead to twist angles φ, which represent a compromise between the maximum conjugation for φ = 0° and minimum steric interaction for φ = 90°. Other bond rotations in the arms A-1–A-9 have very low
energy barriers. The corresponding minima on the energy hypersurface are located in flat wells of planar conformations.

A critical question arises only for continued torsions along oligo(1,4-phenylene) [OP] arms A-3. Based on perturbation theory, the decrease of resonance can be described by \( \cos^2 \phi \) for each torsion angle \( \phi \) [23]. The resonance of an OP chain of \( n \) benzene rings has therefore the attenuation factor \((\cos^2 \phi)^n\). Thus, an average torsion angle \( \phi = 23^\circ \), which is characteristic for unsubstituted OP chains, reduces the resonance in a 1,4-sexiphenyl chain \( (n = 6) \) to 50\%. Moreover, an angle \( \phi = 55.7^\circ \) would implicate already for \( n = 3 \) a 90\% decrease of the resonance energy [24].

Detailed DFT studies on 1,4-phenylene-ethynylene and 1,4-phenylene-butadiynylene chains revealed that a sufficiently large \( \phi \) between two successive segments breaks the through-bond and through-space conjugation and yields weakly coupled chain segments as chromophoric units [25-27]. The corresponding function of the electronic coupling \( EC(\phi) \) has an inflection point whose value \( \phi \) can be used as cutoff angle for the conjugation. Due to the dilution of the wave function for increasing segment length, the cutoff angles decrease with increasing numbers \( n \) of repeat units. Thus, the effective conjugation length in the arm of a compound \( CA_m=C(R_nE)_m \) can be smaller than \( n \). In addition to this effect of statistical torsions, the conjugation of planar as well as non-planar arms shows a saturation phenomenon as any conjugated oligomer chain [14,28]. The effective conjugation length \( n_{ECL} \) defines the number of repeat units, whose exceeding does not lead to a further change of properties such as absorption, fluorescence, etc. [28]. The convergence effect is a consequence of different bond lengths and resonance integrals in the chain. Torsions along the chain accelerate this convergence, real kinks can stop the conjugation [14].

In “normal” series of conjugated oligomers, \( \lambda_{\text{max}}(n) \) of long-wavelength absorption or emission bands increases monotonously with increasing numbers \( n \) of repeat units and approaches to a limiting value \( \lambda_{\infty} \) [14,29]. The earlier used hyperbolic approximation, in which the excitation energy \( E \) is a function of the reciprocal number of repeat units \( n^{-1} \), does not sufficiently represent the saturation phenomenon. Some time ago, Meier et al. [28] suggested empirical exponential functions for the transition energy \( E(n) \), the \( \lambda \) \((n) \) values, and the effective conjugation length (Equations 1-3).

\[
E(n) = E_{\infty} + (E_1-E_{\infty}) \cdot a(n^{-1}) \quad (1)
\]
\[
\lambda(n) = \lambda_{\infty} - (\lambda_{\infty}-\lambda_1) \cdot e^{b(n^{-1})} \quad (2)
\]
\[
n_{ECL} = \ln (\lambda_{\infty}-\lambda_1) \cdot b^{-1} + 1 \quad (3)
\]

\( \lambda_1, E_1 \) : values of the monomer.
\( \lambda_{\infty}, E_{\infty} \) : values of the convergence limit; \( a, b \) : parameters optimized by the method of least squares.

Although 0→0 transitions should ideally be used for \( \lambda \), the \( \lambda_{\text{max}} \) values proved to be satisfactory in most cases. An example is shown in Figure 6.

Recently Gierschner et al. [30] and Bednarz, Bäuerle et al. [31] proposed semi- to non-empirical equations for the long-wavelength band of conjugated oligomers. The Bednarz algorithm is based on Frenkel exciton models. Its accuracy of interpolations is high; however, the prediction of \( \lambda_{\infty} \) and \( E_{\infty} \) by extrapolation can be problematic [17,32].

The optical band gap \( E(n) \) and its limiting value \( E_{\infty} \) is a very important feature for many applications of conjugated oligomers in materials science.
Due to their monodispersity and rigidity, star-shaped oligomers $\text{CA}_m$ have an exactly defined size and shape. Figure 4 demonstrates the situation for benzene cores $\text{C-4}$ with three arms $\text{A-6}$ or $\text{A-8}$. The radius $r$ of the discs can be calculated by equation (4) and the parameters $a$ and $b$ given in Figure 4 [14]. Accordingly the diameter of these discs increases from about 1.6 nm for the first generation ($n=1$) to about 5.6 nm for the fourth generation ($n=4$). Torsions of the benzene rings do not change the size of the nanoparticles.

**Figure 4.** Disc-like shape of [3]star compounds with a benzene core $\text{C-4}$ and $\text{A-6}$ or $\text{A-8}$ arms in 1,3,5-position. The diameter of the discs amounts to $d = 2n \cdot a + (2n+1)b$ for the $n$th generation.

![Diagram of disc-like shape](image)

$$r = n(a + b) + \frac{b}{2} \quad (4)$$

Neighboring olefinic double bonds, in the arms $\text{A-4}$–$\text{A-6}$ can have *cisoid* or *transoid* orientations, which have virtually the same energy content. Solely in $\text{A-1}$, the energy of the *transoid* conformations is significantly lower.

Thus, a variety of conformers is present in systems, which have *trans* configured olefinic double bonds in their repeat units. Table 1 summarizes the number of *transoid/cisoid* conformers. All these conformers contribute for example to the UV/Vis absorption. However, the NMR spectra contain only one set of signals because the equilibration of the conformers is fast in terms of the NMR time scale.

**Table 1.** Number of rotamers in [3]star compounds with different symmetry and arms, which contain repeat units with *trans* configured olefinic double bonds.

| Generation | Core Symmetry | $D_{3h}$ $C_{2v}$ $C_s$ |
|------------|---------------|--------------------------|
| 1          |               | 2 4 8                    |
| 2          |               | 12 32 64                 |
| 3          |               | 88 256 512               |
| 4          |               | 696 512 1024             |
The number of conformers amounts to $2^{3n}$ in the $C_s$ and to $2^{3n-1}$ in the $C_{2v}$ case. Cores with $D_{3h}$ symmetry (for example 1,3,5-trisubstituted benzenes or 2,4,6-trisubstituted 1,3,5-triazines) lead to a number $Z(n)$ of conformers, which can be calculated by the recursive formula of equation 5.

$$Z(n) = 2^3 [Z(n-1)-1]$$

$$n = 2, 3, 4, \ldots Z(2) = 12$$

3. Three-Arm Systems with One Central Atom

3.1. [3]Star Systems with Methylonium Core

Triphenylmethane dyes, which should be better called triphenylmethine dyes [37], are an important class of organic dyes. The extension of the conjugation in their arms can lead to NIR dyes. Figure 5 shows such [3]star compounds. The methylonium salts 1-3 can be prepared from the corresponding carbinols, their ethers or esters. A reasonable stability can only be expected for push-pull systems with electron donating end groups E.

**Figure 5.** Triphenylmethylium structures with extended conjugation.

Several compounds 1 ($n = 2$, $R = H$, alkoxy, dialkylamino) [33-35], 2 ($n = 1$, $R = H$, alkoxy, dialkylamino) [36-40] and 3 ($n = 1$, $R = H$) [36] are known. The effect of cross-conjugation in the center can be characterized by comparison of the UV/Vis spectra with those of related systems, which have only one or two extended arms [36].

A detailed study of the conjugation effect in 2 with extended arms ($n = 1-4$) was made by Meier *et al.* [41,42]. The carbinols 6a-d were prepared by Wittig-Horner reactions of the triphosphonate 4 and the aldehydes 5a-d and spontaneous autoxidation at the central carbon atom. Treatment of 6a-d with CF$_3$COOH yielded the methylonium salts 2a-d (Scheme 1).

The increasing length of the arms in 2a-d results in an increasing bathochromic shift of the absorption from the Vis into the NIR region. According to equation 2, a convergence limit of $\lambda_{\infty} = 879 \text{ nm}$ was calculated (Figure 6).
Scheme 1. Preparation of methylium salts 2a-d with three oligo(1,4-phenylene-vinylene) [OPV] arms.

\[
\begin{align*}
\text{PO(OCH}_3\text{)}_2 & \quad \text{HC} \\
\text{PO(OCH}_3\text{)}_2 & \quad \text{PO(OCH}_3\text{)}_2 \\
\text{HC} & \quad \text{PO(OCH}_3\text{)}_2 \\
\end{align*}
\]

\[
R = \text{OC}_6\text{H}_{13}
\]

\[
\begin{align*}
R & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\end{align*}
\]

\[
\text{F}_3\text{C} \quad \text{O} \\
\text{O} \quad \text{F}_3\text{C}
\]

Figure 6. Maxima of the long wavelength absorption of the carbinols 6a-d (□, measured in CHCl$_3$) and their salts 2a-d (■, measured in CHCl$_3$/CF$_3$CO$_2$H, 7:3) [41].

\[
\begin{align*}
\lambda_\text{max} & = 879 \text{ nm} \\
\lambda_\text{max} & = 415 \text{ nm}
\end{align*}
\]

The delocalization of the positive charge in 2a-d can be registered by down-field shifts $\Delta\delta$ of the $^{13}$C NMR signals. A comparison of 2a-d with 6a-d reveals, that the central carbon atom has a $\Delta\delta$ value
of about $109.9 \pm 1.1$, whereas the carbon atoms b, d and f (Scheme 1) are shifted by $12.5 \pm 0.4$, $14.2 \pm 0.5$ and $9.1 \pm 1.1$ ppm, respectively [41].

When dialkylamino groups, such as the solubilizing bis(2-hexyloctyl)amino group, are attached in $p$-position of the terminal benzene rings, the situation is more complex (Scheme 2) [42]. The lowest generation $7a$ ($n = 1$) forms first by $O$-protonation and elimination of water the corresponding methylium salt $7'a$ before the successive three-fold $N$-protonation to $7''''a$ occurs. The higher members $7b,c$ ($n = 2, 3$) are first $N$-protonated to the carbinols $7''''b,c$ before the methylium ions $7''''b,c$ are generated. The methylium ion $7'a$ is a star-shaped push-pull system with an absorption, which reaches far into the NIR region ($\lambda_{\text{max}} = 1100$ nm). Its extended conjugation causes such an enormous bathochromic shift in comparison to tris(4-dimethylaminophenyl)methylium ions (Crystal Violet: $\lambda_{\text{max}} = 590$ nm). The push-pull effect disappears as soon as (threefold) $N$-protonation occurs. The tetracations $7''''a-c$ have absorption maxima in the visible region ($\lambda_{\text{max}} = 622, 740$ and $790$ nm, respectively). They represent a bathochromic oligomer series with a convergence limit of $\lambda_{\infty} = 827$ nm. Figure 7 demonstrates the generation-dependent protonation behavior by the different red- and blue-shifts in the absorption spectra.

Apart from the application as NIR dyes, the methylium salts promise interesting nonlinear optical (NLO) and two-photon absorption (TPA) properties.

**Scheme 2.** Generation-dependent protonation of the carbinols $7a-d$ with trifluoroacetic acid.
Figure 7. (a) UV/Vis/NIR absorption of 7a in CHCl₃, with 7'a as the major component obtained by primary protonation and 7''''a obtained as the major component in the final protonation (CHCl₃/CF₃COOH). (b) UV/Vis/NIR absorption of 7c in CHCl₃, N-protonated carbinol 7''''c, and methylium salt 7'''c as major component after the final protonation with CF₃COOH (molar ratio 7c/CF₃COOH, 1:200) [42].

3.2. [3]Star Systems with Boron Core

Planar trigonal boron centers seem to be ideal cores for [3]star oligomers, since the empty pₓ orbital of the boron atom guarantees an efficient conjugation. This is particularly valid for the pₓ-π* interaction in the LUMO. The resulting low-lying LUMOs cause low reduction potentials and favor therefore n-doping and good electron-transporting properties. Moreover, the electropositive character of B should enable an intramolecular charge transfer from electron-rich π-conjugated arms to the center. However, the high sensitivity of boranes toward air and water is normally a big disadvantage for their application. Yamaguchi, Tamao et al. [43] overcame this problem by the introduction of durenylene groups, which provoke a kinetic stabilization by steric shielding of the reactive B center. The compounds 10a-e were obtained by Sonogashira-Hagihara reactions (Scheme 3).

The crystal structure analysis [43] of 10a proved a trigonal planar boron center. The duryl groups are arranged in a propeller-like fashion. Their planes and the central boron plane form dihedral angles of 53-55°. The long wavelength absorption maxima (Scheme 3) are red-shifted by the extension of conjugation. The dimethylamino substituted compound 10d exhibits a strong push-pull effect with a significant solvatochromism of the fluorescence band. The blue emission color (λ_max = 457 nm) in
benzene changes to green ($\lambda_{\text{max}} = 512$ nm) in THF, and to orange ($\lambda_{\text{max}} = 530$ nm) in DMF (Figure 8). The fluorescence quantum yields of 10a-e in THF range between $\phi_F = 0.16$ and $0.54$ [43].

**Scheme 3.** Preparation of the triarylboranes (10a-e) with extended conjugation. Absorption maxima in THF.

**Figure 8.** Fluorescence of 10d: (a) The emission spectra in various solvents (benzene, blue line; THF, green line; DMF, orange line) and (b) a picture of the solutions under irradiation of light at 365 nm. The spectrum in DMF is magnified 10× in intensity [43]. (Copyright 2000, reprinted with permission of Org. Lett.).
Wang et al. [44] prepared boranes with 1,4-phenylene repeat units and 2,2′-dipyridylamino end groups, which served for the chelation of metal ions, such as Zn$^{2+}$ (Scheme 4). The final step consisted of a Pd catalyzed Suzuki-Miyaura coupling reaction.

Scheme 4. Preparation of the boranes 13a,b by Suzuki-Miyaura couplings.

According to the crystal structure analysis of 13b, the dihedral angle between the inner and the adjacent benzene rings amounts to 74-75°, whereas the dihedral angle between the outer and the middle benzene rings amounts to 38°. The crystals contain pairs of enantiomers, which interconvert rapidly in solution.

In contrast to the absorption bands, the emission bands are solvent dependent and exhibit a remarkably positive solvatochromism. In addition to the blue fluorescence, the compounds 13a,b show in frozen solution (CH$_2$Cl$_2$, 77 K) low-energy phosphorescence emissions ($\lambda_{\text{max}} = 480$ nm and 506 nm, respectively). The triplet lifetimes of 13a,b amount to 9-10 $\mu$s. When 13a is complexed with ZnCl$_2$, the fluorescence emission in THF is shifted from $\lambda_{\text{max}} = 427$ to 458 nm. This provides new opportunities for applications, such as fluorescent sensors for metal ions and metal ion containing nonlinear optical materials [44].

Related borates with (1-naphthyl)phenylamino end groups were used as hole transport or hole injection materials in OLEDs [45].

3.3. [3]Star Compounds with Nitrogen Core

Goodson et al. [46] investigated push-pull systems with a nitrogen core and 4-pyridyl end groups. Scheme 5 shows the preparation of the compounds 16a,b (with phenylene-ethenylene repeat units) by applying Heck reactions and 18a,b (with phenylene-ethynylene repeat units) by applying Sonogashira-Hagihara reactions.
Scheme 5. Preparation of tertiary amines having extended conjugation.

Electron excitation of 16a,b and 18a,b leads to intramolecular charge transfer (ICT) states. Increasing conjugation in the three arms shifts the absorption and the fluorescence band to longer wavelengths and increases the two-photon absorption cross-sections. Since trans-configured olefinic double bonds have a greater effect than triple bonds, the maximum cross-section (δ = 1937 GM) is reached for 16b. The two-photon absorption (TPA) of 16b was already studied earlier and 16b was used as initiator for two-photon polymerization reactions at 830 nm [47].

The related compound 21 was obtained by a Wittig-Horner reaction [48] (Scheme 6) [49].

Scheme 6. Preparation of tertiary amine 21 with extended conjugation by applying Wittig-Horner reactions.
Dissolved in toluene, compound 21 exhibits a one-photon absorption with a long-wavelength maximum at $\lambda = 495$ nm and a one-photon emission maximum at 536 nm. The fluorescence quantum yield amounts to 67%. The system has a very high two-photon absorptivity, which amounts to $5030 \times 10^{-50}$ cm$^4$ s photon$^{-1}$ (GM) at 840 nm [49]. Related compounds N(OPV)$_3$ with cyano groups as end groups or as substituents on the olefinic double bonds were studied by Jeon, Cho et al. [50].

Various applications of TPA – such as 3D optical data storage, two-photon laser scanning microscopy, photodynamic therapy, etc. – enhanced strongly the demand on new materials with high TPA cross-sections.

Blanchard-Desce et al. [51,52] developed two-photon excited fluorescence (TPEF) probes 22a-c, which work in the red-NIR region. Triflate or nonaflate groups served as strong electron-withdrawing end groups. The final step in the preparation of 22a-c consisted of a Heck coupling of tris(4-vinyl-phenyl)amine with the corresponding halogenarenes [51] (Figure 9).

**Figure 9.** Tertiary amines N(OPV)$_3$ with electron-withdrawing SO$_2$CF$_3$ or SO$_2$C$_4$F$_9$ end groups.

|   | 22a | 22b | 22c |
|---|-----|-----|-----|
| $n$ | 1   | 2   | 1   |
| E | SO$_2$CF$_3$ | SO$_2$CF$_3$ | SO$_2$(CF$_2$)$_3$CF$_3$ |
| A: $\lambda_{\text{max}}$ (nm) | 430 | 435 | 440 |
| F: $\lambda_{\text{max}}$ (nm) | 494 | 499 | 517 |
| $\phi_F$ [%] | 71 | 77 | 84 |
| TPA: $\lambda_{\text{max}}$ (nm) | 740 | 755 | 800 |
| $\sigma_{\text{max}}$ (TPA) [GM] | 1340 | 1430 | 2070 |

1 GM = $10^{-50}$ cm$^4$ s photon$^{-1}$

In agreement with time-dependent density functional theory [52], the octupolar fluorophores have an absorbing ground state, which can be understood in terms of Frenkel exciton states, which are delocalized over the three arms, whereas the emitting state is localized on a single arm. The powerful electron-withdrawing end groups provoke a strong dipolar character of the emitting arm, which is expressed by a strong solvatochromic effect [51,52].

In the series of tertiary amines with three OP chains, many phenyl systems (23a, $n = 1$), but few biphenyl (23b, $n = 2$) and $p$-terphenyl systems (23c, $n = 3$) were reported. All these compounds can be used as hole-transporting materials (Scheme 7).
Kim et al. [53] prepared 23b (n = 2) with trifluorethenyloxy end groups and subjected it to a thermal cyclopolymerization. The obtained cross-linked polymer 23b is thermally and electrochemically stable, solvent resistant, and has a high transparency and a good surface smoothness. A fabricated light emitting diode (PLED) with the configuration ITO/23b (30 nm)/ PFO (70 nm)/Ba (15 nm)/ Al (130 nm) had good values for the luminance ($L_{\text{max}} = 1500 \text{ cd m}^{-2}$) and the luminance efficiency ($LE_{\text{max}} = 0.132 \text{ cd A}^{-1}$, but its turn-on voltage of 7 V is relatively high [53].

A further advantage of such materials in LEDs is due to their emission in the blue or blue-violet spectral range [54-56].

4. Star Compounds with a Benzene Core

4.1. Three-armed Stars (C-4)

4.1.1. Structure and Conjugation

Figure 10 displays the different reported types of parent conjugated three-armed star scaffolds; C-4-A-3 (24), C-4-A-6 (25), C-4-A-8 (26), C-4-A-7 (27), C-4-A-9 (28) and C-4-A-1 (29). The molecular structure of 1,3,5-triarylbenzene 24 is determined by the steric interaction between ortho hydrogens of the peripheral ring and the hydrogens of the central benzene. Therefore, such molecules are found to be propeller-shaped, with dihedral angles between 7-49°, depending on the substitution and the packing in the crystal structure [57-59]. In contrast, 1,3,5-trisstyrylbenzenes 25 lack such steric interactions and can consequently arrange in a more planar molecular structure in the crystal of the 1,3,5-tris-(3,4,5-trimethoxyphenylethenyl)benzene 25b [60]. Interestingly, 1,3,5-tris(phenylethynyl)benzenes 26 realize various torsional angles between central and peripheral benzene planes ranging from 0 to 80° in their crystal structures, despite the lack of intramolecular steric interactions [61]. Structures 25 and 26 can establish planar conformations and therefore it can be supposed that the conjugation to the central ring is larger compared with 24.
Indeed the large difference between absorption and emission spectra of triphenylbenzene 24a and the stilbene 25a and tolane 26a derivatives point already to the reduced conjugation with the central benzene unit in 24a (Table 2). A more evident sign of the almost missing conjugation may be revealed by the tolane derivative 28a, with a very small increase in the absorption maximum by only 8 nm compared with the 1,3,5-tris(phenylethynyl)benzene 26a. Studies of the linear molecules at 77 K point to a larger bathochromic shift of 23 nm when comparable vibrational bands are considered [66], however, this value is still smaller than that expected for the addition of a phenyl group to oligophenylenes (cp. compounds 24b,c). A second important feature of 1,3,5-trisubstituted benzenes with conjugated arms is their meta substitution pattern. Meta substitution is known to prevent the conjugation between the individual arms of the star-molecules in their ground state. This is evidenced by the only slightly different absorption maxima compared to the linear derivatives and the threefold higher extinction coefficient (Table 2). Thus, the star-shaped chromophores can be considered as supermolecules consisting of three almost independent arm chromophores including the central ring. Yamaguchi et al. argued recently that the bathochromic shift from the absorption maxima of the linear to the branched molecule 26d would clearly show an increase in conjugation across the central ring. Similar effects can be observed for all chromophores in Table 2. However, such a bathochromic shift can be as well explained by the inductive effect of the additional two conjugated groups at the central benzene ring. Even a single missing methoxy group at the periphery of the arms of molecules 26e-g give rise to a hypsochromic shift of more than 20 nm compared with 26b-d.
Table 2. Photophysical properties of star-shaped conjugated molecules with a 1,3,5-trissubstituted benzene core.

