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Designing highly fluorescent, arylated poly(phenylene vinylene)s of intrinsic microporosity

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Three new polymers containing tetraphenylethylene and diphenyl-dinaphthylethylene cores and their corresponding monomeric model compounds were synthesized and fully characterized aiming to investigate their photoluminescence efficiency, microporosity and Brunauer–Emmett–Teller-derived surface areas ($S_{\text{BET}}$). A comprehensive photophysical characterization was undertaken in the solid state (powder and thin films), tetrahydrofuran (THF) solution and in mixtures of good and “poor solvent” to induce aggregation (THF:water mixtures). Aggregation induced emission (AIE) was found for the tert-butyl-TPE monomer and polymer and diphenyl-dinaphthylethylene monomer with the increase of the water amount in THF:water mixtures and in the solid state. The tert-butyl substituted TPE derivatives display the highest fluorescence quantum yield ($\phi_F$) values: 0.14 to 0.30 (in powder) and 0.46 to 0.64 in thin films. In contrast, with the diphenyl-dinaphthylethylene (meta and para-phenylene) polymers aggregation caused quenching (ACQ) occurs in THF:water mixtures ($\phi_F \leq 0.011$) and in the solid state ($\phi_F \leq 0.012$). The microporosity of the soluble conjugated polymers as potential Conjugated Polymers of Intrinsic Microporosity (CPIPs) was further investigated. The $S_{\text{BET}}$ of the polymers were related to their optical properties. The polymers show an attractive combination of high $S_{\text{BET}}$ surface area (417 m$^2$g$^{-1}$) and the occurrence of distinct AIE effects for the tert-butyl-TPE polymer while the diphenyl-dinaphthylethylene polymers do not exhibit microporosity ($S_{\text{BET}} \leq 17$ m$^2$g$^{-1}$) and show ACQ behavior.

Introduction

Aggregation induced emission (AIE, or even aggregation enhanced emission, AIEE) corresponds to the description of the luminescent phenomenon in which the luminescent efficiency of a luminescent is increased upon its aggregation. The most accepted mechanism for the occurrence of AIE is through a restriction of intramolecular motions (RIM), including rotations and vibrations, that would deactivate non-radiatively the excited state of the luminescent. This phenomenon occurs in some luminescences in opposition to aggregation caused quenching (ACQ) commonly described for traditional fluorophores in which the π-π-stacking of the molecules in high concentration or in solid state leads to the formation of H-aggregates, which decreases the emission efficiency. Typically, low molecular weight AIE chromophores possess a propeller-shaped structure with rotatable peripheral phenyl rings (rotors), such as 1,1,2,3,4,5-hexaphenylsilole (HPS) and 2,3,3-triphenylacrylonitrile (TPAN) and 1,1,2,2-tetraphenylethylene (TPE). TPE derivatives have demonstrated a wide range of applications in optoelectronic devices, biotechnology, bioimaging, biosensors, etc., due to their AIE properties. TPE-based conjugated polymers - poly(arylene-diphenylenevinylene) - are known since the 1960s. Soluble, high molecular weight poly-TPEs (M$_n$ 10 - 40 kDa) can be made in reductive polyolefinations of aromatic, bisgeminal tetrachlorides as diketone derivatives with Cr$_2$Ac$_2$ or Co$_2$(CO)$_8$ as reducing agents or in carbonyl polyolefinations after McMurry with TiCl$_4$/LiAlH$_4$. Some of them show distinct AIE properties leading to high solid state photoluminescence quantum yields of >70% for some of the poly-TPEs. Since 2011, the easily functionalized four phenyl rings of the TPE unit were combined with a variety of reactive groups in construction of TPE-based polymers with inherent porosity. The development of microporous organic polymers (MOPs) with very high surface area is an active field of current research, with high potential in a variety of applications such as energy storage, light harvesting, catalysis and sensing of hazardous chemicals and explosives. Several classes of MOPs, such as amorphous hyper-cross-linked polymers (HCPs), polymers of intrinsic microporosity (PIMs), and conjugated microporous polymers (CMPs), have been reported. In this work, two types of poly(1,4-phenylene-diarylvinylene) with 4-tert-butylphenyl or naphthyl as aryl substituents at the vinylene units as well as the corresponding poly(1,3-phenylene-dinaphthylvinylene) are investigated for their photophysical properties in tetrahydrofuran (THF) and THF:water mixtures (a mixture of “good solvent”, THF, and water, a “poor solvent” to induce the formation of aggregates) as well as in the solid state (powder and films) for studying the effect of aggregation on the photoluminescence efficiency. The results are further rationalized with investigations on monomeric model monomer compounds and with the parent TPE molecule under the same conditions to also elucidate the effect of substituent and polymerization on the photophysical properties of these...
compounds. Furthermore, the porosity of these new TPE-based polymers is also investigated.