| Compound<sup>a</sup> | Substituents E, R | Solvent, T (K) | Absorption $\lambda_{\text{max}}$ [nm] ($\epsilon$ [L cm$^{-1}$ mol$^{-1}$]) | Emission $\lambda_{\text{em}}$ [nm] (Quantum yield $\Phi$) | Reference |
|----------------------|------------------|----------------|-------------------------------------------------|-------------------------------------------------|----------|
| 24a                  | star             | H (dioxane)    | 250 (59,600) | 354 (0.10) | [62]      |
|                      | linear           | H (dioxane)    | 246 (18,600) | 316 (0.18) | [62]      |
| 25a                  | star             | tristyryl (hexane, 293 K) | 317 (47,863) | 410 | [63] [64] |
|                      | linear           | H (methylpentanes, 295 K) EPA,<sup>c</sup> 77 K | 294 (26,000) | 347 | [65] |
|                      |                  |                | 303 (51,500) | 343 | [66] |
| 26a                  | star             | H CHCl$_3$, 295 K | 305 (85,100) | 353 (0.15) | [67]      |
|                      | linear           | H CHCl$_3$ EPA,<sup>c</sup> 77 K | 300 (24,000) | — | [66] |
|                      |                  |                | 284 (42,900) | 302 (44,500) | 326 | [66] |
| 27a                  | star             | H DMF          | 337 (142,000) | — | [70]      |
|                      | linear           | H DMF          | 328 (45,200) | — | [70] |
| 28a                  | star             | H acetonitril  | 308 (158,000) | 365 (0.92) | [68]      |
|                      | linear           | H EPA,<sup>c</sup> 77 K | 307 (55,000) | 352 | [66] |
|                      |                  |                | 325 (51,400) | — | [66] |
| 24b<sup>b</sup>      | n = 2            | H dioxane      | 288 (103,000) | 364 (0.27) | [62]      |
|                      |                  |                | 276 (30,200) | 342 (0.55) | [62] |
| 24c<sup>b</sup>      | n = 3            | H dioxane      | 307 (136,000) | 375 (0.71) | [62]      |
|                      |                  |                | 294 (48,600) | 369 (0.71) | [62] |
| 25c<sup>b</sup>      | n = 0            | Trisdodecyloxy-phenylethenyl CHCl$_3$, rt | 331 (81,000) | 426<sup>b</sup> | [69] |
| 25d<sup>b</sup>      | n = 1            | Trisdodecyloxy-phenylethenyl CHCl$_3$, rt | 376 (170,000) | 447<sup>b</sup> | [69] |
### Table 2. Cont.

| Compound<sup>a</sup> | Substituents E, R | Solvent, T (K) | Absorption $\lambda_{\text{max}}$ [nm] ($c$ [Lcm$^{-1}$mol$^{-1}$]) | Emission $\lambda_{\text{max}}$ [nm] | Quantum yield $\Phi$ | Reference |
|----------------------|------------------|----------------|---------------------------------|---------------------------------|----------------|------------|
| linear               | Trisdodecyloxy-phenylethenyl, R = Methyl |                  | 366 (64,000) |                  |                  | [70]       |
| 25e<sup>c</sup><br>n = 2 | star Trisdodecyloxy-phenylethenyl CHCl<sub>3</sub>, rt | | 397 (313,000) | - |                  | [69]       |
| linear               | Trisdodecyloxy-phenylethenyl, R = CH$_2$OH CH$_2$Cl$_2$, 298 K | | 390 (67,000) | 468 nm |                  | [71]       |
| 26b<sup>c</sup><br>n = 1 | star H, OCH$_3$ CHCl$_3$, 295 K | | 334 (64,600) | 384 (0.46) |                  | [67]       |
| 26c<sup>c</sup><br>n = 2 | star H, OCH$_3$ CHCl$_3$, 295 K | | 380 (128,800) | 409 (0.85) |                  | [67]       |
| 26d<sup>c</sup><br>n = 3 | star H, OCH$_3$ CHCl$_3$, 295 K | | 426 (195,000) | 464 (0.98) |                  | [67]       |
| linear               | H, OCH$_3$ CHCl$_3$, 295 K | | 390 (56,200) | 430 (0.81) |                  | [67]       |
| 26e<sup>c</sup><br>n = 0 | star 2-methoxyphenylethynyl, OCH$_3$ CHCl$_3$, 295 K | | 314 (58,900) | 359 (0.24) |                  | [67]       |
| 26f<sup>c</sup><br>n = 1 | star 2-methoxyphenylethynyl, OCH$_3$ CHCl$_3$, 295 K | | 377 (104,700) | 406 (0.83) |                  | [67]       |
| 26g<sup>c</sup><br>n = 2 | star 2-methoxyphenylethynyl, OCH$_3$ CHCl$_3$, 295 K | | 405 (128,800) | 433 (0.97) |                  | [67]       |
| 29a<sup>c</sup><br>n = 1 | star 3,4-dibutoxyphenyl | | 340 |                  |                  | [72]       |
| linear               | 3,4-dibutoxyphenyl | | 325 |                  |                  | [72]       |
| 29b<sup>c</sup><br>n = 2 | star 3,4-dibutoxyphenyl | | 360 |                  |                  | [72]       |
| linear               | 3,4-dibutoxyphenyl | | 350 |                  |                  | [72]       |
| 29c<sup>c</sup><br>n = 3 | star 3,4-dibutoxyphenyl | | 380 |                  |                  | [72]       |
| linear               | 3,4-dibutoxyphenyl | | 375 |                  |                  | [72]       |

<sup>a</sup> star refers to the star-shaped molecules as shown in Figure 10; linear refers to the red substructures highlighted in Figure 10, without the additional arms. <sup>b</sup> in CH$_2$Cl$_2$<sup>c</sup> EPA solvent mixture (diethylether:isopentane:ethanol = 5:5:2).
Nevertheless, there is an influence of the 1,3,5-trisubstitution to photophysics and photochemistry. For the tristyrylbenzene derivative 25a, a forbidden transition from the ground state $S_0$ to the excited state $S_1$ has been discovered, which results in a very long average fluorescence lifetime $\tau$ in the nanosecond range of up to 43.6 ns [64]. The latter is two orders of magnitude larger than that of the linear chromophore stilbene and depends on the solvent, temperature, substitution pattern and the conformers. The latter can be monitored for 25a in hexane at 50 K, for which the fluorescence decay can only be fitted with two different values $\tau$ (43.6 ns, 16.4 ns). This long lifetime allows for the formation of dimers (cyclophanes) even at very low concentration [63,73,74].

The influence of the central core appears to decrease the fluorescence quantum yield of almost all small stars compared to their linear counter parts. This influence becomes negligible with increasing size of the arms (Table 2, 26a-g).

The lacking conjugation across the central benzene core is also demonstrated for OPV and oligoethenylene stars, end-capped with redox active ferrocene [75] or with tetrathiafulvalene derivatives [76]. These groups are oxidized at one single potential, thus the oxidized, conjugated species disclose no visible influence on the oxidation of the other groups. Theoretically, Fukutome et al. proposed the 1,3,5-trisubstituted benzene derivative as ferromagnetic coupling unit for polaronic high spin compounds [77]. Dougherty et al. could indeed confirm a high-spin system for a doped polymer consisting of oligoenes 1,3-meta substituted to benzene centers [78]. However, studies of stilbenoid star derivatives such as 25d (cp. Table 3, n = 2) revealed that although the first oxidation or reduction produces a paramagnetic radical anion or cation (polaron) the second reduction or oxidation step results always in a diamagnetic dianion [69,79]. Obviously, a diamagnetic bipolaron is always more stable within a stilbene scaffold 25 than two polarons in the triplet state. Ferromagnetic coupling might be more successful in compounds like 27 in which the conjugation to the centre is prevented. This has been demonstrated for a two-arm derivative exhibiting a triplet state for the double charged compound [80].

4.1.2. Synthesis

Stars with oligophenylene arms A-3 can be prepared by an acid catalyzed cyclization of acetophenones 30 (Scheme 8) [58,81]. Functional groups such as Br, CHO, CH$_3$ or phosphonate CH$_2$PO(OH)$_2$ allow a further conversion. For example, Suzuki-Miyaura reaction of 1,3,5-tris(4-iodophenyl)benzene with boronic acid substituted oligophenylene building blocks result in the elongation of the scaffold [82]. Wittig-Horner reaction of aldehyde 24f with phosphonate 31 or phosphonate 24h with aldehydes 32 afforded stars with OPV arms and a 1,3,5-triphenylbenzene core 27 [83]. Hagihara-Sonogashira reaction with terminal alkynes 33 produced compounds 28 [58,84,85].
Scheme 8. Preparation of three-arm oligophenylene stars 24 with a benzene core and the related oligo(phenylenevinylene) and oligo(phenylene ethynylene) stars 27, 28 based on a triphenylbenzene core.

Scheme 9. Synthesis of stars 25 with OPV and 26 with oligo(phenylene ethynylene) (OPE) arms.
Stilbene stars with arms A-6 can be prepared by Heck-, Wittig-, Wittig-Horner-, Siegrist-, McMurry- reaction [86] or by the Stille coupling [87]. Commonly the convergent synthesis, coupling the arms with terminal aldehydes to a phosphonate core 34 (Wittig-Horner) afford the materials in excellent yields (Scheme 9) [69,88,89]. Another synthetic route applied a double stage strategy. First, core 34 was elongated in a divergent step using the THP ether 36 and subsequently converted to the phosphonate 37. In a final convergent step, the three-fold Wittig-Horner reaction affords the target compounds 25 of higher generation. The Hagihara-Sonogashira palladium catalyzed cross-coupling is the most commonly used reaction to assemble three arms with terminal acetylenes 39 in a convergent step to 1,3,5-triiodo- or tribromobenzene 38 to obtain stars 26 with oligo(phenylene ethynylene) arms (A-8) [58,67,90].

Scheme 10. Synthetic routes to stars 29 with oligoethenylene arms. TTF 4',5'-bisdodecylsulfanyltetrathiafulvalene-4-yl; Te thiophencarboxylate.

![Chemical structure](image)

The synthesis of stars with oligoethenylene arms (A-1) is similar to the one of stilbene derivatives since a threefold Wittig or Wittig-Horner coupling reaction of the oligo(ethenylene)aldehyde-arms 41 with the CH-acidic component 40 delivers the target compounds (Scheme 10) [91-93]. Alternatively, the Stille-coupling of 43 with 44 was applied to obtain compounds 29. A divergent three-step synthesis using butadienoltrimethylsilyl ether 46 as a key reagent afforded the target compounds in good yields with terminal aldehyde functions 29g (E = CHO). Acetalization of the aldehydes and repetition of the reaction sequence yielded the elongated compound with four ethenylene groups 29h. The synthesis of
the oligoethynylene stars with arms of type A-2 is somewhat more sophisticated (Scheme 11). Starting from 1,3,5-trisethynylbenzene 42 a star with an uneven number of ethynyl groups can be obtained by a five step synthesis via compound 47 using the Fritsch-Buttenberg-Wiechell rearrangement as final key step to obtain target molecule 48a [94,95]. A star-shaped diethynylbenzene derivative 48b can be prepared in a one step synthesis by the Cadiot-Chodkiewcz reaction [96] converting either the 1,3,5-trisethynylbenzene with a bromoethyne derivative under basic conditions with a copper(I) salt (Scheme 11) [85] or a copper acetylide with a tris(bromoethynyl)benzene [97].

Scheme 11. Preparation of stars with oligoethynylene arms.

Figure 11. Enyne and ynene stars with a benzene core.
Parent stars with enynes (A-4) or ynenes (A-5) arms are not known. In one case the acidic treatment of an iridacyclopentadiene complex with tris(ethynyl)benzene afforded the vinyl substituted parent enyne 50 (Figure 11) [98]. Cross-conjugated enynes 47 are precursors in the synthesis of oligoynes (Scheme 11) [94,95]. Different cross-conjugated enynes with donor and acceptor groups have been also obtained by a tandem reaction sequence including cycloaddition of tetracyanoethylene to an electron rich triple bond and a subsequent retroelectrocyclization to yield 51. In the series of ynenes only a branched star 52 is known, obtained by a six-fold Sonogashira-coupling of the acetylene component to tris(2,2-dibromovinyl)benzene [99].

4.1.3. Three-arm Stars with Benzene Centers and Materials Science

1,3,5-Triphenylbenzene Derivatives (C-4-A-3): In many star molecules the oligophenylene scaffold were only used as a rigid spacer, because of the limited conjugation along the arms and across the centre [100,101]. For example carboxylate substituted derivatives 24i (E = COO-, n = 2) were applied to produce metal-organic frameworks (MOF’s) [102], star scaffolds with peripheral metal complexes were investigated with respect to their intramolecular energy transfer [103,104] and stars with peripheral amino acid substituents as biological active materials were synthesized [105]. The parent structures 24a-c were studied with respect to their potential as laser dyes [62]. The performance of the stars were inferior compared to linear derivatives, however, their potential usage as scintillators have been emphasized. In a further study, oligophenylene (n = 2) stars with acceptor substituents (E = F, CN) have been successfully applied as hole-blocking materials in LED devices based on fluorene/carbazole copolymers with a deep blue emission [106].

1,3,5-Tris(ethenylphenyl)benzene Derivatives (C4-A-7): Burn and Samuel et al. investigated the potential of compound 27h (E = 2-(3,5-(di-tert-butyl)phenyl)ethenyl) for LED applications [107]. This molecule possesses a high tendency to aggregate and consequently produced a broad emission spectrum. The fabricated LED device, however, was not stable. Brunel et al. studied a series of molecules 27b-g (see Scheme 8) with donor or acceptor substituents E [83,108]. They observed a strong solvatochromic effect upon increasing the solvent polarity which revealed a multidimensional intramolecular charge transfer (MICT) between the core and the periphery, increasing with increasing size and the type of substituents. The very large first order hyperpolarisability $\beta(0)$ of up to $510 \times 10^{-30}$ esu (compound 27g) was also attributed to MICT. The latter together with the high transparency in the visible range make these materials highly interesting for NLO applications.

1,3,5-Tris(ethynylphenyl)benzene Derivatives (C-4-A-9): 1,3,5-Tris(4-ethynylphenyl)benzene derivatives are mainly applied as synthetic precursors, templates or building blocks owing to their rigid or branched framework. Thus they were used as precursors for the synthesis of carbonanoparticles [109], precursors for the preparation of phenylquinoxazoline electron transport materials [90], successfully applied as templates for the synthesis of macrocycles [84], as building block for the self-assembly to MOFs [85] and as components for thermosets [110]. However, the very high fluorescence quantum yield of 0.92 for the parent structure 28a makes such molecules highly attractive for LED applications [68].
1,3,5-Trisoligo(phenylene ethenylene)benzene Derivatives (C-4-A-6): A series of 1,3,5-tris(oligo-(phenylenevinylene)benzenes with peripheral 3,4,5-trisalkoxyphenyl and internal 2,5-bisalkoxyloxyphenyl groups has been prepared to study mesomorphic properties and photochemistry in liquid crystal phases [69,88,89,111-113]. Table 3 presents the thermotropic properties of the mesogens. Only molecules with long hexyloxy or dodecyloxy side chains reveal lamellar and columnar liquid crystal phases, driven by nanosegregation of aliphatic chains and conjugated scaffold. In the hexagonal columnar phases the column diameters are in accordance with the molecular diameters of the star-shaped mesogens. This is interesting since the empty space between the arms must be filled in the condensed phase [18]. As a consequence, two or more mesogens must stack in a columnar unit with a height of about 4 Å without change of the star conformation. A preliminary model shows that nevertheless the relatively rigid oligo(phenylenevinylene) scaffold can accommodate in a structure with an appropriate density, by slight folding and with only few distances which are smaller than the sum of the van der Waals radii [114]. An unusual mesogen design was realized in nematogens 25i-m [112,113]. The aliphatic chains are incorporated in the internal structure of the stilben compounds. Rather shape anisotropy than nanosegregation dominates the mesomorphic behavior, resulting only nematic mesophases.

The photochemistry of peripheral substituted mesogens 25b-h was studied in thin spin coated films and showed that in the glassy or liquid crystal phase almost all double bonds were consumed. A comprehensive study in liquid crystal cells revealed that in contrast to the photochemistry of 1,3,5-trisstyrylbenzenes in solution, the polymerization reaction of long lived radicals is the dominating reaction path resulting in polymethine structures [115]. Irradiation in the crystal did not result in a photoreaction; only the mobility of the molecules in the LC phase allows the close approach of the olefinic reaction centers [115]. Such photoreactions alter the mesomorphic properties and thus can be applied as imaging technique [74]. Highly interesting supramolecular properties of an amphiphilic trisstyrylbenzene derivative 25n have been shown in water solution. The critical micelle concentration amounts to 3.17 mgL⁻¹. The lower critical solution temperature (LCST) is 32.2 °C at a concentration of 15.5 mM. Above the latter temperature the solution becomes turbid due to micelle formation, whereas at lower temperature the solution is optically isotropic. The stimuli responsive material reveals also consistent changes of the absorption and emission spectra upon micelle formation [116].

Alkylsulfanyl end-capped OPV stars have been prepared as candidates for elements in future nanocircuits [117]. Materials with peripheral ferrocene groups show no significant interaction of the metal centers upon oxidation, as it would be expected for the meta substitution at the core [75]. Donor-acceptor substituted star-shaped OPVs 25 o-r, which are octupolar molecules, are highly attractive as NLO materials in the crystalline solid (Figure 13). The first hyperpolarizbilities β of the star molecules are superior over the values of their linear counterparts. The stilbenoid stars show larger values compared to the related tolane systems discussed in the next section, however, the maximum value of β(0) = 89 × 10⁻³⁰ esu for 25q is smaller than that of OPV compound 27g, were the conjugation to the benzene core is limited [118].
Table 3. Thermotropic properties of stilbenoid stars.

![Chemical structures of stilbenoid stars]

| Compound | Thermotropic behavior (T [°C] / ΔH [kJ/mol])a | Ref. |
|----------|--------------------------------------------|------|
| 25b (n = 1) | Cr 38/39 Colh 75/10 I | [88,111] |
| 25c (n = 2) | g 21 (Tg) Colh 108/4 I | [89] |
| 25d (n = 3) | g 55 (Tg) Colh 199/3 I | [69] |
| 25e (n = 1) | g -15 (Tg) Colh 74/4 I | [111] |
| 25f (n = 2) | g 21 (Tg) L 129/3 I | [89] |
| 25g (n = 1) | Cr 189/45 I | [111] |
| 25h (n = 2) | Cr 216/40 I | [89] |
| 25i (n = 1) | g 140 (Tg) N 260 1b | [113] |
| 25j (n = 2) | g 246 (Tg) N 296 1b | [113] |
| 25k (n = 1) | Cr 209/40 N 232/1 I | [112] |
| 25l (n = 1) | g 2 (Tg) N 114/0.2 N 126/0.4 I | [112] |
| 25m | g 140 (Tg) N 226 1b | [113] |

a Values given for the second heating cycle at a heating rate of 10 °C/min. b data obtained from polarized optical microscopy; Tg are approximate values, determined at temperatures when the phase was not anymore shearable.

Figure 12. Textures of liquid crystal phases between crossed polarizers. Left: Mosaic texture of compound 25e at 99 °C typically observed for columnar phases. Right: Texture of discotic lamellar phase of 25f at 88 °C.
Figure 13. Compounds 25n and 25o-r. The structure of the linear counterpart, whose properties are investigated for comparison, is highlighted as red substructure in the star molecules.

1,3,5-Tris(oligo(phenylene ethynylene))benzene Derivatives (C-4-A-8): The rigid scaffold of the 1,3,5-tris(oligo(phenylene ethynylene))benzene derivatives plays an important role in materials science. These structures were consequently used as spacers in model compounds for the distance measurements between spins in a defined geometry [119-121]. They find applications as building blocks for MOFs [85,122,123] and pure organic supramolecular networks [61,124]. They were also used to prepare new large cyclophanes which are cage compounds apt as new supramolecular hosts [125]. Porphyrine end-capped scaffolds were investigated as rigid guest molecules for porphyrine hexamer macrocycles with high binding constants [126]. Acetylsulfanyl end-capped stars were employed to assemble three gold or silver nanoparticles around the conjugated core with defined distances [127]. Defined structures are also required in nanotechnology. Tour et al. prepared carborane end-capped 1,3,5-tris(oligo(phenylene ethynylene))benzenes [129]. The carboranes are the wheels at the rigid scaffold to form nanocars which are proposed to show defined motions at smooth surfaces. Tripodal small stars with peripheral amino acids have been synthesized and their complexation with metals has been investigated [130,131]. Such supramolecular interacting molecules with defined structure may be of interest in pharmacology or as chiral catalyst. Phosphine functionalized stars were converted to palladium complexes, however, the multi metal catalyst exhibited only a low performance [132].

A highly defined shape can be one precondition for the design of liquid crystal materials. In the series of the OPE stars there are only few examples. Moore et al. prepared an oligoethylenoxy decorated derivative 53, which can be regarded as discotic mesogens forming a hexagonal columnar mesophase (Figure 14) [133]. A different crowded mesogen 54 containing the 1,3,5-tris(phenylethynyl) benzene motif and an additional amid functionalization at the core leads to a switchable columnar liquid crystal phase and to columnar aggregation in solution by three hydrogen bonds along the stack [134,135].
Especially interesting are the studies of functionalized OPE stars showing electron energy transfers and might be applied as energy traps to mimic photosynthetic light harvesting complexes. Vauthey and Gossauer et al. investigated different porphyrine arrays with a OPE star core [136,137]. The similarity of the absorption and emission spectra with the single chromophore suggested that there is only a very weak interaction between the porphyrins. However, the introduction of porphyrins with different metals or without metals revealed a fast energy transfer. With short spacer length the energy transfer occurred via a mixed mechanism-through bond (Dexter) and through space (Förster). With longer spacers the latter became dominant. However recently the same authors highlighted in a further study that with longer spacers there is an efficient energy transfer from the OPE scaffold to the chromophore [138]. This active role of the conjugated scaffold might be promising for the energy transport over longer distances. N,N-dimethylaminonaphthalen groups were also attached to a star OPE scaffold [139]. The chromophore absorption and fluorescence dominated the photophysical properties of these molecules. Moreover, the fluorescence quantum yield appeared to decrease with longer OPE arms, which is in contrast to the observations for the parent structures (cp. Table 3). Complex palladium containing star OPEs were presented by Yam et al. Figure 15 shows two examples 26h and 26i. The palladium assembled the OPE core and in trans position a peripheral chromophore via an acetylene linker [140]. The presence of of the heavy metal resulted in an absorption dominated by a metal-to-ligand charge transfer and a predominately intraligand emission from a triplet state. Depending on the LUMO energy levels, the emission could be tuned to originate from the OPE core (e.g., 26h) or the peripheral chromophore (e.g., 26i). Fluorescent properties of methoxy substituted OPE stars 26b-d and 26e-g of various lengths were studied by Yamaguchi et al. (see figure 10 and table 3) [67]. Derivatives with three phenylene ethynylene repeating units reveal excellent fluorescence quantum yields of 0.98 and 0.97 and make such materials extremely attractive for the application in LED devices.
Figure 15. Complex star-shaped supramolecules with a OPE center of Yam et al. (26h, 26i) and Humphrey et al. (26j-m) showing tunable phosphorescence and non-linear response.

In a different work, redox active fullerenes were attached to the ends of the three arm OPE stars [141, 142]. The close resemblance of CV curves for the mutilfullerene-OPEs to C\textsubscript{60} suggested only a weak electronic communication of the fullerene groups.

Active research on three-armed star OPE is performed in the area of non-linear optics. Kondo et al. recognized already in 1995 the non-linear response of the parent molecule 26a in chloroform at 532 nm [143]. Humphrey et al. designed a series of ruthenium complexes with a 1,3,5-trisubstituted benzene core (26j-m, Figure 15) [144]. For these molecules they found only one oxidation wave pointing to non-interacting metal centers. The octupolar stars revealed superior non-linear properties over the related linear dipolar compounds. The first order and the second order hyperpolarisability approached values of $\beta(0) = 254 \times 10^{-30}$ esu and $|\gamma| = 9500 \times 10^{-36}$ esu for stars with peripheral phenylethynyl ligands substituted with electron donor or acceptor groups. TPA cross sections of up to 1300 GM were measured for the three arm OPE stars. Interestingly the non-linear response can be tuned electrochemically be oxidation of the metal centers which opens the way for nonlinear electrochromism [144, 145]. A similar concept was pursued by Yam et al., who incorporated palladium as a metal, however, the TPA cross section were considerably lower, with a maximum value of 32 GM (26h) [146]. As mentioned earlier, acetylsulfanyl end-capped OPE stars self-assembled gold or silver nanoparticles in star-shaped arrays. Owing to the plasmon absorption of these nanoparticles these defined materials are highly attractive for the study of non-linear effects. Hupp, Feldheim et al. reported extremely high first order hyperpolarisabilities of $\beta' = (3800 \pm 410) \times 10^{-30}$ esu, even though the $\beta$ value has been normalized ($\beta' = (\beta_{\text{particle}}^2/\text{atom})^{1/2}$) [147].

Tour et al. suggested that OPE stars might be also useful as components for molecular electronics, thus they could act as molecular interconnects or molecular field-effect-transistors [148].

1,3,5-Tris(oligoethenyl)benzene Derivatives (C-4-A-1): Investigation of the electronic interaction of redox centers showed that ferrocene [75, 91] and thiafulvalene [76] derivatives do not communicate
upon oxidation revealing only a single oxidation and reduction wave. Non-linear optical studies of oligoethenylene derivatives with methoxy and methylsulfanyl substituents at different positions resulted in increasing first order hyperpolarizabilities with increasing size of the conjugated scaffold and reach a maximum of $100.5 \times 10^{-30}$ esu for compound 29o ($n = 4$, $E = 3$-methoxy-4-methylsulfanylphenyl) (Figure 16) [92]. Third order non-linear properties have been studied for similar derivatives with two $n$-butoxy groups (29a-c), with second order hyperpolarisabilities $\gamma$ up to $7.96 \times 10^{-38}$ esu [72,149]. Theoretical studies of the parent 1,3,5-tris(oligoethenyl)benzene suggest that such compounds could be potential wave mixer in coherent ac electronic circuitry [150].

**Figure 16.** 1,3,5-Tris(oligoethenyl)benzene derivatives showing nonlinear optical response.

1,3,5-Tris(oligoethynyl)benzene Derivatives (C-4-A-2): 1,3,5-Tris(oligoethynyl)benzene derivatives are rarely investigated. They were applied as precursors for metallofullerene synthesis [97] or CT-Chromophores [151,152]. In one example a cyanophenyl capped derivative were employed to produce porous MOFs with silver salts [85].

1,3,5-Tris(ethenylethynyl)benzene Derivatives or Ethynylethenes (C-4-A-5 or C-4-A-4): Parent mixed ethenylethynyl or ethynylethenyl derivatives are essentially unknown in materials science. However such structures are apparent as substrucures in highly fluorescent materials [99] and CT-chromophores [151,152].

4.2. Four-arm Systems-Tetrasubstituted Benzene (C-5)

4.2.1. Structure and Conjugation

The capability of star-shaped molecules to form planar scaffolds with maximum conjugation is limited by the steric interactions between the arms and the ortho located hydrogen atoms of the benzene core or between the arms themselves (see CPK models of Figure 17). The tetra arm derivatives are intermediate between the three arm derivatives with almost no steric interaction between the conjugated arms and the hexasubstituted stars with strong steric interactions. Strongest steric interactions in the series of tetra arm derivatives would be expected for the parent molecule 55a ($n = 1$, $E = H$) [153]. In this case steric repulsion between the ortho hydrogens and the interactions between the arms result in relatively large values for the dihedral angles between the core benzene and the peripheral aromatic units in all three polymorphs — one small angle between 39.8°-51.1° and one
large angle from 62.2°-66.2°, which are, however, smaller than the values for hexa-substituted benzenes (see chapter 4.3). The steric interaction in the tolane derivative 57a is reduced to interactions between the arm benzene rings of arm neighbors [143]. The torsional angles disclose to be 11.2° and 36.2°. Different rotamers or conformers impact the conjugation within the two dimensional, cross-shaped molecule and thus also on the photophysical properties. Table 4 collects the optical data for molecules 55b, 56a and 57a and compares it with the data of the linear subunits highlighted in red (see Figure 17). The absorption maxima of the stars 55b, 56a and 57a with the strongest oscillator strength are shifted to smaller wavelengths compared with the linear counterparts which points to a reduced conjugation owing to the large dihedral angles. Relatively small differences for 56a and 57a would be in agreement with a less twisted scaffold shown in Figure 17. Despite the maxima at shorter wavelengths, compounds 55b, 56a and 57a reveal additional maxima and shoulders at longer wavelengths, which might be attributed to conformers with lower twist and extended conjugation. The fluorescence maxima of all star-shaped molecules are bathochromically shifted compared to their linear derivatives. This points to a low lying S1 electronic state compared to the S1 state of the linear molecules, which might be rationalized by the participation of a larger fraction of the conjugated molecule to the excited state. Similar results are revealed for many substituted oligophenylene derivatives 55 [154]. In case of compound 56a, the S0 → S1 transition is not allowed and consequently, the fluorescence life time is rather long, i.e., in the nanosecond regime [64]. This property may be attributed to the meta position of the substituents since even larger life times have been measured in the series of 1,3-distyryl substituted benzene derivatives. Three different charge-transfer pathways have been proposed for a series of donor-acceptor substituted cross-shaped tolane derivatives (Figure 18) in a comprehensive study of photoluminescence and emission after excitation by pulse radiolysis [155-157]: The linear (a), the cross-conjugated (b) and the bent (c) ICT pathways. The emission spectra of stars 56b-d with intramolecular charge transfer (ICT) character depend strongly on the substitution pattern and thus on the available charge transfer pathways. Molecules 56b-d possess both two ICT pathways. Molecule 57d with only bend and cross-conjugated pathways exhibit the maxima at the longest wavelength. Thus it might be speculated that in cross-shaped molecules the linear conjugation across the centre of the molecule is less efficient. The latter is in agreement with the photophysical observations (cp. Table 4).
**Figure 17.** Parent 1,2,4,5-tetrasubstituted benzenes (C-5) with conjugated arms A-3 (55), A-6 (56) and A-8 (57) and their space filling models.

**Table 4.** Photophysical data of cross-shaped conjugated star compounds.

| Compounda | Substituents E, R | Solvent, T (K) | Absorption | Emission | Ref. |
|------------|-------------------|----------------|-------------|----------|------|
|            |                   |                | Substituents E, R | Solvent, T (K) | Absorption | Emission | Ref. |
|            |                   |                | λₘₐₓ [nm] (ε [Lcm⁻¹mol⁻¹]) | λₘₐₓ [nm] (Quantum yield Φ) |
| 55b (n = 2) | star | H (CHCl₃) | 276 (-) | 410 | [158] |
| linear | H (CHCl₃) | 309 (log4.8) | 386 (0.90) | [159] |
| 56a (n = 1) | star | H (Toluene, 293 K) | 337/370 (S) | 450/472 | [64] |
| (Toluene 77K) | 350/365(S)/375(S) | 442/463 | |
| linear | H (Hexane, rt) | 350 | 417 | [160] |
| 57a | star | H (CHCl₃) | 315(134,900)/350 | 391 (0.57) | [143] |
| linear | H (CHCl₃) | 328 (38,900) | 348 (0.83) | [159] |

*a star refers to the star-shaped molecules as shown in Figure 17; linear refers to the red substructures highlighted in Figure 17, without the additional arms.
Structure and conjugation of the cruciform molecules of type 56 and 57 has been theoretically thoroughly studied by energy minimization on the B3LYP/6-311G(d,p) level and natural bond orbital (NBO) analysis [161]. All structures showed a variation in bond lengths on the benzene core, i.e., the bonds between the *ortho*-substituents are calculated to be longer than the four other bonds between the *meta*-substituted positions. These results are confirmed by the molecular structure of 55a obtained from single crystal analysis of various polymorphs [153]. The NBO analysis was performed on smaller subunits as model systems. In unsubstituted compounds, it was found that the delocalization energy is highest for the linear conjugation pathway (a). However, in donor-acceptor substituted systems this changes in favor for the cross-conjugated pathway (b), which is in agreement with results from fluorescence spectroscopy.

4.2.2. Synthesis

Parent stars with enynes (A-4) or ynenes (A-5) arms are not known. In one case the acidic treatment of an iridacyclopentadiene complex with tris(ethynyl)benzene afforded the vinyl substituted parent enyne 50 (Figure 11) [98]. Cross-conjugated enynes 47 are precursors in the synthesis of oligoyynes (Scheme 11) [94,95]. Different cross-conjugated enynes with donor and acceptor groups have been also obtained by a tandem reaction sequence including cycloaddition of tetracyanoethylene to an electron rich triple bond and a subsequent retroelectrocyclization to yield 51. In the series of ynenes only a branched star 52 is known, obtained by a six-fold Sonogashira-coupling of the acetylene component to tris(2,2-dibromovinyl)benzene [99].

The synthesis of the different conjugated tetra-substituted benzene derivatives is performed analogous to the preparation of triarm stars described in section 4.1.2. The most important core reagents 58-62 for convergent or divergent synthesis of the target compounds are presented in Figure 19. Convergent synthesis of tetrakis(oligophenylene)benzene derivatives are executed by Suzuki cross coupling of the arms to a tetrabromo center 58a [154]. Tetrakis(oligo(phenylene ethynylene))benzene and tetrakis(oligo(ethynylene))benzene stars are obtained by Wittig [162,163] or Wittig-Horner reactions [164,165] with cores 61, 62a, 62b or by Siegrist reaction [70] using durene 6.
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Tetrakis(oligo(phenylene ethynylene))benzene and tetrakis(oligoethynylene)benzene molecules were prepared by the Hagihara-Sonogashira reaction from core reagents 58a,b [152,166].

Figure 19. Core building blocks for the synthesis of various tetra-substituted conjugated stars.

Scheme 12. Preparation of tetrakis(oligophenylene)benzenes 55 by an alternative route via an aryne mechanism and the divergent synthetic strategy for the synthesis of stars 57 with different peripheral aryl groups (Ar).

TMSA = trimethylsilylacetylene, TIPSA triisopropylsilylacetylene, Ar aryl group
Tetrakisphenylbenzene derivatives can also be obtained by a simple conversion of halogen substituted benzenes with Grignard reagents (Scheme 12) [167]. The resulting tetrakisaryl substituted benzenes are formed by an aryne mechanism in moderate yields.

The nonsymmetric tetrakis(arylethynyl)benzenes 57b-d were synthesized by a divergent strategy starting from cores 58a,b,c with different activated carbon-halogen bonds [157]. The different introduced silylprotecting groups can be selectively cleaved and converted to terminal alkynes which were coupled subsequently to donor or acceptor substituted aryl iodides.

4.2.3. Four-arm Stars with Benzene Centers and Materials Science

Cross-shaped four arm stars have been studied to a much lesser extent in materials science than three arm (section 4.1) or six arm systems (section 4.3). Materials research focuses on compounds 55-57 (Figure 17). 1,2,4,5-Tetrakis(oligoethenyl)benzene derivatives (C-5-A-1) are prepared only as intermediate products to obtain macrocycles [162] or cage compounds [163]. 1,2,4,5-tetrakis(oligoethynyl)benzene derivatives (C-5-A-2) were of interest for the synthesis of graphdiyne substructures [166,168,169], donor-acceptor-functionalized bis(dehydrobenzo[18]annuleno)benzenes [170] and star-shaped compounds [152].

1,2,4,5-Tetrakis(oligophenylene)benzene Derivatives (C-5-A-3): The rigid and shape-persistent structure of tetraphenylbenzene was exploited as building blocks for MOFs (compound 55c (n = 1, E = SCH3), 55d (n = 1, E = COOH)) [171-176] and in crystal engineering by hydrogenbonds (55e, n = 1, E = diaminotriazinyl) [177]. For example 55d complexed to Zn(NO2)2 was tailored to uptake a remarkable amount of cryogenic hydrogen [174] and could also be postsynthetically modified to adsorb CO2 [175]. A framework containing also metalloporphyrin centers was shown to accelerate esterification reactions, thus can be classified as supramolecular catalyst [176].

Much less frequently tetrakis(oligophenylene)benzene materials have been investigated with respect to their opto-electronic properties. Biphenyl derivative 55b was reported as potential blue light emitting compound [158]. Various substituted derivatives were described as materials for LED applications with improved solubility and processibility compared to linear analogous [154]. Fluorine substituted derivatives have been shown to be excellent hole blocking materials [178]. The latter was rationalized by the large energy gap and the low HOMO energy level.

1,2,4,5-Tetrakis(oligo(phenylene ethenylene))benzenes (C-5-A-6): The 1,2,4,5-tetrakis(oligo(phenylene ethenylene))benzenes possess only a limited shape persistence owing to the rather large number of seven possible conformers (c.p. Table 1) [64], thus they were not exploited for MOFs or crystal engineering. However, conformational variation is advantageous for the self-organization into soft materials. A derivative 56 substituted with long oligoethylenoxy chains exhibit analogous to the amphiphilic trisstyrylbenzene 25i a critical micelle concentration, a lowest critical solution temperature (LCST) and is a stimuli responsive material which reveals consistent changes of the absorption and emission spectra upon micelle formation [116].

Some studies were dedicated towards the usage of tetraarm stars as LED materials [179-181]. Galvin et al. reported larger conjugated cross-shaped stars 56b and 56c (Figure 20). They are excellent
processible and exhibit a large stokes-shift which points to a high electron delocalization in the excited state [181]. Preliminary investigations of mono- and multilayer devices show encouraging data although the efficiencies are rather low. Some additional investigation of the charge transport properties revealed that in these compounds excess positive charges are localized at the alkoxy substituted aromatic rings whereas the negative charges are distributed over the entire star scaffold. According to calculated charge carrier mobility data, these materials are promising.

Figure 20. Stilbenoid materials for OLED and TPA applications.

Theoretical studies suggested that especially cross-shaped stilbenoid stars 56 should reveal high TPA cross sections [182]. The same group reported one year later donor substituted derivatives 56d and 56e (Figure 20), with TPA cross sections of up to 1030 GM which are among the highest reported for organic molecular materials [183]. Interestingly, a slight change in the peripheral chains of the molecule reduces this value to only 97 GM for compound 56f [184]. In a further investigation, Perry, Marder and Rumi et al. confirmed the high TPA cross section but pointed out that compared to the linear analogue the TPA is increasing less then with the factor of two [185]. The combination of two crossed linear units in 56, thus do not efficiently enhance the TPA cross section.

1,2,4,5-Tetrakis(oligo(phenylene ethynylene))benzenes (C-5-A-8): In contrast, to the stilbenoid compounds 56, 1,2,4,5-tetrakis(oligo(phenylene ethynylene))benzenes 57 can be classified as shape-persistent compounds and consequently a methylsulfanyl capped derivatives was applied to form 2D and 3D networks with BiBr3 [171]. Methylsulfanyl and methylsulfanylethynyl capped derivatives have been also employed to mediate the self-assembly of gold nanoparticles [186]. The scaffold was substituted by amino acid derivatives in order to generate new ligands and pharmaceutical active compounds [130,131]. Although the tetra arm substituted core is reminiscent of a disc only three compounds with liquid crystalline behavior has been published (Figure 21) [187,188]. The symmetric mesogen with octyloxy chains 57e revealed only a crystalline (Cr 118 °C I), the elongation of the chains (tridecyloxy) lead to the observation of a monotropic nematic phase for 57f (Cr (74 °C N) 96 °C I) at fast cooling between crossed polarizers. Interestingly, a monotropic phase were detected also for a non-symmetric derivative 57g (Cr (69 °C N) 84 °C I) and an enantiotropic mesophase were formed.
only when one complete arm was missing such as in compound 65 (Cr 69 °C N 88 °C I) [187]. Although, the design of cross-shaped mesogens was unsuccessful for the self-assembly in enantiotropic thermotropic mesophases, an amphiphilic derivative decorated with oligoethyleneoxy chains 57h revealed high association constants of $4.4 \times 10^4$-$5.2 \times 10^5$ M$^{-1}$ in benzene and acetonitrile [189]. These amphiphiles self-organize in unimolecular wires from benzene solution, whereas they form hollow vesicles or 3D toroidal objects in polar solvents.

**Figure 21.** Cruciform nematic mesogens.

- 57g
- 57h
- 57e
- 57f
- 57i
- 57j
- 57k

Optoelectronic properties were thoroughly studied for compounds 57a-d and 57i-l (Figure 22). Their relatively high fluorescence quantum yields and the tunability of the emission maximum make these compounds to promising candidates for the application in organic light-emitting diodes [155-157]. Recently, the acid titration of 57i revealed a two-stage emission switching between $\pi-\pi^*$ and intramolecular charge transfer emissions [190]. The latter is evidenced by a strong bathochromic shift at the beginning dynamic protonation of the first three amino groups. Further increase of the TFA concentration results in the tetra-protonated species revealed by the hypsochromic shift of the emission maximum (Figure 23).

Cruciform conjugated tolane systems are promising for NLO applications as realized already by Kondo et al. for the parent molecule 57a [143]. Recently, the TPA cross section of a donor (57i) and a donor-acceptor substituted compound (57l) have been measured with maximum values of $(520 \pm 30)$ GM at 710 nm for 57i and $(240 \pm 20)$GM at 750 nm for 57l in the optical transparent region [191]. Feng et al. considered such systems theoretically and proposed highest two-photon responses for ortho and meta substituted derivatives such as 57j and 57k, due to the large dipole moment differences between the ground states and the intermediate states [192]. By incorporation of ruthenium complexes in the arm scaffold, Humphrey et al. could obtain cruciform materials with switchable non-linear response by protic and electrochemical stimuli [193].
Figure 22. Donor and donor-acceptor substituted cruciform star molecules for optoelectronic and NLO applications.

Figure 23. Excitation (left) and emission (right) spectra of TFA titration of 57i in CH₂Cl₂ (ca. 20 mM). Inset: photographs of vials of analyte solutions at indicated -log[TFA] under illumination by high-intensity 365 nm lamp. Reprinted from reference [190] Tetrahedron, 64, Spitler, E. L.; Haley, M. M., Dynamic proton-induced two-stage emission switching in donor-functionalized bis(dehydrobenzo[n]annuleno)benzenes and 1,2,4,5-tetrakis-(phenylethynyl)benzene., 11469-11474, (Copyright 2008, reprinted with permission from Elsevier).
4.3. Six-arm Systems-Hexasubstituted Benzenes (C-6)

4.3.1. Structure and Conjugation of Parent Systems

Hexasubstituted benzenes are predominately steric crowed benzenes. Figure 24 collects four parent structures: hexaphenylbenzene 66a (C-6-A-3), hexakis(phenylethenyl)benzene 67a (C-6-A-6) hexakis(phenylethynylene)benzene 68a (C-6-A-8) and hexakis(phenylbutadiyne)benzene 69b (C-6-A-2).

Figure 24. Parent, conjugated, hexasubstituted benzene compounds (C-6).

The space filling models in Figure 24 demonstrate that for steric reasons the phenyl and the phenylethenyl radicals must turn out of plane relative to the central benzene ring. Only the phenylbutadiynyl derivative may arrange the peripheral benzene rings in a coplanar topology. Single crystals were obtained for derivatives of 66, 68 and 69. In the crystal, the molecular structure of hexaphenylbenzene 66a take a propeller shape with a dihedral angle of 62-71°; in the vapor phase this angle increases to about 90° ± 10° [194,195]. Smaller dihedral angles of 1°-26° were reported for the molecular structure of a hexaphenylethynylbenzene derivative 68b (E = NO₂, N(C₆H₁₃)₂) with pseudo D₃h symmetry [195]. No steric interaction becomes evident in the structure of hexa-(tert-butylbutadiynyl)benzene 69a [196].
Table 5. Photophysical properties of hexaarm derivatives.

| Compounda | Substituents E | Absorption $\lambda_{\text{max}}$ [nm] | Emission $\lambda_{\text{max}}$ [nm] | References |
|-----------|----------------|--------------------------------------|-------------------------------------|------------|
| 66a       | star H         | 249                                  | 337                                 | [197]      |
|           | linear H       | 280                                  | 342                                 | [159]      |
| 67b       | star 4-dodecyloxy | 342                               | -                                   | [198]      |
|           | linear 369     |                                      | -                                   |            |
| 68a       | star H         | 349                                  | 449                                 | [143,159]  |
|           | linear H       | 328                                  | 348                                 | [159]      |
| 69c       | star 4-tert-butylphenyl 385/415 | -                             |                                      | [199]      |
|           | linear phenyl  | 335/360                              | -                                   | [200]      |

* star refers to the star-shaped molecules as shown in Figure 24; linear refers to the red substructures highlighted in Figure 24, without the additional arms.

The conjugation via the centre of the molecule is effected by the magnitude of the dihedral angle between the central and peripheral benzene units. Absorption or emission maxima, reflecting the degree of conjugation, are summarized in Table 5 and compared with the maxima found for linear building blocks. The linear building blocks are defined as the para connected segments with maximum conjugation, which Figure 24 highlights in red. The absorption and emission maxima of hexaphenylbenzene 66a and hexastyrylbenzene 67b derivatives are shifted hypsochromically compared to the linear oligomers which points clearly to less efficient conjugation. In contrast, star-shaped compounds 68a and 69c show bathochromically shifted absorption and emission maxima relative to the maxima of the linear building blocks. Marguet et al. predicted qualitatively the absorption spectrum of 68a by exciton theory and CS-INDO-CIPSI calculations [201]. They proposed that the absorption with the largest transition dipole should be delocalized over the whole chromophore and should therefore be affected by peripheral substituents and the dihedral angle. In contrast, the lowest excited state is localized at the hexaethynylbenzene centre of the molecule and should be insensitive to the peripheral substitution pattern. The wavelengths of the calculated absorption maxima were found to be approximately 100 nm lower than the experimental data, which was only rationalized by solvent effects. Recently it has been demonstrated for compounds with donor or acceptor substituents at the peripheral benzene ring, that absorption and emission maxima are both bathochromically shifted [202]. The largest effect with $\Delta \lambda > 100$ nm was observed for donor-acceptor substituted derivatives with alternately attached three donor and acceptors. The authors rationalize this behavior by the conjugation across the benzene centre. However, the linear donor-acceptor substituted chromophore (E = N(n-C_{12}H_{25})_2, CHC(CN)_{2}) for which no steric congestion impedes a planar conformation possesses a strongly blue shifted absorption by 38 nm compared with star 68b (E = N(n-C_{12}H_{25})_2, CHC(CN)_{2}) [202,203]. The reason for the red-shifted absorption of the hexaphenylethynylbenzene derivatives is not yet fully understood. However, it might be related to interactions of $\pi$-orbitals of the arms able to approach each other closely at the centre of the molecule,
which was recently also suggested to mediate electronic interactions between oxidized chromophores at a hexaphenylbenzene core [204]. This is supported by the fact that the absorption maxima shifts stepwise to longer wavelengths with increasing number of arms [143].