Experimental section

Materials

Most chemicals were purchased from Sigma-Aldrich, Fischer Scientific or TCI and used without further purification, unless described otherwise. For the photophysical studies, the solutions were prepared with solvents of spectroscopic grade or equivalent: Tetrahydrofuran (THF, Uvasol – Merck), analytical grade Chloroform (Fischer Chemical) or deionized water (18.2 MΩ-cm at 25 °C, Milli-Q, Millipore).

Synthesis and structural characterization of model compounds and polymers

All reactions were carried out under argon atmosphere using flame dried glassware. The detailed synthetic procedure and structural characterization are provided in the supporting information. NMR spectra were recorded on a Bruker AVANCE 400 or AVANCE III 600. APCI (Atmospheric Pressure Chemical Ionization) and ESI (electrospray ionisation) mass spectra were obtained on a Bruker Daltronik microTOF system. Gel permeation chromatography (GPC) measurements were carried out on a PSS/Agilent SECurity GPC System equipped with polystyrene gel columns using chloroform or THF as eluent. Nitrogen adsorption-desorption isotherms were recorded on a BEL Japan Inc Belsorp-max system at 77 K. The surface areas were calculated using the BET model in the pressure range p/p₀ from 0.05 – 0.25. All samples were degassed offline at >100°C for 16 hours under vacuum. Single crystal X-ray structures were obtained on a Bruker AXS Kappa Mach3 APEX-II-diffractometer housed at a FR591 rotating anode, equipped with graded multilayer optics emitting copper radiation (1.54178 Å) and measured at 100 K. For structure solution and refinement, the SHELX-package was used as integrated in Olex2

Solutions and film preparation

An appropriate amount of powder of each compound was dissolved in THF to prepare a stock solution with an optical density of 1.0 at the excitation wavelength used for the experiments. Then, 100 μL of the stock solution was then diluted with the proper amount of THF or THF:water mixture to obtain the desired water fraction (f_w = 0-95%, v/v) in 2 mL of final volume. Thin films from the compounds were obtained with a desktop precision spin-coating system, model P6700 series from Speedline Technologies, as described elsewhere. Briefly, thin films from the samples were obtained by deposition of ca. 50 μL from a solution of the compounds into a circular sapphire substrate (10 mm diameter) followed by spin-coating (2500 rpm) in a nitrogen-saturated atmosphere (2 psi). The solutions for spin-coating were prepared by adding 2 mg of the samples to 200 μL of chloroform solution, with stirring, at environment temperature, overnight. 15 mg of Zeonex® were added to the chloroform solution of the model compounds, TPE, Mono-tBu and Mono-Np, as polymeric matrix to obtain thin films of these samples.

Steady state and time-resolved fluorescence measurements

The absorption spectra were recorded using Shimadzu UV-2450 or Agilent Cary 5000 UV-Vis-NIR spectrometers. Absorption spectra of the transparent thin films were obtained in absorption mode using a clean sapphire substrate as the reference sample. The absorption spectra of the amorphous powder samples were recorded by collecting diffuse reflectance using the Cary 5000 DRA (integrating sphere accessory with detection in the 200-2500 nm range). Background correction was performed by collecting the baseline with 100 % and 0 % reflectance (using a polytetrafluoroethylene, PTFE, reference sample and the blocked beam, respectively) prior to the determination of the spectra of the solid samples. Conversion to absorption was performed assuming the Kubelka-Munk function, F(R).