4.3.2. Synthesis of the Parent Systems

**Scheme 13. Synthesis of hexaarm derivatives**

The synthesis of the parent star-shaped conjugated molecules is summarized in Scheme 13. The $D_{6h}$ symmetric hexaphenylbenzene derivatives 66 can be efficiently obtained by the trimerization of diphenylacetylenes 70 with a cobalt or palladium catalyst [205,206]. Early attempts to synthesize and isolate hexaphenylenbenzene derivatives by a sixfold Heck reaction failed [207,208]. Efforts to prepare the target compounds by sixfold Suzuki or Stille type cross coupling reactions afforded no or very low yields [208]. Consequently, a two-stage reaction sequence have been developed [209]. In a first step three styryl derivatives were coupled to centre 71 by the Heck procedure. Functional group interconversion of the methyl group in 72 via bromination to a phosphonic acid diethylester allowed in
the final step to form a double bond by the Wittig-Horner reaction to yield the target compounds 67 in moderate over-all yields. Compounds 68 (R = R') were obtained originally by sixfold Sonogashira-Hagihara cross coupling reactions of core 73 with phenylethyynes [207,210,211]. In principle pseudo $D_{3h}$ symmetric compounds (R ≠ R') can be isolated after a two-stage strategy starting with 1,3,5-Bromo-2,4,6-iodobenzene 74 [202]. However, recently Kuck et al. stressed the fact that repetition of earlier sixfold reactions only yielded the pentasubstituted benzene as the principle product [212]. This group could obtain the hexaphenylethenylbenzene only starting from the hexaethynylbenzene core 76. A sixfold coupling of butadiyne derivatives using modified Sonogashira-Hagihara condition (Pd[P(o-Tol)3]2, CuI, Et3N, NMP) afforded compounds 69 in moderate yields [199].

4.3.3. Hexaarm Stars with Benzene Centers and Materials Science

**Hexaphenylbenzene Derivatives (C-6-A-3):** Many applications of hexaphenylbenzenes and hexa(oligo-para-phenylene)benzenes are based on the rigid molecular scaffold in which the conjugation does not play the major role. They are used as synthetic precursors for hexabenzocorones and nanographenes [205,213-216], as oligophenylene dendrimer cores [217], as templates for the preparation of macrocycles [218,219], as star-shaped amphiphiles for the active layer of nanofilters [220,221] and as model scaffolds for natural antenna complexes with a well-defined porphyrine chromophore array [206,222,223]. A rigid scaffold is also a precondition for mesophase formation. Hexaphenyl- and hexabiphenylbenzene were decorated with dodecyl chains or dodecylthienyl groups in order to generate mesomorphic properties. The resulting materials showed complex thermotropic behavior, for which the high temperature phases have been suggested to be columnar mesophases [224].

Hexaphenylbenzene and hexakis(4-n-dodecylbiphenylyl)benzene can be reduced to their hexaanions. In these hexaanions the central benzene ring is twisted and undergoes a dynamic processes which could be monitored with NMR investigations for the thermally surprisingly stable biphenyl system [187].

Much work has been undertaken to functionalize hexaphenylbenzene with electrochemical active groups shown in Figure 25.

**Figure 25.** Hexaphenylbenzene derivatives with electrochemically active peripheral groups.

Compounds 66b and 66c can be six-fold oxidized at a single potential which was attributed to the missing conjugation of the redox-active peripheral units E [225,226]. Indeed the molecular structure of 66b in the single crystal revealed not only the typical dihedral angle of about 66° between peripheral phenyl groups and the central benzene, but also a dihedral angle of 4-31° between ferrocenyli groups...
and the peripheral benzene units. Star-shaped compound 66c was called an electron-sponge which has been successfully applied to oxidize aromatic and olefinic compounds to produce their radical cations. A different situation comes across in compound 66d [204]. The redox-active tetrphenylethen includes a phenyl group from the propeller core. The absorption spectrum is slightly red-shifted to 324 nm and the extinction coefficient is higher than the six-fold extinction of tetrphenylethen. These observations were attributed to a weak electronic interaction of the arm units and could be confirmed by cyclic voltametry revealing three overlapping oxidation waves. This is based on the rapid charge transfer between the active centers of the molecule in a radical cation which consequently affects the removal of further electrons. In compound 66e six trityl cations are arranged about a benzene ring [227]. It can be produced by treatment of the alcohol precursor with methyl sulfonic acid. Again a red-shift (20 nm) of the trityl cation absorption compared with the parent trityl cation suggests a weak interaction between the arms of the star-shaped molecule. The compound can be used as a hydride transfer reagent in Organic Chemistry. Müllen et al. investigated the photophysical properties of higher oligophenylene star homologues, namely stars with terphenyl and quarterphenyl arms substituted with alkyl chains at the para-position [228]. They pointed out that the bathochromic shift of the absorption maxima (303 nm, 316 nm) compared to individual terphenyl (285 nm) or quarterphenyl (299 nm) arms does not account for completely independent chromophores. The materials are highly fluorescent, with high quantum yields, possess a low crystallization tendency, do not form aggregates or excimers and thus are suitable for light-emitting diodes. Donor-acceptor substitution of hexaphenylbenzene makes these stars to NLO materials with high second order polarizabilities [195].

**Hexakis(phenylethenyl)- and Hexakis(oligo(phenylene ethylene)phenyl)benzene Derivatives (C-6-A-6 and C-6-A-7):** Hexakis(phenylethenyl)benzenes 67 have been synthesized due to expected interesting intramolecular or intermolecular photochemical reactions. However, only an unspecific photopolymerization has been observed [198]. Surprisingly, the attachment of long, peripheral alkoxychains does not result in liquid crystalline materials. Meijer and Schenning et al. synthesized a star with six arms based on a oligo(phenylene ethylene) scaffold 66f (Figure 26) [229]. They circumvented the demanding synthesis of a hexa(phenylethenylene)benzene centre 67 by the preparation of the star using the simple high yielding trimerization procedure of ethynylene derivatives resulting in a molecule 66f with hexaphenylbenzene core. Compound 66f reveals remarkable self-assembly properties. Even at concentrations of 10^{-7} mol/l in heptane at 90 °C they stack into helical columnar aggregates. In bulk the mesogen self-assemble in a soft, columnar crystal. The high order in the aggregates of this conjugated oligomer makes these compounds highly appealing for supramolecular electronics.
Hexakisoligo(phenylene ethynylene)benzene Derivatives (C-6-A-8): As mentioned for the hexaphenylbenzene cores, hexa(phenylethynyl)benzene scaffolds are often prepared to utilize their defined and persistent shape. For example, they were employed to design new ligands for multimetal complexes [131,230-234]. Especially the cobalt complexes, were subsequently used to prepare carbon nanomaterials by pyrolysis [235]. The most important property with respect to the shape anisotropy is the self-organization in liquid crystals. The hexa(phenylethynyl)benzene core with peripheral flexible chains is one of the most prominent disk-shaped mesogen, forming exclusively discotic nematic mesophases. Table 6 summarizes the thermotropic behavior of some selected examples. In the series of alkyl ($n$-C$_n$H$_{2n+1}$) substituted mesogens the mesophase range increase until $n = 7$ and decrease with longer chains until it disappears for $n = 12$ [211,236]. With peripheral alkoxy substituents (OC$_n$H$_{2n+1}$) the temperature interval of the nematic mesophases is considerably extended [210,237]. Changing the chain position from para to meta or ortho in the peripheral ring results in the loss of the LC behavior. Although, methyl groups at the meta-position lead to a decrease of the melting transitions, almost room temperature stable discotic nematic liquid crystals have been obtained only by desymmetrization of the star mesogen [237]. Such nematic phases are attractive for the application in wide viewing angle nematic displays [238].

For photophysical applications, not only the shape but also the conjugation paths are important. In a fundamental study, Kondo et al. reported a rather large third order non-linearity for the non-polar parent compound 66a [143]. A substantial second order polarizability of $\beta_{zzz} = (1670 \pm 140) \times 10^{-50}$ Cm$^3$V$^{-2}$ have been recorded for the donor-acceptor substituted hexa(phenylethynyl)benzene 66b [195]. The excellent 2D NLO property have been attributed to the conjugation across the central benzene ring, since related more twisted derivatives exhibit significantly reduced values. Similar relationships have been found when the two-photon absorption properties were studied for compounds 68a,q,r (Figure 27) [239]. The value of the cross section decreased in the series of 68q > 68a > 68r. The larger value for 68q was rationalized by the substitution effect of the donation tert-butyl groups. The lowest value for 68r can be explained by the reduced conjugation across the centre of the molecule due to steric interactions of the methyl groups in meta-position [240].
Table 6. Hexaarm systems with a benzene core and phenylethynyl arms.

| E<sup>a</sup>  | X      | Transition Temperatures /°C<sup>b</sup> | E<sup>a</sup>  | X      | Transition Temperatures /°C<sup>b</sup> |
|----------------|--------|----------------------------------------|----------------|--------|----------------------------------------|
| n-pentyl       | H      | Cr 170 N<sub>D</sub> 185 I            | hexyloxy       | H      | Cr 144 N<sub>D</sub> 216 I            |
| n-hexyl        | H      | Cr 124 N<sub>D</sub> 142 I            | heptyloxy      | H      | Cr 109 N<sub>D</sub> 193 I            |
| n-heptyl       | H      | Cr 98 N<sub>D</sub> 131 I             | meta           | H      | Cr 87 I                               |
| n-octyl        | H      | Cr 80 N<sub>D</sub> 96 I              | hexyloxy       | H      | Cr 63 I                               |
| n-nonyl        | H      | Cr 67 N<sub>D</sub> 83 I              | octyloxy       | CH<sub>3</sub> | Cr 95 N<sub>D</sub> 176 I          |
| n-decyl        | H      | Cr 71 (N<sub>D</sub> 54 I)            | 3,7-dimethyl-octyloxy | H      | Cr 80 N<sub>D</sub> 124 I          |
| n-dodecyl      | H      | no LC                                 | 3,7-dimethyl-octyloxy | CH<sub>3</sub> | Cr 71 N<sub>D</sub> 147-160 I     |

<sup>a</sup> Substituents E are always in para-positions if not otherwise stated.  <sup>b</sup> Cr crystal; N<sub>D</sub> discotic nematic; I isotropic.

Figure 27. Hexa(phenylethynyl)benzene stars for NLO or two-photon absorption applications.
5. Compounds with Heterocyclic Cores

5.1. Pyridine-based Stars (C-7-A-6, C-7-A-7):

A multitude of 2,4,6-triarylpyridines (C-7-A-3) with a large variety of additional substituents on central and the peripheral rings as well as conjugated π-systems incorporating pyridine rings has been prepared in the past. However, only a few star-shaped compounds with larger conjugated branches in the 2,4,6-positions appeared in the literature. Compared to benzene as a core, the pyridine offers a higher electron affinity [241], a subtle difference between substituents in the 2,6- and 4-positions, and the ability to be protonated or quaternized. Nevertheless, 2,4,6-trisubstituted pyridines can be regarded as pseudo-C₃-symmetric.

2,4,6-Trimethylpyridine (sym-collidine) 77a (R⁴ = H) is the most prominent starting material for stars with a pyridine core. The base-catalyzed condensation of sym-collidine with 4-, 3,4-di- and 3,4,5-tridodecyloxy-substituted N-phenylbenzaldimines 78a-c (Siegrist reaction) gives 2,4,6-tristyrylpyridines 79a-c in moderate to good yields and with an extraordinary high E-selectivity (Scheme XIV). Contrary to similar compounds with a benzene core, these stars do not form mesophases [242]. The analogous compound 79d with a 3,5-didodecyloxy substitution was prepared by Attias [243]. Substituted 2,4,6-tristyrylpyridines, e.g., the p-chloro derivative, have been claimed as electroluminescent materials [244].

Scheme 14. Siegrist reaction of 2,4,6-collidine 77 with alkoxybenzanilines 78.

The acid-catalyzed condensation of 3,4-didecyloxybenzaldehyde 78e with 3,5-dicyanocollidine 77b (R⁴ = CN) gave a yellow-orange tristyrylpyridine 79e in 42% yield [245,246].

In dichloromethane solution, the absorption maximum is observed at \( \lambda = 400 \text{ nm} \) (\( \varepsilon > 80,000 \text{ Lmol}^{-1}\text{cm}^{-1} \)) and, separated by a large Stokes shift, a fluorescence maximum at \( \lambda^f = 550 \text{ nm} \) (Φ = 0.40). A
reversible reduction was observed by cyclic voltammetry at -1.19 V (vs. SCE) and an irreversible oxidation wave at 1.28 V. The electron affinity could be calculated to be about 3.6 eV.

Between octadecylsilane treated surfaces 79e shows a fan-shapes texture, characteristic of a hexagonal columnar mesophase that exists between 81 °C and 133 °C (DSC). According to the X-ray diffraction of the mesophase, columns composed of discs with an antiparallel orientation form a hexagonal lattice. The anti-orientation of the discs results from dipolar interactions, these are also responsible for the stability of the columnar structure [245,246].

Related stars with diphenylamine end groups 79f were prepared via piperidine-catalyzed Knoevenagel condensations in 22% to 27% yield [247]. The absorption spectra of these octupolar dyes show maxima between $\lambda = 476$ and 480 nm and an intense ($\Phi = 51-54\%$) orange fluorescence with maxima at $\lambda^\text{Fmax} = 575$-586 nm. Two-photon absorption cross-sections at 800 nm were found to be 187-204 GM. The TPEF is shifted about $\Delta \lambda = 6$-18 nm to the red relative to the single-photon excited fluorescence. Comparing 2,4-di- and 2,4,6-tristyryl-dyes, the authors found a strong cooperative enhancement of the TPA cross-section among the three branches which may be attributed to an electronic coupling among the core and the three individual branches of the octupolar molecule.

Pyridine stars with larger $\pi$-conjugated branches 80 (C-7-A-7-E) have been prepared by Siegrist [248]. Threefold base catalyzed reaction of 2,4,6-tris(4-methylphenyl)pyridine with the Schiff bases of benzaldehydes and aniline 78g, h (g: R$^{1-3} = H$, h: R$^1 = R^3 = H$, R$^2 = C_6H_5$) gave trisstilbenylpyridine 80a (E = phenyl) and tris-4′-phenylstilbenylpyridine 80b (E = 4-biphenyl) in 41% and 55% yield. The acetic anhydride promoted condensation gives similar yields [249]. The absorption of 80a has a maximum at $\lambda = 342$ nm (DMF), a threefold phenyl-substitution in the $p$-positions of the stilbene arms (80b) resulted in a red-shift to $\lambda^\text{max} = 360$ nm.

Tristyrylpyridinium dyes 81 (Scheme 15) were prepared by piperidine catalyzed condensation of the $N,N$-dialkyl-aminobenzaldehydes 82 with a 1,2,4,6-tetramethylpyridinium salt 83 in 10-25% yield [250,251]. Along with the substitution of the pyridinium ring with one, two or three dimethylaminostyryl groups, the absorption maximum is first shifted to the red (mono-$\alpha$: $\lambda^\text{max} = 478$ nm; mono-$\gamma$: $\lambda^\text{max} = 502$ nm; di-$\alpha,\alpha'$: $\lambda^\text{max} = 515$nm, di-$\alpha,\gamma$: $\lambda^\text{max} = 518$ nm) but the threefold styryl-substituted dye 81a absorbs at higher energies (tri-$\alpha,\gamma,\alpha'$: $\lambda^\text{max} = 510$ nm). In the series with dimethylaminophenylbutadienyl groups, the sequence for $\lambda^\text{max}$ is mono-$\alpha$: $\lambda^\text{max} = 508$ nm; mono-$\gamma$: $\lambda^\text{max} = 525$ nm; di-$\alpha,\alpha'$: $\lambda^\text{max} = 552$ nm, di-$\alpha,\gamma$: $\lambda^\text{max} = 557$ nm and the tri(phenylbutadienyl) dye 81b shows $\lambda^\text{max} = 559$ nm [250]. These dyes are negative solvatochromic, the absorption maxima are shifted about 36 and 30 nm resp. to the blue comparing solutions in CHCl$_3$ with those in methanol.

Substituted with six long octadecyl side chains, the absorption maximum of a $N$-methyl-2,4,6-tris(aminostyryl)pyridinium salt 81c in CHCl$_3$ appears at $\lambda^\text{max} = 520$ nm which is shifted to $\lambda^\text{max} = 500$ nm in LB films due to the formation of H-aggregates [251].
Scheme 15. Synthesis of \(N\)-alkyl-2,4,6-tristyrylpyridinium salts 81.

The redox potentials of these LB films are \(-0.73 \text{ V}\) for the reduction and \(-0.384 \text{ V}\) for the reoxidation (vs. SCE). LB films on ITO were used for photocurrent generation.

Aza-analogous 2,4,6-tristyrylpyridinium salts and 2,4,6-tris-(styrylstyryl)pyridinium salts proved to be efficient two-photon absorbing dyes with cross-sections up to 1600 GM at 800 nm [252]. Trisstyrylpyrylium analogues of 81 were prepared by condensation of trimethylpyrrylum perchlorate with dimethylaminobenzaldehyde (97%) or dimethylaminocinnamic aldehyde (5%) [250]. Compared to the pyridinium salts, the absorption maxima are severely shifted to lower energies (\(\lambda_{\text{max}} = 685 \text{ nm}\) and \(\lambda_{\text{max}} = 781 \text{ nm}\) resp.).

A star-shaped three-dimensional cage compound (C-7-A-2) with two pyridine cores and three hexadecaoctayne handles has been observed by negative mode laser desorption TOF mass spectrum of a pyridocyclophane precursor [253]. Additionally, with low intensity, a peak due to a \(C_{58}N_2\) anion was detected representing the first observation of a diazafullerene formed in a size-selective manner.

5.2. Stars with a Pyrimidine Core

Triarylpymidines and Tri(alkynylaryl)pyrimidines (C-8-A-3 and C-8-A-9): Like pyridine, the pyrimidine core displays a higher electron affinity and pseudo-\(C_3\)-symmetry of 2,4,6-trisubstituted derivatives, but the pyrimidine is less basic compared to pyridine [254].

Two general methods for the synthesis of 2,4,6-triarylpyrimidines 84 are described in the literature [255]. The first method consists in the construction of the pyrimidine ring by condensation reactions [256-258], the second involves the functionalization of the pyrimidine ring. Trifluoromethanesulfonic anhydride appeared to be suitable for a co-condensation of benzonitriles with acetophenones yielding 2,4,6-triphenylpyrimidines 84 substituted with alkoxy side chains [259].

Aryl groups can be attached to the 2,4,6-positions of pyrimidine by successive arylation reactions (Scheme 16). Starting with 2-methylthiopyrimidine 85a, an addition of an aryllithium reagent followed by oxidation with DDQ introduced the first aryl group in the 4-position, and the iterative procedure gives the 4,6-diarylpyrimidine 85b. A \(\text{NiCl}_2(\text{dppe})\)-catalyzed substitution of the methylthio
group with aryl-Grignard reagents led to the triphenylpyrimidines \(84\) with symmetrical or non-symmetrical substitution on the periphery [260].

**Scheme 16.** Successive threefold arylation of pyrimidine.

\[
\begin{align*}
&\text{SCH}_3 \\
&\text{N} & \text{N} & \text{N} \\
&\begin{array}{c}
2x \quad 1. \text{PhLi} \\
2. \text{HOAc} \\
3. \text{DDQ}
\end{array} \\
&\text{85a} & \text{85b} & \text{85c} & \text{84}
\end{align*}
\]

The Suzuki cross-coupling reaction on chloropyrimidines [261] has become an important tool for the construction of 2,4,6-triarylpyrimidines \(84\) (Scheme 17). The \(\pi\)-electron deficient character of the pyrimidine ring is advantageous for the Suzuki reactions since it makes easier the oxidative addition of palladium to a carbon-chlorine bond without the use of specialized ligands [255].

Plé et al. synthesized star-shaped triarylpyrimidines \(84b-i\) via Suzuki coupling of 2,4,6-trichloropyrimidine \(86\) and an excess of boronic acids \(87b-i\). With yields in the range of 72-86%, this method is suitable for boronic acids with moderate donor groups, strong donors like dimethylamino strongly reduce the electron deficient character of the pyrimidine and only a mono-coupling could be achieved, but with a modified procedure 2,4,6-tris-(\(p\)-dimethylamino)pyrimidine \(84f\) could be obtained in 54% yield. This strategy is also useful for the construction of pyrimidine stars with biphenyl- (\(84g, h\)), tolanyl- (\(84i\)) and heterocyclic \(\pi\)-conjugated arms, but the yields decrease with increasing conjugation lengths.

The X-ray structure of \(84b\) shows that the molecule is slightly twisted in the solid state, the dihedral angle between the central pyrimidine and the 2-phenyl ring is only 3.6°, but the dihedral angles of the pyrimidine with the 4- and 6-phenyl ring are 13° and 14°. Nevertheless, these angles are sufficiently small to allow conjugation along the arms.

2,4,6-Triphenylpyrimidine \(84a\) is almost non-fluorescent [260]. Stars with moderate donor groups on the phenyl rings \(84b, c, e\) show absorption (\(\lambda = 296-321\) nm) and emission (\(\lambda^F = 372-398\) nm) in the UV, but with low quantum yields (\(84b: \Phi = 0.04, 84e: \Phi = 0.14\) [255]. The stronger dimethylamino donor group on the \(p\)-position of each phenyl ring \(84f\) provokes strong bathochromic shifts absorption (\(\lambda = 349\) nm) and of the emission (\(\lambda = 427\) nm) with a quantum yield of \(\Phi = 0.14\).

An unsymmetrical donor-substitution appears to be superior in terms of fluorescence efficiency. Only one dimethylamino group on the \(p\)-position of the 4-phenyl ring results in a highly emissive triphenylpyrimidine (in CHCl\(_3\): \(\lambda^F_{\text{max}} = 444\) nm, \(\Phi\) ca. 0.6) that is strongly solvatofluorochromic with bathochromic shifts up to 184 nm [260]. The isomer with a 2-(\(p\)-dimethylaminophenyl) group is only weakly fluorescent. Compared to the tris-(\(p\)-methoxyphenyl)pyrimidine \(84b\) the unsymmetrical compound with a 4-dimethylaminophenyl substituent in the 4-position of the pyrimidine and two alkoxyphenyl rings shows a marked hypsochromic shift of the absorption (\(\lambda_{\text{max}} = 269\) nm) and the emission (\(\lambda^F_{\text{max}} = 306\) nm) along with a strong increase of the quantum yield (\(\Phi = 0.53\)).
Scheme 17. Synthesis of 2,4,6-triarylpyrimidines via threefold Suzuki cross-coupling.

![Scheme 17](image)

| R                  | yield | $\lambda_{\text{max}}$ /nm | $\lambda^F_{\text{max}}$ /nm | $\Phi$ |
|--------------------|-------|-----------------------------|-----------------------------|-------|
| 84b OCH$_3$        | 72%   | 296                         | 372                         | 0.04  |
| 84c OC$_{10}H_{21}$| 79%   | 297                         | 387                         | 0.04  |
| 84d Si(CH$_3$)$_3$ | 86%   | 321                         | 427                         | 0.14  |
| 84e SCH$_3$        | 82%   | 349                         | 427                         | 0.14  |
| 84f N(CH$_3$)$_2$  | 67%   | 349                         | 427                         | 0.14  |
| 84g OC$_{10}H_{21}$| 59%   | 323                         | 409                         | 0.54  |
| 84h N(CH$_3$)$_2$  | 39%   | 366                         | 495                         | 0.57  |
| 84i OC$_{10}H_{21}$| 16%   | 348                         | 422                         | 0.48  |

In order to increase the electronic delocalization along each arm, stars with biphenyl and tolanyl groups were prepared by Pd-catalyzed coupling. Tris-4’-decyloxybiphenyl- (84g 53%) and tris(4’-dimethylaminobiphenylyl)- (84h 39%) as well as tris-(4’-decyloxytolanyl)-pyrimidine (84i 16%) have been prepared [255]. Elongation of the $\pi$-system of the arms results in bathochromic shifts of the electronic spectra of $\Delta\lambda \approx 24$ nm for the 84g and $\Delta\lambda \approx 17$ nm for the absorption of 84h, but the emission maximum of the latter is shifted about $\Delta\lambda \approx 67$ nm to the red. The fluorescence quantum yields increased strongly to values of $\Phi = 0.54$ and 0.57. A further increase of the conjugation length by introduction of a triple bond between the benzene rings (84i) results in further red shifts of the absorption ($\Delta\lambda = 25$ nm) and the emission ($\Delta\lambda^F = 13$ nm) and a small decrease of the fluorescence quantum yield ($\Phi = 0.48$).

Absorption and emission properties of pyrimidine based stars with peripheral amino groups are sensitive towards changes of the environment. Compound 84h (biphenyl $\pi$-bridge) with a donor-acceptor structure shows a strongly solvatochromic emission. Increasing the solvent polarity from heptane to DMF results in a bathochromic shift of 146 nm together with a reduction of the fluorescence quantum yield from 0.77 to 0.04. From solutions in methanol, no fluorescence could be detected. Contrary to the highly solvatochromic emission, the absorption maximum shifts only about 19 nm to the red. Addition of TFA to solutions of 84f and 84h results in a strong red shift of the emission of 84f (from $\lambda = 427$ nm to $\lambda = 539$ nm) and a small shift of the emission of 84h ($\Delta\lambda^F = 17$ nm) but the absorption of 84h is shifted to the blue (from $\lambda = 366$ nm to $\lambda = 300$ nm) These shifts are attributed to protonation of the peripheral amino groups of 84f and 84h [255].
In addition to their interesting optical properties, triarylpyrimidines are also electrochemically active compounds. Reversible reduction waves were obtained at $-2.70$--$-2.85$ V (vs. Ag/Ag$^+$), the stars with amino groups showed an irreversible oxidation wave at ca. 0.4 V.

Alkoxy-substituted triphenylpyrimidine derivatives can exhibit hexagonal columnar mesophases. Comparing discs with identical numbers of side chains, those with an unsymmetrical substitution exhibit better mesomorphic properties. The improved LC behavior of the pyrimidine derivatives over the analogous discs with a benzene core is attributed to the greater polarization of N atoms in the ring [259].

**Trialkynylpyrimidines** (*C-8-A-2 and C-8-A-8*): Threefold alkynylation of pyrimidine was not possible via Sonogashira or Negishi coupling, even when triiodopyrimidine was used as substrate. Molander [262] developed a Suzuki coupling of alkynyltrifluoroborates 88 with 2,4,6-trichloropyrimidine 86 and obtained 2,4,6-trihexynylpyrimidine 89a in 70% yield (Scheme 18). Plé successfully applied this method for the synthesis of 2,4,6-tris-(phenylethynyl)pyrimidines, the unsubstituted star 89b (74% yield), its trimethoxy 89c (35%), and tris-(dimethylamino)-substituted derivatives 89d (51%) [263].

**Scheme 18.** Synthesis of 2,4,6-tri(arylethynyl)pyrimidines via Suzuki coupling.

DFT 6-31G* calculations of the geometry of tris-(phenylethynyl)pyrimidines 89 resulted in absolutely planar geometries with enforced conjugation whereas the triphenylpyrimidine derivatives 84 have a twisted geometry with dihedral angles in the range of 8-16°.

The absorption maxima of these compounds are in the UV ($\lambda_{\text{max}} = 335-368$ nm), only the dimethylamino derivative 89g has an absorption maximum in the blue ($\lambda_{\text{max}} = 433$ nm). A comparison with banana-shaped 2,4- and 4,6-bis-(dimethylaminophenylethynyl)pyrimidines revealed bathochromic shifts of $\lambda_{\text{max}}$. The maximum of the emission of these stars is strongly influenced by the donor substitution. A methoxy or dimethylamino group shifts $\lambda_{\text{F}}$ from 370 nm to 406 nm and 522 nm, respectively. But Stokes shift and fluorescence quantum yield increase in the order H< dimethylamino< methoxy. A 3,4,5-trimethoxy-substitution on each phenyl ring (89e) results in the largest Stokes shift (7681 cm$^{-1}$) with $\lambda_{\text{F}}$ = 513 nm in CHCl$_3$.

Compared with the 2,4,6-triphenylpyrimidines 84 [255,260] the elongation of the conjugated system provokes significant red shifts of the absorption and emission spectra (up to 95 nm for the dimethylamino derivatives) and increasing fluorescence quantum yields.

**Tristyrylpyrimidines** (*C-9-A-6*): 2,4,6-Tristyrylpyrimidine 90 has been prepared by base-catalyzed condensation of benzaldehyde with the N-oxide of 2,4,6-trimethylpyrimidine followed by reduction
with PCl$_3$ [264]. Better yields (44%) were obtained using ZnCl$_2$ as catalyst for the condensation of benzaldehyde with 2,4,6-trimethylpyrimidine [265].

**Figure 28.** 2,4,6-Trisstyryl- and 2,4,6-trisstilbenylpyrimidines.

![Figure 28](image)

*Trisstilbenylpyrimidine (C-8-A-7):* Threefold Siegrist reaction of 2,4,6-tris(4-methylphenyl)pyrimidine 84k (R = CH$_3$) with benzalanilines gave 2,4,6-trisstilbenylpyrimidine 91a and tris-4′-phenylstilbenylpyridine 91b in 33% yield [248].

The absorption of 91a has a maximum at $\lambda = 349$ nm (DMF), extension of the $\pi$-system as in 91b resulted in a red-shift, $\lambda_{\text{max}} = 367$ nm.

5.3. Pyrazine as Core (C-10-A-6)

Pyrazine as a core is an electron-deficient center for stars with a $C_{2h}$-symmetry and the shape of St. Andrew’s cross. A multitude of tetraphenylpyrazines substituted with different functional groups has been prepared in the past, the first report about a tetraphenylpyrazine dates back to 1888 [266]. The typical procedure is the condensation of benzils or benzoins with ammonia from different sources. Some of these compounds have been suggested for application in high-temperature functional fluids [267], as photoconductive material for electrophotography [268], or as electron transporting layer in OLEDs [269].

Only a few pyrazines with four identical $\pi$-conjugated branches larger then a phenyl ring are known. The first syntheses of star-shaped-or cruciform-pyrazines with four styryl groups 92a (R$^1 = \text{N(CH}_3\text{)}_2$, R$^2 = \text{H}$) was reported by Takahashi and Satake as part of their search for new photosensitizers [270]. Acid-catalyzed condensation of 4-dimethylaminobenzaldehyde (95a R$^1 = \text{N(CH}_3\text{)}_2$) and tetramethylpyrazine 93 gave the pyrazine 92a with four $p$-dimethylaminostyryl branches as orange-yellow prisms. Similarly, the higher homologue with 4-$p$-dimethylaminophenylbutadienyl branches 92b and the $N,N$-dioxide 92c of the tetrastyryl compound 92a were prepared.
Scheme 19. Condensation of tetramethylpyrazine 93 and benzalanilines 94 or benzaldehydes 95.

4-Substituted tetrastyrylpyrazines 92 (R = H, Cl, CH₃) have been used as emissive layer in OLEDs with the configuration ITO/TPD/92/Alq₃/Mg. High luminescence (1516-4069 cd/m²) was achieved at low dc voltages [271].

Several 2,3,5,6-tetrastyrylpyrazines with alkoxy side chains in the 4-, the 3,4-, or the 3,4,5-positions of the peripheral benzene rings 92d, 92e, 92f have been prepared via Siegrist reaction of tetramethylpyrazine 93 with benzalanilines 94 [272]. An eight-fold hexyloxy substitution of the tetrastyrylpyrazine 92d is sufficient for the formation of a mesophase between 102 °C and 210 °C.

Table 7. Transition temperatures and enthalpies of liquid crystalline tetrastyrylpyrazine cruciforms (DSC, first heating scan).

| Compound         | Transition T ΔH (cal/g) | Transition T ΔH (cal/g) |
|------------------|-------------------------|-------------------------|
| 92d: 3,4-dihexyloxy | Cryst → Col 102 °C (14.0) | Col → i 210 °C (0.4) |
| 92e: 3,4-didecyloxy | Cryst → Col 101 °C (19.3) | Col → i 173 °C (1.5) |
| 92f: 3,4-didodecyloxy | Cryst → Col 95 °C (18.8) | Col → i 172 °C (0.7) |

Tetrastyrylpyrazines with an alkoxy side chain in the p-position of all peripheral benzene rings show a broad absorption spectrum with λmax = 390 nm (CH2Cl2) and a second maximum at λmax = 461 nm. A peripheral 3,4-dialkoxy substitution (e.g., 92d) shifts both maxima about 4 to 7 nm to the red. Further alkoxy groups in all 5-positions provoke an additional small hypsochromic shift (λmax = 389 nm, λ’max = 455 nm) [272]. The fluorescence of tetrastyrylpyrazines with a 4-alkoxy substitution is slightly solvatochromic, increasing solvent polarity shifts the fluorescence maximum from λFmax = 509 nm (cyclohexane) to λFmax = 527 nm (ethanol) [273].

Within this tetrastyrylpyrazine series, compounds substituted with dialkylamino groups in the 4-positions of the benzene ring appear to be most attractive. Several syntheses of these compounds have been reported [185,270,273,274]. Acid- or base-catalyzed condensation of tetramethylpyrazine 93 with dialkylamino benzaldehydes or their aniline derived Schiff bases gives these cruciforms 92a, 92g, in moderate to very good yield.

X-ray analysis of the dimethylamino derivative 92a shows a nearly planar molecule [273], but the two linear distyrylpyrazine subunits are not equivalent (Figure 29). Whereas one shows small dihedral...
angles between the aromatic rings and the vinylene groups of $-0.3^\circ$ and $-177.7^\circ$, the other is more distorted. Torsion angles of $8.6^\circ$ and $174.4^\circ$ have been measured.

**Figure 29.** X-ray structure of 2,3,5,6-tetrakis($p$-dimethylaminostyryl)pyrazine 92a.

The absorption spectrum of 2,3,5,6-tetrakis(4-diethylaminostyryl)pyrazine 92g shows a structured main absorption band with $\lambda_{\text{max}} = 452$ nm and a structureless separate peak at $\lambda_{\text{max}} = 498$ nm. The fluorescence in toluene peaks at $\lambda_{\text{max}}^{F} = 563$ nm with a fluorescence quantum yield of 0.67 [185].

Compared to the linear 2,5-bis-(4-diethylaminostyryl)pyrazine 96, ($\lambda_{\text{max}} = 462$ nm, $\lambda_{\text{max}}^{F} = 518$ nm, $\Phi = 0.77$) the emission is shifted to the red side and occurs only from the lower lying of the two states observed in the absorption spectrum.

A pronounced sensitivity of the fluorescence of tetrakis(dialkylaminostyryl)pyrazines 92a,g was reported [273,274], e. g. the emission maximum of 92a appears in cyclohexane at $\lambda_{\text{max}}^{F} = 535$ nm and in ethanol at $\lambda_{\text{max}}^{F} = 588$ nm.

The two-photon absorption properties of these stars with strong ICT transitions have been studied. Harper reported a two-photon absorption cross-section of $\delta = 1600$ GM at $\lambda = 800$ nm [274]. According to the results from two-photon spectroscopy, Marder et al. [185,275] could show that the TPA properties of the linear 2,5-bis(diethylaminostyryl)-pyrazine 96 and the cruciform 92g are quite similar, a TPA cross-section $\delta_{\text{max}}$ of 1250 GM has been measured for both compounds, the TPA absorption maximum of the linear compound $\lambda_{\text{TPA}}^{\max} = 770$ nm is shifted about 20 nm to the red for the cruciform ($\lambda_{\text{TPA}}^{\max} = 790$ nm). The similar TPA cross-sections of linear and cruciform dye result from a significant coupling of the branches through the common central ring.

5.4. 1,3,5-Triazine as Core

*Triaryltriazines (C-9-A-3):* Within the series of star-shaped oligomers with a heterocyclic core, the 1,3,5-triazine ring C-9 plays the most prominent role. In these stars, the $\pi$-conjugated branches are connected with $C_{3h}$-symmetry to a highly electron-deficient core. Synthetic approaches include the formation of triazines via cyclotrimerization of nitriles, nucleophilic and palladium-catalyzed substitutions on trifluoro- or trichloro-1,3,5-triazines as well as transformations of functional groups in the periphery.
The trimerization of nitriles 97 (Scheme 20) catalyzed by acid [277] or base [278,279] is the classical synthetic strategy for the preparation of symmetrically substituted 2,4,6-triaryl-1,3,5-triazines 98. Recently, coupling reactions of organometallic reagents with cyanuric chloride 101a (Scheme 21), direct [280] and palladium-catalyzed [255,281,282], have become the preferred way.

**Scheme 20.** Cyclotrimerization of benzonitriles.

Tris-(4-hydroxyphenyl)-1,3,5-triazine 98a was prepared from p-hydroxybenzonitrile 97a using trifluoromethane sulfonic acid in 93% yield. Alkylation of the hydroxy groups with 3,5-di- and 3,4,5-trialkoxybenzylchlorides 99a, b gave star-shaped compounds 98b, c [277]. Contrary to the pure tris-tridodecyloxybenzyl substituted compound 98c, its orange-red CT complex with trinitrofluorenone forms a columnar mesophase between 50.6 °C and 101.5 °C (first heating scan) which remains stable at room temperature.

3,4,5-Trialkoxybromobenzenes were converted to the boronic acids 100a, b and threefold Suzuki coupling reactions with cyanuric chloride 101a in toluene gave the triphenyltriazine 98d with nine decyloxy side chains in 52% yield and the isomer 98e with (3S)-3,7-dimethyloctyl side chains in 33% yield [281]. Both compounds show enantiotropic LC behavior with mesophases from 36 to 145 °C (98d) and −15 °C to 56 °C (98e) on heating. According to the textures observed in POM and to X-ray diffraction, the former star exists in a hexagonal columnar mesophase whereas the LC phase of the latter has a rectangular columnar structure.

UV-vis absorption shows a broad absorption band at 318 nm. A strong circular dichroism of 98e suggests that the discotic molecules are stacked along the columns, while tilted with respect to the column axis, to form a left-handed helix within the column. The non-centrosymmetric arrangement of these discs should result in nonzero bulk second order NLO properties.

The threefold Suzuki coupling of 4-dimethylaminobenzeneboronic acid 100c with cyanuric acid chloride using Cs₂CO₃ as a base provided 2,4,6-tris-(4-dimethylaminophenyl)-1,3,5-triazine 98f in 42% yield [255]. In CHCl₃ the absorption maximum appears at 368 nm and the fluorescence maximum at 419 nm with a quantum yield of Φ = 0.15.
Scheme 21. Synthesis of 2,4,6-triaryl-1,3,5-triazines 98d, e, f via Suzuki coupling.

Fujita [278] used drastic conditions (NaOH, 200 °C, 36h, Scheme 22) for the oligomerization of \(N,N\)-di-(p-cyanophenyl)-\(N\)-methylamine 97b, giving a mixture of branched oligomers including 11\% of the star-shaped compound 98g. The absorption spectrum is dominated by a long-wavelength ICT band with \(\lambda_{\text{max}} = 387\) nm-about 100 nm at longer wavelengths compared with the analogous stars without peripheral amino groups. Though intramolecular charge transfer occurs, the compounds show a negligible solvatochromism. A pronounced acidochromism results from the successive addition of trifluoroacetic acid: in the first step, a new maximum at \(\lambda_{\text{max}} = 480\) nm appears-attributed to protonation of the triazine core and therefore enhanced acceptor strength. At higher TFA concentrations a third compound with \(\lambda_{\text{max}} = 577\) nm appears, changing the solution from colorless (neutral) and orange (10\% TFA) to wine-red (60\% TFA). The authors suggest a protonation on the nitriles. An intense blue fluorescence (\(\lambda_{\text{F max}} = 434\) nm, \(\Phi = 0.66\)) is emitted from neutral solutions, bathochromic shifts occur in protic solvents and acids efficiently quench the fluorescence.

Scheme 22. Base-catalyzed trimerization of dinitrile 97b.

The trifluoromethane sulfonic acid catalyzed cyclotrimerization of \(p\)-bromobenzonitrile 97c to 2,4,6-tris-4-bromophenyl-1,3,5-triazine 98h has become a key step in the preparation of stars with a 1,3,5-triazine core [275,282-285].

Lithiation of the tribromo compound 98h and addition of 2-methyl-2-nitrosopropane 102 followed by Ag\(_2\)O oxidation gave the triradical 98i in 77\% yield (Scheme 23). The triangular triradical shows dihedral angles between the phenyl rings and the central triazine units of 9.96, 10.29 and 5.37°, respectively. In solution, 98i gives an EPR signal with a seven-line hyperfine structure at \(g = 2.0061\).
suggesting that the exchange interaction is larger than the hyperfine coupling [275]. Compared to the analogous triradicals with a benzene core, 98i exhibited stronger intramolecular ferromagnetic interaction than the benzene analogue.

Scheme 23. Synthesis of 98i, a triazine-based triradical.

2,4,6-(Tris-diethylaminophenyl)-1,3,5-triazine 98k was prepared by the reaction of 4-lithio-N,N-diethylaniline and 101a in 20% yield [280]. The strong donor effect of the diethylamino group is visible in the UV-vis spectrum as $\lambda_{\text{max}} = 375$ nm (acetone) and gives a large second-order polarizability (hyper-Rayleigh-scattering) with $\beta = 162 \times 10^{-50}$ Cm$^3$V$^{-2}$, six times larger than that of $p$-nitroaniline ($\beta = 27.4 \times 10^{-50}$ Cm$^3$V$^{-2}$).

The first hyperpolarizabilities of symmetrically substituted 1,3,5-triazines are higher than those of corresponding octupolar benzenes [286]. The triazine ring seems to be a better acceptor than the benzene ring but if it acts as a donor as in symmetrically substituted triphenyltriazines the nonlinearity improves further. \textit{Ab initio} calculations (HF/6-31G) of donor-substituted 2,4,6-triphenyl-,2,4,6-tristyryl-, and 2,4,6-tris(phenylbutadienyl)-1,3,5-triazines resulted in planar structures and significant $\beta$ values [287].

98h is a suitable substrate for three-fold copper-catalyzed N-arylations, e.g., with 7-azaindole [288]. Ullmann reaction with di-2-pyridylamine gave a star 98l with triarylamine branches in 60% yield. This compounds has a melting point at 267 °C, DSC shows a glass transition at 121 °C, and a second heating scan revealed a broad crystallization peak around 180 °C [289].

The UV absorption appears with a double maximum at $\lambda = 322$ and $\lambda = 386$ nm and the blue fluorescence, both, from solution or the solid state, has a maximum at $\lambda^F_{\text{max}} = 440$ nm ($\Phi = 0.78$).

In diodes with the configuration ITO/CuPc/98l/PBD/LiF/Al blue light was emitted with a turn-on voltage of 15 V. This turn-on voltage is higher than that of the analogous compound with a benzene core, probably due to poor electron/hole mobility.

2,4,6-Tris-4-pyridyl-1,3,5-triazine 103 has been prepared by base-catalyzed (KOH/18-crown-6, decaline, 200 °C) cyclotrimerization of 4-cyanopyridine [279]. It has been used as a tridentate ligand in supramolecular nanocages [290] and 2,4,6-tripyridyl-1,3,5-triazines have been found to be efficient materials for electron injection layers in transparent OLEDs [291].
Triazines with Biaryl Arms (C-9-A-3): **98h** is a key compound for the synthesis of triazines with biaryl branches [292-294]. 2,4,6-tris(4-(4-pyridyl)phenyl)-1,3,5-triazine **98n** was obtained in 66% yield via Stille coupling with 4-pyridylstannanes in the presence of LiCl [292].

Threefold Suzuki coupling reactions of **98h** (Scheme 24) with benzeneboronic acids **100d-h** substituted in the 4-position with phenyl, 2,4-difluorophenyl, 1- and 2-naphthyl or pyrene gave the star-shaped compounds **98o-s** in good yields [293].

The half-wave reduction potentials of these compounds are close to –2.1 V (vs. Fc/Fc+) suggesting that the electron affinity of the triazine core is only slightly affected by the terminal groups. The 1-naphthyl derivative **98p** possesses a high glass transition temperature at 133 °C, time-of-flight measurements on vacuum-deposited films of this star showed a high electron drift mobility of \(8 \times 10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) at 25 °C, therefore, this compound is an attractive amorphous glassy electron transporting material.

Wang described a 2,4,6-tris-biphenyltriazine star **98t** with six N-indolyl groups on the 3,5-positions of the terminal rings [288]. The key step for the synthesis is a Suzuki coupling of the 3,5-bis(N-indolyl)benzeneboronic acid **100i** with **98h** (61%). DSC reveals that this star has a glass transition at 175 °C, the melting point is above 330 °C. In CH₂Cl₂, the long-wavelength absorption band appears at \(\lambda = 306 \text{ nm}\) and the fluorescence with \(\lambda_F^{\max} = 481\). The analogous compound with a benzene core has a similar absorption, but hypsochromically shifted emission (\(\lambda_F^{\max} = 427 \text{ nm}\)) due to a reduced charge transfer.

The inverted functionalization, a central trisboronic acid **98u** and 5-bromoquinolines **104a, b** as coupling partners proved to be suitable for the synthesis of stars **98v, w** with a 8-alkoxyquinoline periphery (Scheme 24) [294]. The absorption maximum of **98v** with three 8-methoxyquinoline end groups appears at \(\lambda = 340 \text{ nm}\) and the emission peaks at \(\lambda_F^{\max} = 443 \text{ nm}\) (CH₂Cl₂, \(\Phi = 0.63\)), characterized by a strongly positive solvatochromism. The electrochemical oxidation of this compound occurs at 1.51 V (vs. AgCl/Ag) and the quasi-reversible reduction at –1.73 V. Star **98x** with unprotected 8-hydroxy groups forms complexes with triphenylboron. Complexation shifts absorption and emission spectra about \(\Delta\lambda \approx 80 \text{ nm}\) to longer wavelengths.

Acid-catalyzed cyclotrimerization [289] of 4-bromo-4’-cyanobiphenyl **97d** gives 2,4,6-tris(4’-bromobiphenyl)-1,3,5-triazine **98y** (80%). Using a Cu-catalyzed Ullmann reaction with 2-(2’-pyridyl)benzimidazole **105**, triazine-based star **98z** with three chelating pyridylbenzimidazole end groups was obtained in 68% yield [295]. After complexation with ruthenium, **98z** was used in red light-emitting devices.