Fluorescence spectroscopic studies were performed using Horiba-Jobin-Yvon Fluorolog 3-22 spectrofluorimeter. The fluorescence quantum yields (Φ_F) of all compounds, in solution or in solid state, were measured using the absolute method with a Hamamatsu Quantaurus QY absolute photoluminescence quantum yield spectrometer, model C11347 (integration sphere). A clean sapphire substrate was used as reference for the Φ_F measurements of solid-state thin films.

Fluorescence decays were measured using a home-built Time-Correlated Single Photon Counting (TCSPC) apparatus described previously. An IBH nanoLED (339 nm, 1.0 kHz) was used as excitation source. The fluorescence decays and the instrumental response function (IRF) were collected using 1024 channels in a time scale up to 48.8 ps/channel; alternate measurements (500 counts) of the pulse profile at the excitation wavelength and the sample emission were performed until 3000 counts at the maximum were reached. Deconvolution of the fluorescence decay curves was performed using modulation function method in the SAND program, as previously described

Results and discussion

Synthesis and physical characterization of polymers and monomeric model compounds

The structures and acronyms of the investigated compounds are depicted in Scheme 1.

Three new polymers comprising tetraphenylethylene and diphenyl-dinaphthylethylene backbones together with their corresponding monomeric analogues were synthesized according to the general strategic methodology described in...
Scheme 2. These polymers were inspired on the well-known aggregation induced emission, AIE, luminogen, 1,1,2,2-Tetraphenylethylene (TPE)\(^1, 7, 24, 35-37\). All polymers were synthesized via reductive polyolefinations of aromatic, bisgeminal tetrachlorides following a procedure initially described by Hörhold and co-workers in the 1970ies\(^14, 38, 39\). In difference to the original procedure dicobalt octacarbonyl was used as condensing agent, a variation of Hörhold’s method developed by us in the 1990ies\(^15\). The required tetrachlorides where generated starting from the commercially available tere- or isophthaloyl chlorides in two steps (Scheme 2a). In the first step diketones were synthesized following a modified Friedel-Craft-Acylation procedure using tere-/isophthaloyl chloride and tert-butylbenzene or naphthalene\(^40, 41\). Next, the bisgeminal tetrachlorides were obtained by reaction of the diketones with phosphorous pentachloride as described by Hörhold et al.\(^14, 38\).

The monomeric model compounds were prepared in a two-step synthesis. First benzoyl chloride and naphthalene or tert-butylbenzene were converted to the corresponding diaryketones in a Friedel-Craft-acylation protocol\(^2, 2\)(Scheme 2b). In case of the naphthalene, the resulting mixture of 1-Benzoylnaphthalene and 2-Benzoylnaphtalene was separated using flash column chromatography. In the second step the desired tetraarylethylenes were obtained by reductive coupling of the ketones using titanium tetrachloride and zinc\(^23\). The 1:1 mixtures of E/Z-Isomers in the products (as determined from the \(^1\)H-NMR spectrum) were separated by recrystallization.

The average molecular weight, \(\overline{M}_n\), weight average molecular weight, \(\overline{M}_W\), and polydispersities (PD) values of the polymers are listed in Table 1. Based on the \(\overline{M}_n\) values the degrees of polymerization (DP) have been calculated. The two naphthyl-substituted polymers, Poly-Np1 and Poly-Np2, can be assigned to the same model compound, Mono-Np, Poly-Np1 incorporates para-phenylene main chain linker units, while Poly-Np2 contains meta-phenylene main chain units (Scheme 1). Poly-Np1 and Poly-Np2 display reduced molecular weights, most probably caused by the increased steric demand coupled with decreased polydispersity (PD) values. Table 1 also lists the BET-based surface areas (SBET) of the solid polymer powders extracted from nitrogen sorption/desorption isotherms (Figures S11 and S12). Obviously, only Poly-t-Bu exhibits an intrinsic microporosity with a high SBET surface area of up to 417 m²/g as so-called conjugated polymer of intrinsic microporosity (CPI)\(^23\).