Lithiated 2-bromo-7-diphenylamino-9,9-dialkylfluorenes **106a-c** reacted with cyanuric fluoride **107** to the tris-(diphenylaminofluorenyl)-1,3,5-triazines (Scheme 25) with six allyl (**98aa**), 3,7-dimethyloctyl (**98ab**) or decyl groups (**98ac**) in 51 to 60% yield [296]. The UV-vis absorption of these aminofluorene stars peaks around 413 nm and emission shows maxima between 500 and 518 nm with high quantum yields (\(\Phi \approx 0.47\)). The two-photon absorption cross-sections (excitation at \(\lambda = 800 \text{ nm}\)) were found to be in the range of 278-395 GM, compounds with longer aliphatic chains gave higher cross-sections.
Scheme 24. Synthesis of tris(biaryl)triazine stars via Suzuki coupling.

\[
\begin{align*}
\text{Ar-B(OH)₂} & \\
\text{Pd(PPh₃)₄} & \\
\text{Na₂CO₃} & \\
98h & \\
\end{align*}
\]

100 d - h

\[
\begin{align*}
\text{E = phenyl} & \\
\text{E = 1-naphthyl} & \\
\text{E = 2-naphthyl} & \\
\text{E = 1-pyrenyl} & \\
\text{E = 2,4-difluorophenyl} & \\
\end{align*}
\]

Scheme 25. Triazin-star 98z with chelating pyridyl-benzimidazole periphery.

\[
\begin{align*}
\text{F₃CSO₃H} & \\
\text{CuI, Cs₂CO₃} & \\
\text{phenanthroline} & \\
97d & \\
98y & \\
98z & \\
\end{align*}
\]

The photophysical properties of star 98ab were thoroughly analyzed by Rogers [297]. A slight solvatochromism of the absorption spectrum (e.g., in hexane $\lambda_{max} = 418$ nm, in THF $\lambda_{max} = 414$ nm) and a strong solvatochromism of the fluorescence (hexane: $\lambda^f_{max} = 432$ nm, $\Phi = 0.75$; 2-propanol $\lambda^f_{max} = 516$ nm, $\Phi = 0.25$) was observed. In hexane, the fluorescence occurs predominantly from the
S	extsubscript{1} state, in more polar solvents, the emission occurs from both, the S	extsubscript{1} and the \(^1\)ICT state. Ultrafast transient absorption spectra revealed a multiexponential decay. In the presence of methyl iodide (20% in methylcyclohexane) a phosphorescence with \(\lambda_{\text{Ph}}^\text{max} = 546\) nm was detected. \(98\text{ab}\) has a triplet excited-state absorption in the region of 800 nm that enhances the effective two-photon absorption cross-section.

**Scheme 26.** Triazine-stars with fluorene branches.

![Scheme 26](image)

Tris-(spirobiphenyl)-1,3,5-triazine \(98\text{ad}\), an electron transport host materials for green phosphorescent OLEDs, has been prepared by the acid-catalyzed cyclotrimerization of 2-cyano-9,9\(^{\prime}\)-spirobifluorene \(97\text{e}\) in 63% yield [298]. The time-of-flight electron mobility was higher than \(10^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). A relatively low triplet energy of 2.54 eV and a HOMO energy level of 5.69 eV (PES) were found. An OLED with \(98\text{ad}\) as electron transporting material and (PPy)\(_2\)Ir(acac)/1,3,5-tris-N-benzimidazolylbenzene gave only a low external efficiency of 5.1%.

Some triazine stars carrying heterocyclic biaryl branches exhibiting interesting optical and nonlinear optical properties have been prepared by triple nucleophilic aromatic substitution of \(\alpha\)-lithiated bithiophenes and cyanuric chloride in up to 90% yield [299]. Also the Stille coupling [300] proved to be useful.

**Triazines with Three Stilbene Arms (C-9-A-7):** Threefold condensation of 2,4,6-tris(4-methylphenyl)-1,3,5-triazine \(98\text{ae}\) with benzalaniline \(78\text{g}\) has been developed by Siegrist [248] for the synthesis of trisstilbényl-1,3,5-triazine \(108\text{a}\) and derivatives \(108\text{b-e}\) with substituents in the 4\(^{\prime}\)-positions of all stilbene arms in 14-35% yield (Scheme 27) The absorption spectrum of \(108\text{a}\) has a maximum at \(\lambda = 360\) nm (DMF). Whereas a chlorosubstitution in the 4\(^{\prime}\)-positions of all stilbene units \((108\text{b})\) provokes only a small hyperchromic effect, donor-substitution \((108\text{c}: 4^{\prime}\)-phenoxy, \(\lambda_{\text{max}} = 380\) nm) or extension of the conjugated system \((108\text{d}: 4^{\prime}\)-phenyl, \(\lambda_{\text{max}} = 375\) nm) led to significant red shifts of the absorption spectrum.
Scheme 27. Three-fold Siegrist and Horner olefinations to tristilbenyltriazines.

Similarly, a three-fold Siegrist reaction was used by Tian [301] for the synthesis of a tristilbenyltriazine star 108e with three peripheral N-4-methoxyphenyl-N-phenylamino groups (50% yield). An absorption peak at $\lambda = 312$ nm corresponds to a localized excitation, the band centered at $\lambda = 430$ nm to a $\pi-\pi^*$ transition of the whole molecule. Compared to stars with only one or two stilbene arms absorption and emission suffer minor shifts to lower energies. The absorption of star 108e is slightly solvatochromic, a red-shift of 7 nm in DMSO was recorded. Upon irradiation at $\lambda = 415$ nm, an intense fluorescence was emitted, with $\lambda^F_{\text{max}}$ at 550 nm in CHCl$_3$ ($\Phi = 0.47$) and hypsochromically shifted-with $\lambda^F_{\text{max}} = 530$ nm in DMSO [302]. The state responsible for the photoluminescence is the ICT state. The transient absorption shows a biexponential decay with much higher decay rates in DMSO. The long decay time is attributed to the lifetime of the ICT state, and the shortening of the decay time was explained by a TICT model. From Z-scan measurements the TPA cross-section $\sigma_2$ at $\lambda = 800$ nm was calculated to be $\sigma_2 = 410$ GM and therefore five times higher than the triazine with only one stilbene unit. The two-photon excited emission is located at $\lambda^\prime_{\text{max}} = 577$ nm.

An independent approach for the synthesis of triazine stars with three arylethenylphenyl branches has been reported by Martín [303]. The triflic anhydride catalyzed cyclotrimerization of $p$-bromomethylbenzonitrile 97f followed by Michaelis-Arbuzov reaction gave a triphenyltriazine 98af with three methylenephosphonate groups as useful building block. Threefold Horner reaction with formylferrocene or formyltetrathiafulvalene resulted in redoxactive stars 108f, g in 45% and 23% yield.

Ferrocene-star 108f absorbs with $\lambda_{\text{max}} = 484$ nm (CHCl$_3$) and the TTF-star 108g with $\lambda_{\text{max}} = 471$ nm (CHCl$_3$). The intramolecular charge transfer in 108f was confirmed by solvatochromic studies, a positive solvatochromic shift of 25 nm was recorded from hexane to ethanol. Both stars show an amphoteric redox behavior, with the oxidation features of the donor moieties and the reduction of the triazine acceptor. A significant electronic communication between the triazine and the TTF was observed.
Tris(ethynylaryl)triazines (C-9-A-9): 1,3,5-Triazines with three tolane branches 109 were successfully prepared by threefold Sonogashira-Hagihara cross-coupling reactions on tris-(p-bromophenyl)-1,3,5-triazine 98h. The stepwise approach (coupling with TMS-acetylene to 109a (E = TMS), deprotection to tris(ethynylphenyl)-1,3,5-triazine 109b (E = H) and second coupling of the deprotected star with iodoarenes [282] as well as the direct coupling with phenylacetylenes 110a-g [283-285] have been used (Scheme 28).

An X-ray structure analysis of 2,4,6-tris-(4'-cyanotolanyl)-1,3,5-triazine 109c reveals a non-planar structure with a sphere-surface like shape. The average deviation of the atoms from the mean plane of the molecule is 0.789 Å [284]. The UV-Vis spectrum of 2,4,6-tris-(4'-cyanotolanyl)-1,3,5-triazine 109c peaks at 353 nm and a sharp emission peak is observed at $\lambda_F = 386$ nm.

Tris-tolanyl-1,3,5-triazines with three peripheral alkoxy side chains (109d-i) have been prepared by Lee and Yamamoto [285]. Chains lengths of 6, 10, 12, 14, and 16 carbons as well as (S)-2-methylbutyl were investigated. Whereas the compounds with short linear or chiral side chains 109d, i are not liquid crystalline materials, the stars with the longer chains exhibited columnar hexagonal disordered mesophases (Colhd). Stars with decyl (109e) or dodecyl chains (109f) showed a transition into a smectic phase at 57 °C and 116 °C, followed by a transition into a Colhd phase at 67 °C and 124 °C and a transition into the isotropic melt at 141 °C and 129 °C. Upon cooling, all transitions were shifted about 5-10 °C to lower temperatures. The homologs with longer chains 109g, i showed transitions to their Colhd phases at 66 °C (109g) and 105 °C (109h) and into the isotropic phases at 105 °C and 116 °C.

The UV-vis absorption of tris-(4'-alkoxytolanyl)-triazine stars 109d-i peaks at $\lambda = 360$ nm and the fluorescence maximum appears at $\lambda_F = 432$ nm (CHCl$_3$; $\Phi = 0.85$). In cast films, the absorption and emission spectra are shifted to longer wavelengths (typically $\lambda_{max} = 385$ nm, $\lambda_F_{max} = 491$ nm). Due to the high quantum yields and the stability, these compounds have a potential applicability as laser dyes.

Analogous tris-tolanyl-1,3,5-triazines 109k-o with six peripheral alkoxy side chains of 9-14 carbon length on the 3,4-positions of the outer benzene rings were investigated as LC materials. Only compounds with decyl 109l or undecyl chains 109m showed mesogenic properties. Transition into the columnar hexagonal disordered mesophase occurred at 85.6 °C (109l) and 92.0 °C (109m) and to the isotropic liquid at 99.4 °C and 102.7 °C, respectively. Compared to the related compounds with only one alkoxy group in the 4-position of the peripheral rings 109e, f, the electronic transitions are shifted to lower energies. Dissolved in CHCl$_3$, their UV-vis absorption peaks at $\lambda_{max} = 365$ nm and their fluorescence at $\lambda_F_{max} = 476$ nm. Cast films showed similar absorption maxima but shifts of the emission about 30 nm to the red. These shifts are associated with the formation of excimer-like adducts.

A threefold Pd-catalyzed coupling of tris-(ethynylphenyl)-1,3,5-triazine 109b with an p-iodophenyl benzoate carrying tolyloxy esters in the 3- and 5-positions gave star-burst compounds with a tris-tolanyl-1,3,5-triazine core and branched tolanylester groups 109p-s [282]. Liquid-crystalline phases with columnar hexagonal disordered structure (POM) were obtained between 132 °C (cryst. to mesophase) and 229 °C (mesophase to isotropic) depending on the nature of the peripheral alkoxy side chains.
Scheme 28. Synthesis of tris-tolanyl-1,3,5-triazines via Sonogashira cross-coupling reactions.

Tristyryltriazines (C-9-A-6): The first report of a 2,4,6-tristyryl-1,3,5-triazine 111a \((R_{1-3} = H)\) dates back to 1953 [304]. Changing the original conditions for the threefold condensation of 2,4,6-trimethyl-s-triazine 112 with benzaldehyde from KOH/methanol to concentrated sulfuric acid as dehydrating agent by Elias [305] increased the yield from 31% to 99% of analytically pure material. Nevertheless, the base-catalyzed aldol condensation is the generally applied strategy for the synthesis of tristyryl-substituted

1,3,5-triazines 111. Higher homologues are accessible either via Horner olefination of a tristyryltriazine carrying methylene phosphonates on the benzene rings \((111b \; R^1 = R^3 = H, R^2 = CH_2PO(OEt)_2)\) or, generally more efficient, via direct aldol condensation of 112 and stilbenoid aldehydes 107 [306].

The acceptor effect of the triazine causes an intramolecular charge transfer which results in a bathochromic shift of the lowest-energy transition. The parent tristyryltriazine 111a has an absorption at \(\lambda = 327\) nm, the methoxy derivative 111c at \(\lambda = 356\) nm and the dimethylamino derivative 111d at \(\lambda = 425\) nm \((CH_2Cl_2)\).
Scheme 29. Threefold aldol-condensations of 2,4,6-trimethyl-1,3,5-triazine.

| R¹  | R²  | R³  | yield | reagent   | λ_max |
|-----|-----|-----|-------|-----------|-------|
| 111a | H   | H   | H     | 99%       | H₂SO₄ | 327   |
| 111c | H   | OCH₃| H     | 94%       | KOH/CH₃OH | 356 |
| 111d | H   | N(CH₃)₂| H | 39%     | KOH/CH₃OH | 425 |
| 111e | H   | OC₈H₁₇| OC₈H₁₇| 82%   | KOH/CH₃OH | 366 |
| 111f | OC₈H₁₇| OC₈H₁₇| OC₈H₁₇| 87%   | KOH/CH₃OH |
| 111g | H   | H   | CH₃  | 96%       | KOH/CH₃OH |

2,4,6-Tristyryl-1,3,5-triazines 111 with 3, 6, or 9 peripheral alkoxy side chains (linear and branched) are disc-like molecules which can exhibit a regular aggregation by π-stacking and by the interaction of the side chains. Whereas three side chains, irrespective of their length, are not sufficient for the formation of thermotropic liquid crystals, six octyloxy side chains (111e) result in the formation of a narrow mesophase (75°-82 °C) [307]. The compounds with nine linear hexyloxy side chains (111h) shows transition temperatures Tₘ = 68.4 °C and Tₑ = 112 °C. Elongation of the side chains gives a minimum of the transition temperatures for 9 decyloxy groups (111i) with Tₘ = -23 °C and Tₑ = 90 °C. Further elongation results in an increase of Tₘ = 50.3 °C for hexadecyloxy (111k), but Tₑ is lowered to 77.9 °C. All mesophases were recognized as hexagonal columnar phases Colhd. The star with nine hexyloxy side chains 111h exists in the solid state in a helical columnar arrangement, which is transformed to disordered hexagonal columns in the mesophase.

Irradiation (λ = 366 nm) in the mesophase of tristyryltriazines with nine alkoxy groups 111f, h-k provokes partial cyclodimerization reactions which cause lower clearing points. Since the diffusion processes of the dimers are very ineffective, the borderline between the irradiated and the original LC phase is preserved, even in the molten state. In the solid state, the compound proved to be photostable, dimerization occurs only if the mobility of the molecules is enhanced, e.g., in the mesophase. Thus, the compounds seem to be suitable for an optical data storage in LC materials.
Meier et al. [112] prepared tris(styrylstyryl)-1,3,5-triazines 111l, m with a unique substitution pattern (Scheme 30): the alkoxy side chains are attached to the 2,5-positions of the inner rings of the conjugated arms and not in the periphery of the molecules. These compounds exhibit nematic mesophases 111l: \( T_g = 95 \, ^\circ\text{C} \) \( N_D \) and \( T_c = 107 \, ^\circ\text{C} \) and 111m between 210 \(^\circ\text{C} \) and 236 \(^\circ\text{C} \). The peripheral cyano groups on 111m lead to an acceptor-donor-acceptor character resulting in a strong increase of the phase transition temperatures. The undercooling and the \( \Delta H \) high values of 35 kJmol\(^{-1} \) (111l) and 49.8 kJmol\(^{-1} \) for the isotropization indicate \( N_{\text{col}} \) phases.

The LC phases are light-sensitive, irradiation with UV (\( \lambda = 366 \) nm) or daylight leads to a breakdown of the mesophases due to intermolecular C-C-bond formation generating cross-linked oligomers and polymers. This can be useful for imaging techniques with liquid crystals. In the crystalline state irradiation provokes a chemoselective \([2\pi + 2\pi]\) cycloaddition between the inner, more polar double bonds with a head-to-tail regioselectivity and stereoselective syn arrangement and a preservation of the trans configuration from the olefinic double bonds in the cyclobutanes.

**Scheme 30.** Synthesis of triazine stars with alkoxy groups in the inner sphere.

The extension of the \( \pi \)-conjugated system in a homologous series of tris(oligostyryl)-1,3,5-triazines (Scheme 31) 111n-q with a peripheral 3,4,5-trialkoxy substitution leads to a systematic bathochromic and hyperchromic effect (\( n = 1: \lambda = 367; n = 2: \lambda = 398; n = 3: \lambda = 414; n = 4: \lambda = 420 \) nm; \( n = \) styryl units per arm) [306]. The convergence limit, calculated on the basis of exponential functions [28] is predicted as 427 ± 3 nm. The analogous stars 111t-v with a stronger \( p \)-dihexylamino donor and one to three styryl units per arm (\( n = 1-3 \)) behave different [308].
Scheme 31. Homologous series of donor-substituted tris(oligostyryl)triazines.

![Chemical structure](image)

| R¹ | R² | n | yield | λ<sub>max</sub> /nm (CH₂Cl₂) | λ'<sub>max</sub> /nm |
|----|----|---|-------|-----------------|-----------------|
| OC₆H₁₃ | OC₆H₁₃ | 0 | 79%   | 367             |                 |
| OC₆H₁₃ | OC₆H₁₃ | 1 | 61%   | 398             |                 |
| OC₆H₁₃ | OC₆H₁₃ | 2 | 44%   | 414             |                 |
| OC₆H₁₃ | OC₆H₁₃ | 3 | 15%   | 420             |                 |
| H   | N(CH₃)₂ | 0 |       | 438 (CHCl₃)    | 518             |
| H   | N(CH₃)₂ | 1 | 34%   | 457             |                 |
| H   | N(CH₃)₂ | 2 | 3%    | 442             |                 |

The unsubstituted 2,4,6-tristyryl-1,3,5-triazine 111a has an absorption maximum in the UV (λ = 327 nm), the absorption spectra of compounds with amino end groups 111r-v are strongly shifted to the red due to an intramolecular charge transfer from the amino groups to the acceptor core. This ICT depends strongly on the distance of lateral donors and the central triazine ring (n = 1: λ<sub>max</sub> = 442 nm; n = 2: λ<sub>max</sub> = 457 nm; n = 3: λ<sub>max</sub> = 442 nm).

The transition energy ΔE(S₀→S₁) of push-pull oligomers is lowered by the extension of the conjugation and by the ICT. Both effects are superimposed and can lead to four different functions λ<sub>max</sub>(n) where n represents the number of repeat units in a conjugated oligomer series [14]

a) ΔE (n+1) < ΔE (n) monotonous bathochromic shift
b) ΔE (n+1) > ΔE (n) monotonous hypsochromic shift
c) ΔE (n+1) ≈ ΔE (n) borderline case between a) and b)

a) ΔE goes through a minimum for a certain n

The fifth case, in which ΔE passes a maximum for a special n is still unknown.

The series 111t-v belongs to category d) [308]. The decrease of the ICT with increasing conjugation length provokes a hypsochromic effect which cannot be compensated for n = 3 by the bathochromic effect caused by the extension of the conjugated system. This result is in contrast to the analogous stars with terminal alkoxy groups 111n-q, which belong to category a) [307]. Alkoxy groups are weaker electron donors than dialkylamino groups; therefore the extension of the chromophores can overcompensate the decrease of the ICT.
The absorption of 111t-v depends unusually strongly on the concentration. This deviation from Lambert-Beer law is attributed to a pronounced aggregation even at concentrations as low as $5 \times 10^{-5}$ M. The J-aggregates formed absorb with higher $\lambda_{\text{max}}$ and lower $\varepsilon$.

An important point concerns the influence of protic media. An addition of trifluoroacetic acid to solutions of alkoxy-substituted stars 111n-q causes bathochromic shifts of about 82-93 nm of the absorption maximum due to protonation on the central triazine ring and enhanced ICT [306].

Protonation of amino groups should lead to a disappearance of their donor character, whereas protonation of the 1,3,5-triazine ring enhances the acceptor capability. Thus, protonation can strengthen or weaken the push-pull effect depending on the preferred site. The protonation behavior of tris(dialkylaminostyryl)-triazines 111t-v has been investigated by NMR spectroscopy: A preservation of $C_3$ symmetry indicates a fast exchange of protons.

Star 111t is first protonated on the 1,3,5-triazine ring resulting in a strong bathochromic shift of the absorption maximum (CH$2$Cl$2$: $\lambda_{\text{max}} = 564$ nm, 111t/TFA = 1/2.8: $\lambda_{\text{max}} = 564$ nm). A large excess of trifluoroacetic acid turns the violet solution colorless with a $\lambda_{\text{max}} = 373$ nm. The higher homologue 111u behaves totally different: The first protonation occurs at the amino groups and causes a hypsochromic shift ($\lambda_{\text{max}} = 394$ nm), and a high excess of TFA gives rise to a strong band with $\lambda_{\text{max}} = 451$ nm. 111v behaves similar, a hypsochromic shift ($\lambda_{\text{max}} = 412$ nm) is followed by a bathochromic shift ($\lambda_{\text{max}} = 485$ nm) upon further protonation. Indications for aggregation of protonated 111t have been found.

Theoretical studies (ab initio coupled Hartree-Fock) on 1,3,5-triazine and 2,4,6-trivinyl-1,3,5-triazine 113 resulted in second-order polarizabilities of $|\beta| = 64.7 \times 10^{-32}$ esu for $s$-triazine and $|\beta| = 2110.1 \times 10^{-32}$ esu for 113. Similarly, the extension of the conjugated system results in a strong enhancement of the third-order polarizability from $<\gamma> = 2304.5 \times 10^{-39}$ esu for $s$-triazine to $<\gamma> = 29,381.7 \times 10^{-39}$ esu for 113 [309]. Ab initio calculations (HF/6-31G) [287] of a series of donor-substituted 2,4,6-triphenyl- (98), 2,4,6-tristyryl- (111a) and 2,4,6-tris(phenylbutadienyl)-1,3,5-triazines (114) revealed that the first hyperpolarizabilities increases with the conjugation length, probably because the electronic charge becomes more delocalised and the HOMO-LUMO energy gap and the bond length alternation decrease with variation of the chromophore structure. Also, the susceptibility of $\beta$ to the donor strength (e.g., methyl, methoxy, dimethylamino) is found to be larger for the more elongated substrates.

The second harmonic generation of 2,4,6-tristyryl-1,3,5-triazine was studied by Fang [310]. 111a in acetonitrile absorbs with $\lambda_{\text{max}} = 322$ nm, no absorption above 370 nm was observed. Upon irradiation with a laser beam ($\lambda = 1064$ nm) a SHG signal was detected with an efficiency 1.8 times higher than that of urea.

According to a X-ray analysis, the molecule adopts the shape of a slightly curved planar triangular kite with a molecular three-fold rotation symmetry. The rings are essentially planar, but all vinylene linkages are disordered. Nearly all bond lengths are between that of typical C-C or C-N single and C = C or C = N double bonds. A non-centrosymmetric packing of four molecules in the unit cell is believed to be the main origin of optical nonlinearity.