![Scheme 2. General synthesis of polymers (a) and phenyl-terminated monomers (b).](image)

The investigated phenyl-terminated monomeric model compounds, Mono-t-Bu and Mono-Np, are both of E-configuration as determined by single crystal X-ray crystallography (see Figure 1). In the crystalline state, Mono-t-Bu adopts a propeller like conformation with dihedral angles between the plane subtended by the central double bond and the phenyl rings of 52.3° and 55.9°. The ring planes of the two t-butyl groups are rotated slightly less, by 38.8° and 41.1°. The molecular configuration of Mono-Np is similar to that of Mono-t-Bu. The molecule is located on a crystallographic twofold axis and consequently only one independent dihedral angle between the two phenyl rings and the olefinic bond exists. This amounts to 56.2°. The same symmetry restriction holds for the naphthyl rings, which are rotated by 53.3° against the plane of the double bond. While the molecular conformations of the two propeller shaped molecules is similar, a marked difference is observed regarding the intermolecular interactions. Mono-t-Bu does not form π-π interactions, neither between the t-butyl rings nor the phenyl rings. In contrast, Mono-Np exhibits π-stacking between the naphthyl rings. The shortest C-C contact between rings is 3.32 Å and slightly shorter than in graphite (Figure 2). The distance between the centroids of the overlapping halfs of the naphthyl rings is 4.8 Å. Indicating ring slippage and reduced overlap of π-systems. However, the π-stacking is not limited to pairs of molecules but extends infinitely through the crystal along the c-axis. Also, the observed differences in the surface area values of the polymers should result from the different packing behaviour of the 4-tert-butylphenyl vs. naphthyl side groups. Indeed, while the naphthyl side groups tend to aggregate (π-stack) with neighbouring side groups in the solid state, the 4-tert-butylphenyl groups with their bulky tert-butyl substituents create free volume and microporosity (please see also the discussion of the X-ray crystal structures of the monomers).

### Electronic Spectral data

The photophysical properties of the polymers and model compounds, TPE and phenyl-terminated monomers, were investigated in the solid state (amorphous powders and thin...
films), in tetrahydrofuran (THF) solution and in mixtures of good and poor solvent (THF:water mixtures) to evaluate the effect of aggregation on the fluorescence emission efficiency.

Figure 3 presents the absorption and fluorescence emission spectra of the polymers and model compounds in the solid-state (powder and thin films) and in THF solutions. The spectroscopic data in Figure 3 is designed and structured in order to compare the polymer with the respective monomeric model compound plus the model AlGen, TPE.

The absorption and emission spectra of the investigated compounds in the amorphous powders are red-shifted and broader than in THF solution, indicating an extent of conjugation through intermolecular packing in solid state (see Figure 3 and Table 2). Additional observation of the spectral behavior shows that there is a good match between the solution absorption bands profiles and those obtained in thin films for the polymers and monomers (although with a different maximum, Table 2).

Observation of Figure 3 and Table 2 shows that the emission spectra of the polymers are red-shifted relative to the monomeric model compounds, emitting in the visible green region of the light spectrum: in solution, the emission maxima correspond to 530 nm, for Poly-t-Bu, and 545 nm and 518 nm to Poly-Np1 and Poly-Np2, respectively. In films, Poly-Np2 presents the highest emission wavelength found for the studied compound, with maxima at 611 nm (Table 2). Generally, the polymers also have higher Stokes shifts compared to their respective monomers, in the same medium. Since charge transfer bands cannot occur in these polymers this behavior points to the adoption of different conformations in the ground- and excited-state of the polymers (probably adopting a more planar conformation in the excited-state, which can lead to an extended degree of conjugation). The more extended nature of the π-conjugation in PolyNp1 compared to PolyNp2 in THF solution may be explained by the fact that π-phenylene units, in Poly-Np1, formally allows extended π-conjugation along the main chain (not much due to its strongly distorted conformation), while in Poly-Np2, the m-phenylene main chain units act now as effective conjugation barriers. This is further reflected in the differences observed in the solution absorption and emission (solvent: THF) spectra (Figure 3, bottom right hand panel). In contrast with these results, a different behavior is found in thin films (Figure 3, middle right hand panel) where the fluorescence spectrum of Poly-Np2 is red-shifted when compared to Poly-Np1. While THF solution and thin film emission maxima of PolyNp1 are quite similar (545 nm in THF