According to PM3 calculations, tris-(p-diethylaminostyryl)-1,3,5-triazine 111s takes a planar $C_{3h}$ conformation [311]. The absorption maximum in CHCl$_3$ appears at $\lambda = 438$ nm, the emission maximum at $\lambda^E = 518$ nm. Comparing this star with compounds having only one or two arms,
absorption and emission maxima shift about 18 nm to the red with increasing number of arms. Upon irradiation with $\lambda = 1064$ nm, no SHG effects were detectable. Two-photon absorption and two-photon excited fluorescence were studied at the excitation wavelength of 800 nm. TPEF is similar to SPEF and the two-photon absorption cross-section at 800 nm amounts to 671 GM. The structurally related 1,3,5-tricyano-2,4,6-tris-(4-aminostyryl)benzenes [312] show two-photon absorption maxima in the range of $\lambda_{\text{TPA max}} = 840-990$ nm with TPA cross-sections around 1400 GM at $\lambda_{\text{exc}}$.

The absorption maximum of 2,4,6-tris-(4-dimethylaminostyryl)-1,3,5-triazine $111r$ in CHCl$_3$ appears at $\lambda_{\text{max}} = 426$ nm and the fluorescence at $\lambda_{\text{F max}} = 511$ nm ($\Phi = 0.066$) [313]. In THF, a negative solvatochromism shifts the absorption to $\lambda_{\text{max}} = 418$ nm, but the fluorescence is bathochromically shifted to $\lambda_{\text{F max}} = 516$ nm ($\Phi = 0.033$) [314]. Two-photon absorption cross-sections of $\sigma = 534$ GM in CHCl$_3$ [313] and of $\sigma = 2405$ GM in THF at $\lambda_{\text{exc}} = 800$ nm [314] were reported. The analogous star with piperidine end groups $111w$ shows a $\sigma = 2523$ GM in THF. Comparing triazines with one, two or three aminostyryl branches, the increase of the extinction coefficients and the TPA cross-sections is about 1:2.6: 4 and 1:3.5: 7 indicating a large cooperative enhancement relative to the number of branches 1:2: 3.

Trialkynyltriazines (C-9-A-2 and C-9-A-8): the synthesis of trialkynyl-1,3,5-triazines 115 (C-9-A-2) and 116 (C-9-A-8) appears to be a special challenge. These stars are generally prepared from lithium acetylides 117 and require cyanuric fluoride 101b as coupling partner. Nevertheless, only moderate yields [315] were obtained. The palladium-catalyzed coupling of alkynylstannanes 118, introduced by Faust [316], allows the use of cyanuric chloride 101a and gives similar yields.

**Scheme 32.** Synthesis of triethynyl-1,3,5-triazine 115b via nucleophilic substitution.

By reaction of cyanuric fluoride 101b with lithium trimethylsilylacetylide 117a, a highly soluble triyne 115a was isolated in 55% yield. X-ray structure determination of this compound shows parallel sheets of individual planar molecules with small distortions of the triazine ring due to packing effects [315]. Desilylation results in 2,4,6-triethynyl-1,3,5-triazine 115b [317]. Sublimed 115b crystallizes in a layered structure. The triethynyltriazine molecules are connected by self-complimentary hydrogen bonding. All triazine-N atoms participate in short and linear CH-N contacts with a neighboring alkyne forming a unique two-dimensional hexagonal structure. The interplanar separation of 3.23 Å is shorter than that of graphite (3.4 Å) and therefore, there would be significant $\pi$-stacking interaction between the layers of 115b.

A tris(phenylethynyl)1,3,5-triazine with three dodecyloxy groups on the 3,4,5-positions of each benzene ring 116a has been prepared by Meijer [318] in 23% yield from the lithio salt of the
phenylacetylene $117b$ and $101b$ (Scheme 333). This star shows a LC phase between 22.9 °C and 60.3 °C (DSC and POM). The X-ray diffraction pattern was unlike those seen for other discotic molecules, but an exact determination was not possible. Bathochromic shifts of the excitation ($\lambda_{\text{max}} = 358$ nm in hexane, $\lambda_{\text{max}} = 370$ nm in CHCl$_3$) and fluorescence spectra ($\lambda_{\text{Fmax}} = 399$ nm in hexane, $\lambda_{\text{Fmax}} = 514$ nm in CHCl$_3$) with increasing solvent polarity indicate a strong charge transfer in the excited state.

Scheme 33. Synthesis of 2,4,6-tris(phenylethynyl)-1,3,5-triazines.

Similarly, tris-(4-diethylaminophenylethynyl)-1,3,5-triazine $116b$ ($R^1 = H$, $R^2 = N(C_2H_5)_2$) was successfully prepared by Wolff [280] from lithium $N,N$-diethylaminophenyl acetylide $117c$ and $101b$ in 37% yield. Compared to the tris(diethylaminophenyl)-1,3,5-triazine $98k$, the absorption maximum is shifted about 50 nm to longer wavelengths ($\lambda_{\text{max}} = 425$ nm in acetone)

The elongation of the $\pi$-system of $98k$ by an acetylene unit to $116b$ also increased the large second-order polarizability to $\beta = 404 \times 10^{-50}$ Cm$^3$V$^{-2}$ (hyper Rayleigh scattering), 2.5 times higher than the $\beta$ value found for the smaller analogue $98k$.

2,4,6-Trisstilbazolium-1,3,5-triazines (C9-A-7’): A unique series of $\pi$-conjugated stars $119a$-c has been reported by Cherioux. The triazine core is connected to three cationic stilbazolium arms with electron releasing groups in the periphery. The nucleophilic substitution on cyanuric chloride with donor-substituted stilbazoles $120a$-c (2h, 80 °C, ethyl acetate) gave the tricationic stars in excellent yields (>90%) [319].
The charge on the nitrogen atoms is extremely delocalized. The only band in the UV-vis spectra of these tris-stilbazolium ions peaks at $\lambda_{\text{max}} = 440$ nm (119b), 470 nm (119c), or 547 nm (119a) with extinction coefficients in the range of $2.8 \times 10^8$ L mol$^{-1}$ cm$^{-1}$. Like the UV-vis absorption, the first reduction potential is strongly controlled by the peripheral groups: from -0.485 V (vs. SCE) for 119c to -0.71 V for 119a [319].

NLO measurements have been performed via harmonic light scattering (HLS). The nonlinearities obtained are slightly higher than those of the classical p-nitroaniline with $\sqrt{<\beta^2>}$ = $5 \times 10^{-30}$ esu. The highest value was obtained for the star with methylthio end groups 119c $\sqrt{<\beta^2>}$ = $45.6 \times 10^{-30}$ esu which can be readily accounted for by a more favourable charge transfer by the stronger donor end group [320]. In the case of the dimethyamino star 119a the harmonic wavelength signal was buried within a broad two-photon emission peak around 650 nm (irradiation wavelength 1.34µm). In this case, the HLS signal could not be discriminated from the two-photon fluorescence background. Contrary to the dimethyamino dye 119a, stilbazolium stars with less electron-releasing donor groups 119b, c did not present any two-photon fluorescence.

Melamines (C-9-N-A-3): Stars with a 2,4,6-triamino-1,3,5-triazine core 121 are generally prepared by nucleophilic substitution of the chlorine atoms of cyanuric chloride 101a with anilines 122.
Scheme 35. Synthesis of alkoxyphenyl- and alkoxytolanylmelamines.

![Chemical Structures]

These melamines, if substituted with three dialkoxyphenyl groups [321], exhibit enantiomorphic mesophases irrespective of the length of the peripheral side chains. Fan-like structures were observed by POM for 121a and 121b whereas the compound with hexadecyl side chains 121c exhibited a broken, mottled structure. A reluctance to recrystallize was observed for all compounds. The clearing temperatures decrease as a function of the increasing length of the side chains. X-ray scattering reveals disordered hexagonal columnar structures for 121, b substituted compounds but an ordered rectangular columnar phase of the hexadecyl substituted 121c.

Table 8. Phase transition temperatures of tris-3,4-dialkoxyarylmeamines 121a-c and their 1/1-mixtures with non-mesomorphic compounds. 123a: 3,5-didexyloxy benzoic acid, 123b: 3,5-didodexyloxy benzoic acid, 123c: 3,5-dihexadexyloxy benzoic acid; 123d: 3,4-didodexyloxy benzoic acid, 124: 2,4,7-trinitrofluorenone, 125: (2,4,7-trinitrofluorenylidene)malodinitrile.

| Star | 2. compound | Tm /°C | Tc /°C | Structure |
|------|-------------|--------|--------|-----------|
| 121a |             | 70.4   | 154.6  | Colhd     |
| 121b |             | 54.4   | 90.8   | Dhd       |
| 121c |             | 68.4   | 76.9   | Dro       |
| 121a | 123a        | 32.4   | 64.8   | Colhd     |
| 121a | 123b        | 34.5   | 75.1   | Colhd     |
| 121a | 123c        | 18.7   | 73.6   | Colhd     |
| 121a | 123d        | 62.2   | 88.7   | Colrd     |
| 121a | 124         | 68.1   | 110.4  | SmA       |
| 121b | 124         | 68.6   | 115.9  | SmA       |
| 121b | 125         | 93.7   | 147.2  | Colr      |
These compounds form monolayers on the air/water interface. The surface pressure-area isotherms show collapse ranges between 1.15 and 1.25 nm² per molecule, the area does not depend on the length of the peripheral side chains. The central melamine ring lies flat on the water surface and the peripheral side chains are oriented perpendicular to the water surface.

A mixture of tris(3,4-didecyloxyphenyl-1-amino)-1,3,5-triazine 121a and 3,5-dihexadecyloxybenzoic acid 123e showed transition temperatures at 18.7 (cryst. to mesophase) and 73.6 °C (mesophase to isotropic). X-ray diffraction reveals disordered hexagonal columnar structures [322]. This combination of two principles of structure formation, form anisotropy and intermolecular hydrogen bonding allows a control of the formation of columnar liquid crystalline structures.

Sixfold alkoxy-substituted 2,4,6-triarylamino-1,3,5-triazines 121a-c are “open-sided” core systems that have the capacity to form columnar mesophases of the single components and also allow the docking of a second component to a molecular recognition site located in the inner core region [323]. Mesomorphic aggregates from 121a-c as electron donors and non-mesogenic acceptors 2,4,7-trinitrofluoren-9-one 124 form enantiotropic mesophases between 68 °C and 115 °C with smectic A structure. Both transitions are shifted to higher temperatures when (2,4,7-trinitrofluorenylidene)malodinitrile 125 was used as acceptor. Additionally, the structure of the mesophase changed to rectangular columnar.

Even nonmesomorphic 2,4,6-triarylamino-1,3,5-triazine 121e (R¹ = H, R² = OC₁₂H₂₅) and TNF gave columnar as well as smectic liquid crystalline structures [324].

Polymerizable liquid crystal molecules are very useful in the preparation of anisotropic materials. The ordered array of mesogenic monomers in the LC state can be fixed by polymerization which results in stable polymeric materials with a two or three dimensional order. Diphenyldiacetylene 125 with an octyloxy chain and an amino group in the peripheral positions was condensed with 101a in the presence of potassium carbonate to give the star 121d composed of a melamine core with three rigid diphenyldiacetylene branches and octyloxy side chains [325]. 121d forms a liquid crystalline phase with a crystal to crystal transition at 189 °C followed by a transition into a hexagonal columnar mesophase at 197 °C. Further heating resulted in thermal polymerization at 280 °C. When the LC phase was quenched to room temperature, the texture was maintained. UV irradiation in the LC state resulted in a polymer with an ordered structure.

Similar compounds without alkoxy side chains or the diphenyldiacetylene connected via ether linkages to the triazine did not show mesophases. For the formation of mesophases, the outer benzene rings appeared to be essential. Related compounds 121e-g with different alkyl chains replacing the peripheral alkoxyphenyl groups, obtained by base-induced condensation of 101a with the respective anilines, did not show a thermotropic LC-behavior. Mixed with 124 in a 1:1 molar ratio, the second DSC heating and cooling curves gave only a mesophase-isotropic transition at 121 °C (121e: R² = decadi-1,3-ynyl), 130 °C (121f: R² = dodeca-1,3-diynyl), and 137 °C (121g: R² = tetradeca-1,3-diynyl) [326]. POM shows the typical textures of columnar mesophases in the LC state that was maintained even at room temperature. X-ray scattering reveals a long-range ordering of columns with an intercolumnar spacing of 35.3 Å (121f). UV irradiation in the LC state (125 °C) of 121f resulted in oligomerization through the diacetylene units. The oligomers still show LC behavior similar to the monomers but with a much higher viscosity of the LC state.
5.5. Borazine as a Core

Borazine, a carbon-free aromatic heterocycle has been used by Yamaguchi [327] as a core connecting six aryl groups. The synthesis of these molecules 126 with a threefold symmetry axis starts with a cyclocondensation of butyl amine or \( p \)-substituted anilines and boron trichloride to \( B,B',B'' \)-trichloro-\( N,N',N'' \)-tributyltriazine 127a and the \( N,N',N'' \)-triaryl derivative 127b-d followed by the threefold substitution of chlorine using 9-lithioanthracene 128a, b. The yields of this one-pot procedure are generally high, up to 70%. Dihedral angles between the borazine plane and the aryl substituents are about 72°-76° giving the molecules a gear-shaped motif.

Relative to anthracene, the fluorescence spectrum of 126b is shifted about 17 nm to the red and the fluorescence intensity (\( \Phi = 0.62 \)) increases by a factor of two. This increase in quantum yield was attributed to the sterically congested bundle preventing conformational disorder leading to nonradiative decay. The interaction of the aromatic groups is also responsible for a shift of the oxidation potential to less positive potential (\( E_{pa} = 0.94 \) V for 126a (trianthryl-tributyl) and \( E_{pa} = 0.85 \) V for 126b (trianthryl-tri-\( p \)-hexylphenyl).

Scheme 36. Synthesis of hexasubstituted borazines 126a-e.

Several tri-9-anthryl-tri-\( p \)-hexylphenyl-borazines (126f: \( R^2 = p \)-diphenylaminophenyl, 126g: \( R^2 = \) diisopropylsilyl, 126h: \( R^2 = \) and dimesitylboryl) were prepared via lithiation of 125e (\( R^2 = Br \)). Notably, the boryl-substituted derivative 126h shows three reversible reduction waves between -2.29 and -2.52 V (versus ferrocene) and a reversible oxidation wave at + 0.72 V. Since the first reduction
potential is comparable to that of Alq$_3$ (-2.36 V), this material indicates a potential as electron transporting material in OLEDs. On the other hand, diphenylaminophenyl-substituted 126f shows three oxidation waves ($E_{pa} = 0.60, 0.80, 1.03$ V). These data are promising for the application of trianthrylborazines as active materials in electronic devices.

6. Condensed Ring Systems as Cores

Condensed rings systems are common anisotropic cores in the area of liquid crystals inducing columnar mesophases [328,329]. Their sound investigation started at the end of the last century when columnar liquid crystals and their high charge carrier mobilities compared to disordered conjugated polymers were discovered [328]. With respect to star-shaped molecules with conjugated arms we focus here on one of the smallest systems-the triphenylenes (C-12) their heterocyclic counterparts (C-13), as well as triazatruxenes (C-14) and tristriazolotriazines (C-15). For these materials the variation of the supramolecular and optoelectronic properties by attachment of conjugated arms is highly attractive and consequently will be subject of the next sections.

6.1. Triphenylene Star Compounds (C-12)

6.1.1. Structures and Synthesis

Figure 30 summarizes the reported parent star-shaped triphenylene structures with conjugated arm scaffolds (C-12-A-3 (129), C12-A1 (130), C-12-A-8 (131)) and illustrates their space filling models. Steric demands force the arm scaffolds of molecules 129-131 out of plane with respect to the triphenylene core, analogous to structures found for the three-, four- or six- arm stars with a benzene core (see chapter 4). However, even the hydrogens in the bay position may result in a twist of the triphenylene disk itself by several degrees, which was revealed from single crystal structure analysis [330]. Crystal structures are not known for compounds 129 and 131. The structure analysis of a single crystal of 130a reveals a statistical rotation of the double bonds out of plane of the core [209]. However, the packing of the molecule in the crystal demands also an almost coplanar arrangement of two tert-butylethenyl units. The spatial arrangement of the arms dominates the supramolecular properties of this molecular family as will be discussed in the subsequent section.
The synthesis of compounds 129-131 is illustrated in Scheme 37. Although many synthetic strategies allow the preparation of symmetrically substituted triphenylenes [331], all members of this molecular family were obtained in a semi divergent/convergent approach [209,211,234,332]. In all cases 2,3,6,7,10,11-hexabromotriphenylene was converted in a convenient transition metal catalyzed cross-coupling reaction, in which six arms were attached. A yield of 93% which is reported for the synthesis of 130a implies that each single coupling step require a conversion of 98.8%[209].
Scheme 37. Synthesis of triphenylene stars. Suzuki (compounds 129, 130) and Hagihara-Sonogashira (compound 131) reactions had to be optimized for efficient sixfold couplings.

6.1.2. Triphenylene Derivatives and Materials Science

Oligophenylene Substituted Triphenylenes (C-12-A-3): Oligophenylene substituted triphenylenes 129 are the most frequently studied systems, due to their high stability and shape persistence. The latter is a feature of interest in the design of coordination networks, which has been attempted for 129a (E = S\text{CH}_3) with BiBr₃ [171] and AgOTf. [333] Only the latter salt resulted in the formation of a 3D network.
Figure 31. Extended triphenylene stars showing efficient energy transfer in mixtures.

Optoelectronic properties have been studied for triphenylenes 129b-d and hexaazatriphenylenes 132b-d [334]. Absorption and fluorescence maxima at long wavelength of 129b are bathochromically shifted (356 nm, 445 nm) compared with triphenylene derivatives. The absorption maximum of the donor-acceptor compound 132b at 421 nm overlaps considerably with the fluorescence spectrum of 129b, which results in an efficient energy transfer. The blue emission of 129b is quantitatively quenched in an equimolar mixture and only the green emission of 132b with a maximum at 543 nm is observed.

Evidently the most comprehensive work has been done in the area of columnar liquid crystals as semiconducting materials for optoelectronic devices. Table 9 collects all the different reported hexaphenyltriphenylene derivatives and their mesomorphic behavior. Interestingly only the dodecaalkoxy substituted derivatives 129e-h revealed columnar mesophases [332,335,336]. When these mesogens were converted to extended condensed triphenylenes by an oxidative cyclisation (Scholl reaction) [332,335], the resulting planar compounds showed a much broader LC temperature range than the parent non planar structures. The other compounds 129i-n with only six flexible peripheral chains did not show any mesomorphism [332,337]. However most of these compounds exhibited a remarkable behavior when mixed 1:1 with the triphenylenes with six flexible chains [336-340]. For example, compound 129m formed with hexahexyloxytriphenylene 133a (Cr 70 °C Col h 100 °C I) in a 1:1 mixture a hexagonal columnar mesophase from 66 °C to 155 °C. This new mesophase was not miscible neither with an excess of triphenylene 133a nor with 129m. The enormously stable 1:1 aggregates could not be explained by simple quadrupole interaction, but were rationalized by complementary polytopic interactions (CPI), which is the sum of the atom centered van der Waals and multipole interactions between the two components [338,341]. The hexaphenyltriphenylenes form a cavity with the twisted phenyl groups and can be regarded as supramolecular hosts for the smaller planar triphenylenes. This interaction is even enforced when the electron poor hexaazatriphenylene host 132a is applied (see last entry Table 9). A library of different triphenylenes 133 with alkoxy, oligoethylenoxy and chains with ester connecting groups has been tested. The temperature range of liquid crystal phases has either been extended for triphenylenes 133 or mesophases have been induced for non-mesomorphic derivatives. Not any new, stabilized liquid crystal phase revealed, when the
aggregate formation was prevented by steric demanding groups such as in hexaphenyltriphenylenes 129e-h, 129l or in mixtures with the 2,3,6,7,10,11-hexahexyloxy-1-nitrotriphenylene [337,338]. The columnar mesophases created by CPI exhibited a remarkable high order [336], an enhanced charge carrier mobility [342-346] and a rather low temperature dependence of the latter [347,348]. The charge carrier mobilities increased from $7.1 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (353 K) for 133a by almost two orders of magnitude to $2.3 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (393 K) for the CPI mixture 133a with 129m [342]. The weak temperature dependence was rationalized by the Holstein small polaron model in the non adiabatic limit [347,348]. Note that the best charge carrier mobility in a liquid crystal was found for a perylene derivative and amounts to $1.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [328,349]. Charge carrier mobilities of up to $15.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been predicted based on Marcus theory (hopping transport) for perfect structures of small graphenes [350].

**Table 9.** Mesomorphic properties of triphenylenes 129.

| Compound | E        | X        | Y | phase transitions [°C]       | reference   |
|----------|----------|----------|---|-------------------------------|-------------|
| 129e     | OC$_6$H$_{13}$ | OC$_6$H$_{13}$ | H | Cr 111 Col 126 I Cr 65 Colh 135 I | [335,336]  |
| 129f     | OC$_8$H$_{17}$ | OC$_8$H$_{17}$ | H | Cr 85 Col 104 I              | [335]       |
| 129g     | OC$_{10}$H$_{21}$ | OC$_{10}$H$_{21}$ | H | Cr 74 Col 103 I              | [335]       |
| 129h     | OC$_{12}$H$_{25}$ | OC$_{12}$H$_{25}$ | H | Cr 47 Col 101 I              | [335]       |
| 129i     | OC$_6$H$_{13}$ | H        | H | Cr 153 I                     | [332]       |
| 129j     | OC$_{11}$H$_{23}$ | H        | H | Cr 66 I                      | [332]       |
| 129k     | H        | OC$_6$H$_{13}$ | H | Cr 11 I                      | [337]       |
| 129l     | H        | H        | OC$_6$H$_{13}$ | Cr 81 I                     | [337]       |
Table 9. Cont

| Compound     | E         | X  | Y  | phase transitions [°C] | reference |
|--------------|-----------|----|----|------------------------|-----------|
| 129m         | C₆H₁₉     | H  | H  | Cr 59 I                | [332]     |
| 129n         | C₁₂H₂₅    | H  | H  | Cr 37 I                | [332]     |
| 129m + 133a  | 1:1       |    |    | Cr 66 Col₁b 155 I      | [336]     |
| 132a         | C₆H₁₉     |    |    | Cr 81 I                | [336,338] |
| 132a + 133a  | 1:1       |    |    | Col₁b 240 I            | [336,338] |

Oligoethenylene and Oligo(phenylenevinylene) Substituted Triphenylenes (C-12-A-1 and C-12-A-6): there are no reports on oligoethenylene derivatives, but only on the hexa(tert-butylethenyl)triphenylene 130a of Meijere et al. [209]. This type of compound was suggested to be useful as ligand or supramolecular host. Oligo(phenylenevinylene) derivatives of triphenylenens were only considered theoretically [351]. For the octupolar donor or acceptor end-capped 2,6,10-trisoligo(phenylenevinylene)triphenylenes a high two-photon absorption was predicted.

Figure 32. Praefkes multiyne nematogens.