The same wavelength scale is presented for all the compounds, which further allows a direct comparison between the two types of polymers.
solution vs. 553 nm in the thin film), PolyNp2 shows a distinctly red-shifted PL maximum when compared to the solution value (611 nm in the thin film vs. 518 nm for the THF solution). This finding may be explained by an increased side chain aggregation (and AQC) in PolyNp2 with the aggregate emission as the dominating feature. This explanation is supported by the reduced thin film $\Phi_f$ for PolyNp2 ($PLOY_f$: 0.02 for PolyNp1 vs. 0.001 for PolyNp2, that will be further discussed on the next section on Table 3).

Upon going from the monomeric model compound, mono-t-Bu, to the polymer Poly-t-Bu a significant red shift of the absorption spectra is observed (39 nm in powder, 35 nm in film and 52 nm in THF). The same is not found for the Poly-Np polymers in THF and thin films where a small red shift is observed when compared to mono-Np (see Table 2). This shows that the chromophoric unit is in these polymers limited to the monomeric counterpart.

In the case of Mono-Np two bands at maxima 407 nm and 498 nm (Figure 3, right hand bottom panel) indicating the coexistence of monomer and aggregate species. This is further complemented with a concentration dependence study on Fig S13. It is also worth noting that in the solid state (powder and thin films) the investigated phenyl-terminated monomers retain the electronic spectral absorption features and maxima found for TPE (Figure 3). On going to solution (THF) although red-shifted (~6 nm for Mono-t-Bu and ~26 nm Mono-Np, see Table 2) similar broad absorption bands are observed for the monomeric model compounds when compared with TPE. The higher bathochromic shift found for Mono-Np can be attributed to the increase in the conjugation segment promoted by the naphthyl moieties when compared with the phenyl units in TPE.

Clearly contrasting with the behavior found for TPE in good solvents, where fluorescence emission is almost negligible (with $\Phi_f$ values of 0.002 or 0.0024 and of 0.003 in Table 3)37, 45, 46, the phenyl-terminated monomeric model compounds, Mono-t-Bu and Mono-Np, display fluorescence both in solution and in solid state (Figure 3 and Table 3). Indeed, TPE itself fluoresces when aggregated in solution37, 47 or in the solid state (Figure 3), i.e., when restriction of intramolecular rotation (RIR) occurs thus hindering the excited state radiationless processes.

In THF solution, when TPE is compared with the t-butil-TPE (Mono-t-Bu) derivative, the absorption spectra almost totally match and the emission is absent in TPE. However, in the case of Mono-t-Bu, the emission spectrum presents two bands: a vibronic resolved band with maxima at ~358 nm (corresponding to the monomer) and a second broad band with maxima at ~490 nm correspondent to the emission of the aggregate. This last band increases and red-shifts with the addition of water (Figure 4). Moreover the $\Phi_f$ value of Mono-t-Bu in THF is one order of magnitude higher than that of TPE (Table 3). Although the emission spectra of the model compounds Mono-t-Bu and Mono-Np in films quite overlaps with that of TPE, in powder the emission of Mono-t-Bu is blue-shifted when compared to TPE, with emission maxima of 441 nm and 454 nm for Mono-t-Bu and TPE, respectively (Figure 3 and Table 2). In the case of Mono-Np and again compared with TPE, there is now a red-shift of the emission maxima of 14 nm (Table 2). For the latter monomer the observed red-shift together with the increase in the fluorescence quantum yield on going from

### Table 2. Room temperature spectroscopic data (absorption and fluorescence emission maxima together with Stokes-shift, $\Delta_{SS}$) for the polymers and model compounds in THF, amorphous powders and thin films.

| Compound      | Medium | $\lambda^{ab}$ (nm) | $\lambda^{em}$ (nm) | $\Delta_{SS}$ (cm$^{-1}$) |
|---------------|--------|---------------------|---------------------|---------------------------|
| TPE           | Powder | 381                 | 454                 | 4220                      |
|               | Film   | 243/312             | 482                 | 11306                     |
|               | THF    | 238/310             | -                   | -                         |
| Mono-t-Bu     | Powder | 382                 | 441                 | 3052                      |
|               | Film   | 245/320             | 473                 | 10108                     |
|               | THF    | 242/314             | 358/490             | 3914                      |
| Poly-t-Bu     | Powder | 421                 | 546                 | 5438                      |
|               | Film   | 252/355             | 537                 | 9547                      |
|               | THF    | 250/356             | 530                 | 8454                      |
| Mono-Np       | Powder | 362                 | 468                 | 6257                      |
|               | Film   | 226/337             | 479                 | 8797                      |
|               | THF    | 220/334             | 407/490 (sh)        | 5370                      |
| Poly-Np1      | Powder | 391                 | 590                 | 8626                      |
|               | Film   | 222/351             | 553                 | 10407                     |
|               | THF    | 222/343             | 545                 | 10806                     |
| Poly-Np2      | Powder | 346                 | 511                 | 9332                      |
|               | Film   | 268/348             | 611                 | 12369                     |
|               | THF    | 221/335             | 518                 | 10546                     |

* Data from reference37, 45. * Prepared using Zeonex® as polymeric matrix.
solution to the solid state give support to the formation of J-aggregates.

Aggregation induced emission (AIE) studies

To further explore the occurrence of AIE in the investigated compounds, the emission behavior was studied in THF:water mixtures (Figure 4). TPE blue emission is only visible in high water content, either in acetonitrile:water or in THF:water mixtures. The broad emission band associated to this emissive aggregate, centered ca. 470 nm, becomes detectable at a water fraction ($f_w$) ≥ 85%.

Enhancing the steric effect is an efficient means to activate the phenomenon, directly validating the RIM hypothesis. The emission spectra and fluorescence quantum yields ($\phi_F$) for Mono-t-Bu were obtained in THF:water mixtures. Naphthalene-substituted ethenes, such as Mono-Np, are AIE-active luminogens. The spectral behavior of the investigated model compounds and polymers in THF:water mixtures, aiming to observe the presence and to quantify the AIE effect, is shown in Figure 4 and Table 3. From Figure 4, it can be seen the Mono-t-Bu presents a structured emission spectra in THF:water mixtures up to $f_w = 60\%$ ($f_w$: water:THF fraction, v/v), increasing in intensity with the addition of water. From $f_w ≥ 70\%$, the emission maxima for Mono-t-Bu red-shifts and the $\phi_F$ value increases with the addition of water, up to $\phi_F = 0.2$ for $f_w = 90\%$, i.e., ~1 order of magnitude higher than in pure THF (Table 3).

Mono-Np shows a similar behavior (to that found for Mono-t-Bu), i.e., a vibronic resolved spectra up to $f_w = 60\%$ and a red-shift emission band, followed by an increase in the $\phi_F$ values for $f_w ≥ 70\%$. This observation is likely due to the formation of J-aggregates in the two phenyl-terminated monomers. Indeed, although the presence of the naphthalene rings could favor $\pi-\pi$ interactions, leading to the formation of H-aggregates and consequently to aggregation caused quenching (ACQ), an opposite behavior was found.

The $\phi_F$ values for TPE and Mono-Np in films have been previously reported as 0.49 and 0.30, respectively. Our values in Table 3 are 0.24 (TPE) and 0.46 (Mono-t-bu). While for TPE in THF:water mixture a $\phi_F = 0.14$ in $f_w = 95\%$ was previously reported in comparison with our of 0.25 (for $f_w = 90\%$). The values obtained in this study are slightly different from those reported previously in films. This is likely because the photophysical properties are intrinsically dependent of the morphological properties of the films. Indeed, and exemplifying this the $\phi_F$ of TPE in powder was described as 24.1%, found in good agreement with the value previously obtained by us (23%) with the same equipment that was used to perform all the $\phi_F$ measurements.