Oligo(phenylene ethynylene)triphenylene (C-12-A-8): Like triphenylenes with oligo(phenylenevinylene) arms the derivatives with oligo(phenyleneethynylene) arms were rarely studied. Huang et al. synthesized triphenylenes with 2-(4-ethynylphenyl)ethynyl arms [234]. Upon complexation with the transition metal entities the absorption and fluorescence spectra were bathochromically shifted by a simultaneous decrease of the fluorescence quantum yield. Praefke et al. studied the 4-alkylphenylethynyl substituted triphenylenes 131a,b (Figure 32), which they called the multiyne
mesogens [211]. Without any exception they self-assembled in nematic mesophases, the mesophase with the lowest order, which can be rationalized considering the non-planar structure in the periphery of the disk (cp. Figure 30) and the small fraction of flexible aliphatic chains. The mixture with dipole bearing groups and even chlorocyclohexane can induce a columnar mesophase which is stable up to 250 °C [352]. The authors suggested that the latter is induced owing to the filling of free space between the arms of the multiynes in the periphery.

6.2. Hexaazatriphenylenes (C-13-A-3 and C-13-A-6)

Dipyrazinoquinoxaline, the hexaaaza analog of triphenylene, amalgamates the structural features of the hydrocarbon and the electron affinity of the pyrazine ring. The general synthetic approach is based on the construction of the three pyrazine units, reports about functionalization of existing triazatriphenylenes are only sparse [353,354]. Praefcke [355] developed the most important route to hexaazatriphenylenes: the threefold condensation of 1,2-diketones \( \text{134} \) with hexaaminobenzene \( \text{135} \). Compounds with six peripheral (\( p \)-substituted) phenyl rings \( \text{132} \) were obtained in 14-68% yield. Upon irradiation into the absorption (\( \lambda_{\text{max}} = 396 \) nm) of the \( p \)-methoxy derivative \( \text{132f} \), an intense emission with \( \lambda_{\text{F, max}} = 461 \) nm was observed.

**Scheme 38.** Synthesis of hexaazatriphenylenes \( \text{132} \) via threefold condensation of benzils with hexaaminobenzene.

![Scheme 38](image)

| \( \text{132e} \) | \( \text{132f} \) | \( \text{132g} \) | \( \text{132a} \) |
|---|---|---|---|
| \( R \) | \( \text{H} \) | \( \text{OCH}_3 \) | \( \text{C}_5\text{H}_{11} \) | \( \text{C}_6\text{H}_{19} \) |
| yield | 43% | 14% | 31% | 68% |

Fages [356] could show that the condensation of hexaaminobenzene with three benzil units, connected via two pentaethyleneglycol tethers, allows the formation of \( C_2 \)-symmetrical hexaphenylhexaazatriphenylenes with macrocyclic bridges \( \text{132h} \). Hexaazatriphenylenes \( \text{132} \) are planar trifunctional chelating ligands for transition metals [357]. Substituted with six phenyl or six \( p-t \)-butylphenyl groups (\( \text{132e}, \text{132i}: R = \text{C(CH}_3)_3 \)), hexaazatriphenylenes have been used by Lehn [358,359] in combination with bis-bipyridyl and \( \text{Cu}^+ \) for the formation of supramolecular architectures of nanometric size.

Hexaphenyl substituted hexaazatriphenylenes with peripheral flexible side chains can form liquid-crystalline mesophases, as pure compounds or in mixtures with hexakis(hexyloxy)triphenylene.
Bushby [336] reported that a 1:1 mixture of the triphenylene with hexakis(p-nonylphenyl)hexaazatriphenylene 132a shows a mesophase between 130 °C and 240 °C with a hexagonal columnar structure. The LC behavior of triphenylene/hexaazatriphenylene mixtures is discussed in detail in chapter 6.1. 132a shows semi reversible reduction above 1.80V and oxidation below –0.6 V (in benzonitrile, vs. Ag/AgCl) [360].

Hexaazatriphenylenes with six biphenyl arms and peripheral donor groups (132c:R = C₆H₆OC₆H₅; 132b: R = C₆H₆N(C₆H₅)₂; 132j:R = C₆H₆N(C₆H₅)-2-C₁₀H₇) were obtained from condensation of 135 and the substituted benzils 134f-g [361-363]. These compounds, though missing any flexible side chain, form liquid-cystalline phases at high temperatures [361]. Hexagonal columnar phases between 343 °C and 385 °C for the diphenylamino derivative 132b, 278-398 °C for 132c and 357 °C-464 °C for the N-phenyl-N-2-naphthylamino derivative 132j were found. The self-assembling of these molecules is also responsible for gelation of 10⁻² M solutions of these stars in aniline or nitrobenzene.

132b forms an amorphous type solid preserving the one-dimensional ordering in a cooling process from the liquid crystalline state [361]. In spin-coated films of mixtures of this star and the analogous triphenylene, these compounds form an efficient energy transfer system due to a strong spectral overlap of the triphenylene emission ($\lambda_{\text{F max}} \approx 450 \text{ nm}$) and the long-wavelength absorption ($\lambda'_{\text{max}} \approx 420 \text{ nm}$) of the hexaaza derivative. With a decreasing ratio (100:1-0:100) of triphenylene donor / hexaazatriphenylene acceptor, the emission of spin-coated films gradually shifts from $\lambda'_{\text{max}} = 500 \text{ nm}$ to 543 nm.

The UV-vis absorption maximum of hexaphenyl substituted hexaazatriphenylenes 132 is shifted to longer wavelengths with the extension of the $\pi$-system (132e: $\lambda_{\text{max}} = 366 \text{ nm}$, 132d: $\lambda_{\text{max}} = 392 \text{ nm}$) [363]. In combination with strong donors this lowered transition energy $\Delta E$ is overcompensated by a reduced ICT and a hypsochromic shift of the absorption band occurs (132k: $\lambda_{\text{max}} = 453 \text{ nm}$, 132b: $\lambda_{\text{max}} = 417 \text{ nm}$). Whereas the UV-vis absorption is nearly unbiased by solvent polarity, the fluorescence of diphenylamino substituted 132b is strongly solvatochromic. 132b shows a remarkable solvatochromic shift of 39.344 cm⁻¹ comparing solutions in toluene and dichloromethane, nearly twice as high as that of the lower homologue 132k. The fluorescence quantum yields of 132 benefit from peripheral donor substitution but become sensitive towards solvent polarity. The fluorescence is characterized by a single exponential decay and solvent polarity reduces the compounds with an ICT.

### Table 10. Optical data of substituted hexaphenylhexaazatriphenylenes 132.

| R             | $\lambda_{\text{max}}$ /nm (toluene) | $\varepsilon$ /l/mol×cm | $\lambda'_{\text{max}}$ /nm (toluene) | $\Phi$ | $\lambda'_{\text{max}}$ /nm (CH₂Cl₂) | $\Phi$ |
|---------------|-------------------------------------|--------------------------|---------------------------------------|--------|-------------------------------------|--------|
| 132e          | H                                   | 366                      | 21.000                                | 419    | 0.01                                | 424    | 0.03 |
| 132k          | -N(C₆H₅)₂                           | 453                      | 98.000                                | 502    | 0.95                                | 563    | 0.75 |
| 132d          | -C₆H₅                               | 392                      | 68.000                                | 438    | 0.43                                | 449    | 0.50 |
| 132b          | -C₆H₄- N(C₆H₅)₂                    | 417                      | 129.000                               | 501    | 0.96                                | 624    | 0.27 |
Hexakis-(biphenylyl)-hexaazatriphenylene stars with six perylenediimide end groups \(132p\) have been prepared and investigated as light-harvesting systems. Two strategies have been used: either the via sixfold Suzuki reactions of hexakis(\(p\)-bromophenyl)hexaazatriphenylene \(132q\) (\(R = \text{Br}\)) with \(p\)-substituted benzene boronic acids [353] or the threefold condensation of substituted bis(biphenylyl)diketones with hexaaminobenzene [364].

Compounds with six alkyl or alkoxy groups or twelve alkoxy groups provide two absorption bands around \(\lambda = 401\) and 360 nm in chloroform. In cyclohexane solution and in the film state, self-assembling to H-aggregates occurs. The fluorescence maximum is sensitive towards peripheral donor substitution: millimolar solutions of the octyl derivative \(132n\) in \(\text{CHCl}_3\) emit with \(\lambda_{\text{F}}^{\text{max}} = 461\) nm, a \(p\)-alkoxy substitution (\(132m\)) shifts the emission about 18 nm to the red and with a sixfold 3,4-dioctyloxy substitution (\(132l\)), the emission peaks at 504 nm. In hexane, the fluorescence of the alkoxy derivatives is hypsochromically shifted, upon dilution to 0.1 and 0.01 mM, further shifts to the blue indicate deaggregation.

The hexaazatriphenylene \(132p\) with six biphenyl branches and perylenediimide end groups forms stable dimer aggregates that allow an efficient energy transfer from the azatriphenylene core to the...
peripheral perylene diimide units. The synthesis starts with a Suzuki coupling of a Boc-protected $p$-aminobenzeneboronic acid and $132r$ followed by a condensation with a perylenedicarbox anhydride. The UV-vis spectrum of $132p$ is dominated by the absorption of the perylendiimide unit ($\lambda = 511$ nm, $544$ nm), the hexaazatriphenylene core gives a band at $\lambda = 390$ nm. Aggregation results in concentration and temperature depending absorption spectra. Irradiation into the absorption bands of the core or of the end groups results in an emission of the PDI acceptor moiety. Similarly, spin-coated films of mixtures of $132m$ and $132p$ show the PDI emission [353].

Hexastyryl substituted hexaazatriphenylenes $136a$, $b$ were obtained by the condensation of unsaturated diketones $137a$, $b$ and $135$ [365]. With an increasing donor strength, the absorption maximum shifts to longer wavelengths ($132a$: $\lambda_{\text{max}} = 460$ nm; $132b$: $\lambda_{\text{max}} = 526$ nm (DMSO)) the hyperpolarizability increases from $\beta = 18 \times 10^{-30}$ esu to $\beta = 50 \times 10^{-30}$ esu. Upon threefold complexation with Cu(I)/phenanthroline, further red shifts of the absorption and increased nonlinearities of $\beta = 31 \times 10^{-30}$ esu and $197 \times 10^{-30}$ esu were found resulting from a strengthened acceptor effect of the core.

Scheme 39. Hexakis(styryl)hexaazatriphenylenes.

Starburst compounds with a tribenzohexaazatriphenylene core $138$ were investigated by Gao et al. [366]. The key step of the synthesis is a threefold condensation of 3,4-disubstituted o-phenylenediamines $139$ with cyclohexanhexaone $140$ (70-85%). The electronic spectra of the hexaphenyl substituted tribenzohexaazatriphenylene $138a$ show $\lambda_{\text{max}} = 413$ nm and $\lambda^F_{\text{max}} = 432$ nm ($\Phi = 0.23$), extension of the conjugation ($138d$)as well as peripheral donor groups ($138b,c$) provoke significant bathochromic shifts of the absorption and, much more pronounced, of the emission. E.g. a sixfold triphenylamino substituted core $138c$ absorbs at $\lambda = 530$ nm and fluoresces with $\lambda^F_{\text{max}} = 700$ nm. The potential of the first reduction wave is nearly unbiased by the peripheral donor substituent, for $138a$: $E_{1/2} = -0.81$ and for $138c$: $E_{1/2} = -0.77$ (vs. Ag/AgCl).
6.3. Triazatruxenes (C-14-A-3 and C-14-A-8)

Carbazolyl groups have long been recognized in the construction of highly photoconductive amorphous materials. They undergo reversible oxidation processes and are able to transport positive charges via radical cation species. The triazatruxene (C-14) can be treated as an overlapping framework of three carbazole units and act as an electron donating unit for π-conjugated branches like oligofluorenes, improving hole injection and transport.

Hexabromotriazatruxene 141 [367] is the central starting material for triazatruxene based stars 142, the attachment of conjugated arms is possible via Stille [368], Sonogashira [369] or Suzuki [370] coupling reactions.

Six-armed stars with a triazatruxene core 142a-c have successfully been prepared by microwave-assisted multiple Suzuki coupling reactions [371]. 141 was coupled with oligofluorenyl boronic acids 143a-c to give the first, second and third generation in good yields (Scheme 41). With an increasing generation, the absorption maximum is gradually shifted to lower energies. In the fluorescence, a small red shift was recorded comparing the 1st and the 2nd generation, the latter represents the convergence limit. The stars form amorphous solids with glass transitions at 51 °C for the first and 144 °C for the third generation [372-374].

Blue light-emission from diodes with the configuration ITO/PEDOT:PSS/142/Ba/Al started at turn-on voltages of 4.0, 3.5, and 3.3 V with external quantum efficiencies of 0.24%, 1.35%, and 2.16% [368,373,374]. OLEDs with blends of this star in polyfluorene matrices showed an improved electroluminescence stability and external quantum yields close to 3% [375].
Scheme 41. Synthesis of triazatruxenes with oligofluorene branches.

\[
\begin{align*}
\text{R} = \text{hexyl} \\
\text{Pd(PPh}_3)_4 \quad \text{K}_2\text{CO}_3
\end{align*}
\]

| n | yield (THF) | ɛ_{max} /nm (THF) | ɛ_{max} /nm (film) | ɛ_{max} /nm (film) | ɛ_{max} /nm (film) | ɛ_{max} /nm (film) | T_g/°C |
|---|---|---|---|---|---|---|---|
| 142a | 1 | 89% | 348 | 429 | 0.72 | 355 | 438 | 0.37 | 51 |
| 142b | 2 | 86% | 360 | 440 | 0.85 | 366 | 439 | 0.73 | 87 |
| 142c | 3 | 84% | 366 | 440 | 0.88 | 373 | 437 | 0.75 | 144 |

Scheme 42. Hexacarbazolyl-triazatruxenes.

| R | ɛ_{max} /nm (THF) | ɛ_{max} /nm (film) | THF/ Film |
|---|---|---|---|
| CH\_2Cl\_2 | CH\_2Cl\_2 | Film |
| 144a | C\_6H\_13 | 350 | 422 | 428 |
| 144b | C\_6H\_5 | 350 | 422 | 428 |

| 145a | H | 344 / 349 | 423 / 428 | 0.65 / 0.35 |
| 145b | tBu | 345 / 350 | 423 / 434 | 0.68 / 0.40 |
Similarly, six phenyl groups with a 9-carbazolyl substituent 145 have been attached to the triazatruxene [377] (Scheme 42).

Related stars with six 9-substituted carbazole moieties 144 (R = phenyl or hexyl) have been prepared from hexabromotriazatruxene 141 in about 50% yield [376]. The optical properties of these stars are nearly independent from the substituent on the 9-position of the carbazoles, the long-wavelength absorption maximum appears at $\lambda_{\text{max}} = 350$ nm and blue light ($\lambda_{\text{F}}^{\text{max}} = 422$ nm) is emitted from solution in dichloromethane and from the solid material ($\lambda_{\text{F}}^{\text{max}} = 428$ nm).

141 is also a suitable substrate for multiple Sonogashira couplings (Scheme 43). Stars with six octylethynyl 148a as well as phenylethynyl groups with a variety of $p$-substituents 148b-e could be obtained in 60-73% yield [369,378].

For a sixfold substitution with peripheral acceptor groups 148h, i (R = CN, NO$_2$), a Sonogashira reaction with TMS-acetylene followed by deprotection of 148f and coupling of 148g with iodonitrobenzene proved to be advantageous. In the electronic spectra, the absorption maximum is shifted from about $\lambda_{\text{max}} = 320$ nm of the hexakis-ethynyl star 148i and $\lambda_{\text{max}} = 350$ nm for electroneutral 148c or donor-substituted 148b phenylethynyl derivatives to 420 nm for the compound with a $p$-nitro substitution 148g. A significant aggregation in polar solvents was reported.

**Scheme 43.** Hexaalkynyl-triazatruxenes. (a) Deprotection of the TMS-protected hexayne (b) Pd(PPh$_3$)$_4$ as catalyst.

| R             | yield | R     | yield |
|---------------|-------|-------|-------|
| 148b          | 63%   | 148f  | 71%   |
| 148c          | 60%   | 148g  | 51%$^a$|
| 148d          | 90%   | 148h  | 47%$^b$|
| 148e          | 78%   | 148i  | 13%$^b$|
6.4. Tristriazolotriazines (C-15-A-3 and C-15-A-9)

The threefold annulation of 1,2,4-triazoles to a 1,3,5-triazine can result in two $C_3$-symmetric tristriazolotriazines (TTT) \(149, 159\). Until recently, only two compounds containing the TTT core were known. Whereas the structure of the first reported TTT \(149a\) (\(R = \text{NH}_2\)) remains ambiguous [379,380], Huisgens triphenyl-TTT has structure \(150\) (\(R = \text{C}_6\text{H}_5\)) [381]. Tristriazolotriazines \(151\) with 1,2,3-triazole rings are still unknown.

A triphenyl-TTT \(149b\) (\(R = \text{C}_6\text{H}_5\)) was obtained in 46% yield by thermal cyclocondensation of \(152a\) (\(R^1 = R^2 = \text{H}\)) at 230-270 °C. This procedure is also applicable to 3,5-dichloro-1,2,4-triazole [382] as well as to 3-chloro-4-hexyloxyphenyltriazole \(152b\) (39%) [383].

Tristriazolotriazines with peripheral alkoxy side chains have been prepared via the Huisgen route in reasonable yields [383,384]. A threefold nucleophilic substitution of the chlorine atoms in cyanuric chloride \(101a\) with \(153\) followed by ring opening of the tetrazoles with elimination of nitrogen and subsequent ring closure gives tristriazolotriazines of structure \(150\).
The X-ray structure [384] of the tris-p-methoxyphenyl derivative 150b (R1 = R3 = H, R2 = OCH3) shows that the peripheral rings are in a non-planar conformation with respect to the triazine core. The mean plane angles for the twist of the three rings from the central ring are 19°, 29°, and 62°. Molecular packing is mainly due to van der Waals and dipole interactions.

Molecular π-stacking is sterically inhibited in the solid phase which improves the potential for these materials to be applied as good solid state emitters, since the formation of excimers via π-stacking is known to suppress the emission in solids. Alkoxy-substituted TTTs 150b-e absorb in solution and in the solid state with λmax in the range of 286-316 nm. In solution, an intense fluorescence (Φ = 0.25-0.47) with λFmax between 360 and 387 nm is emitted. With an increasing number of alkoxy donors, absorption and emission maximum are shifted to lower energies and the fluorescence quantum yields increase. Whereas the absorption spectra are nearly unbiased by the solvent, the emission of donor-substituted triphenyl-TTTs is positive solvatochromic. Comparing solutions in cyclohexane and dichloromethane, shifts from λ = 381 nm to λ = 410 nm for 150e and from λ = 412 to λ = 465 nm for the 4-diphenylamino derivative 150f were observed [383].

Electrochemically, trimethoxy-TTT exhibited only an irreversible oxidation wave peaking at 1.6 V vs. SCE, suggesting that the tristriazolotriazine core potentially has electron-transporting characteristics [384]. The high band gap of these blue-emitting materials is advantageous for their application as hosts in electroluminescent devices.

The TTTs with a single alkoxy side chain in the 4-position of the benzene rings are non-mesomorphic, but they form stable molecular glasses with Tg = 55.4°C (150c:R2 = O-hexyl), 46.7 °C (150g:R2 = O-octyl) and 70.3 °C (1510:R2 = O-dodecyl). This is a further evidence of non-aggregation.
in the solid state. But TTT 150i with two dodecyloxy side chains forms a liquid crystalline phase between 92.2 °C and 207.6 °C with hexagonal columnar structure (POM and X-ray).

Since the cell parameter a was calculated to be 30.4 Å, smaller than the van der Waals diameter of the molecule in the most extended conformation, either interdigitation or folding of the side chains occurs.

According to TGA, decomposition of TTTs starts only above 400 °C [384], but Tartakovsky reported a thermal rearrangement (350 °C, 30 min) of the triphenyl-TTT 150a to an unsymmetrical isomer 154 [382].

**Scheme 46. Isomerization of tristriazolotriazine 150a.**

Similarly, tristriazolotriazines with longer π-conjugated arms have been prepared. Stilbene [385] and tolane [383,386], substituted with alkoxy groups on the peripheral rings have been attached to the TTT core. Compared to the p-hexyloxyphenyl derivative 150c (\(\lambda_{\text{max}} = 289, \lambda_{\text{F,max}} = 347\) in cyclohexane), the absorption and emission spectra of the TTT with tolane branches are shifted to lower energies (\(\lambda_{\text{max}} = 334, \lambda_{\text{F,max}} = 372\) in cyclohexane). Whereas the absorption of the tolane derivative is negative hypsochromic (\(\Delta\lambda = 10\) nm from cyclohexane to ethanol), the emission is characterized by a significant positive solvatochromism (\(\Delta\lambda = 56\) nm).

### 7. Summary and Conclusion

The present review reports on star-shaped conjugated compounds, monomers and oligomers, which consist of a cross-conjugated core and three, four or six linear conjugated arms.

After the introductory chapter 1, a general discussion of the molecular architecture and the conjugation effect of these compounds is presented in chapter 2. The uniform, monodisperse structures are essentially planar, have a relatively rigid shape-persistence and a well-defined size – even when numerous conformers exist.

The core of the here selected compounds is represented by single atoms (B, C\(^+\), N: chapter 3), benzene rings (chapter 4) or azine rings (pyridines, pyrimidines, pyrazines, 1,3,5-triazines: chapter 5). Additionally some polycyclic cores (triphenylenes, hexazaatriphenylenes, triazatruxenes, tristriazolotriazines: chapter 6) are discussed.

The arms of the selected compounds consist of olefinic double or acetylenic triple bonds and/or benzene rings.

According to the literature, various further building blocks for the core and the arms have been used. Prominent examples are truxene cores [387] and oligothiénylene arms [388], for which comprehensive reports already exist. Fluorenediyyl and porphyrindiyyl segments represent further repeat
units for the conjugated arms. The latter building blocks can also serve as cores. However, these systems are beyond the scope of this article, which is defined in chapter 1.

The preparation of the monomeric or oligomeric \([n]\)stars (\(n = 3, 4, 6\)) with emphasis on the final reaction steps is discussed in the Schemes 1–46. Despite of the large number of here described compounds, there is a big challenge for novel syntheses. The majority of conceivable combinations of core structures and repeat units for the arms is still unknown.

Among the spectroscopic properties of the star-shaped systems, the UV/Vis/NIR absorption and emission play an important role, because the long-wavelength transitions reflect the conjugation effect.

In comparison to linear conjugated chains, the \([n]\)stars have a higher solubility and better film-forming properties. Their applications in materials science are wide-spread. The high \(\pi\) electron density and the \(\pi\) stacking tendency conveys the systems interesting optical, electrical and optoelectronic properties. Solar cells, field-effect transistors, light-emitting diodes, devices, which make use of non-linear optics including two-photon absorption, are typical application areas. Quite new is the use of supramolecular \([n]\)star structures that are able to intercalate and release dye molecules [389].

Self-organization and (rotated) \(\pi\) stacking in crystals and liquid crystals are certainly outstanding properties of \([n]\)stars in future multidisciplinary research and development projects. This review shall be a contribution to stimulate such projects.

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