Usually, when AIEgens, such as TPE and its derivatives, are chemically incorporated into polymeric structures, polymers with AIE characteristics could be obtained. Thus, it was anticipated that Poly-t-Bu and Poly-Np1 and Poly-Np2, whose monomeric model compounds are AIE active, would also maintain AIE properties. Although Poly-t-Bu presents an increase of fluorescence quantum yield upon the increase of water fraction, the fluorescence of the naphthyl polymers is quenched with the addition of water in THF:water mixtures. Indeed, as can be seen from Fig. 2 Poly-Np1 and Poly-Np2 present ACQ. Moreover, as shown in Table 3, the $\phi_F$ of Poly-Np2 is smaller than Poly-Np1 in solution, solid state and when compared at the same $f_w$ in THF:water mixture. The ACQ behaviour of Poly-Np1.2 may be caused by the stacking tendency of the naphthyl groups, leading to the formation of H-type aggregates. This is supported by the observed intermolecular $\pi$-interactions of the naphthyl substituents in the single crystal structure of Mono-Np.

In the solid state, the highest photoluminescence efficiency was obtained for Poly-t-Bu, with $\phi_F = 64\%$ in film—an increase of ca. 14x when compared to THF and higher than TPE and Mono-t-Bu— and when aggregated in THF:water mixtures with a value of $\phi_F = 62\%$ for $f_w = 90\%$.

The combination of TPE and carbazole groups also have generated porous organic polymers with higher $S_{\text{BET}}$ area, varying form 472-2200 m²g⁻¹ with fluorescence quantum yields of up to 40% in films (see also Table S15 for a literature revision of $S_{\text{BET}}$ and fluorescence quantum yield values for porous TPE based polymers). In our set of TPE derivatives polymers, a new compound with moderate surface area (412 m²g⁻¹), but higher fluorescent quantum yields (64% in spin coated films) is described.
Figure 4. Room temperature fluorescence emission (photoluminescence, PL) spectra for the model compounds (TPE, Mono-t-Bu and Mono-Np) and polymers (Poly-t-Bu, Poly-Np1 and Poly-Np2) in THF:water mixtures and their respective correlation of fluorescence quantum yield and emission maxima with increasing water fraction, $f_w = 0$-95%. The lines in the right hand panels is just meant to be a guideline to the eye.
The decay time values together with the fractional contribution of each species (C_i) at the aggregate emission wavelength (525 nm) changes with the increase of the water fraction in the mixture (Figure 5). For Poly-t-Bu in THF a fast decay component, \( \tau_1 \), in the 0.23-1.2 ns range and a longer decay time, \( \tau_2 \), ranging from 1.5 ns to 3.3 ns were found on going from 0% to 90% of water content (Table 4). As shown in Figure 5 the fluorescence quantum yields and the fluorescence lifetimes follow similar trend, i.e., a concomitant increase of these parameters with the increase of the water fraction. In addition, the determination of the radiative (k_\text{R}) and radiationless (k_\text{NR}) rate constants clearly shows a decrease of k_\text{NR} and an increase of the k_R with \( f_w \). This is valid for the two decay components, but in Table 4 the data is only showed for the longer (\( \tau_2 \)) component. The radiationless decay is therefore dominant up to a \( f_w = 70 \% \), and from there on the radiative deactivation begins to dominate.

Conclusions

In summary, in this work we have synthesized propellated shaped structures derived from tetraphenylethylene (TPE). The optical and PL properties of these compounds were studied in solid state (powder and films) and in solution (THF and THF:water mixtures). Their properties were compared the model

### Table 3. Room temperature fluorescence quantum yields (\( \phi_i \)) for the investigated model compounds and polymers in different medium.

| Solvent     | THF | 90W:10THF | powder | Film |
|-------------|-----|-----------|--------|------|
| Mono-t-Bu   | 0.94 | 0.25      | 0.23\(^a\) | 0.26\(^b\) |
| Poly-t-Bu   | 0.04 | 0.62      | 0.30   | 0.64 |
| Mono-Np    | 0.03 | 0.043     | 0.14   | 0.64 |
| Poly-Np1   | 0.02 | 0.011     | 0.012  | 0.010 |
| Poly-Np2   | 0.008 | 0.003    | 0.004  | 0.002\(^c\) |

\(^a\) Data from reference\(^H\). \(^b\) Prepared using Zeonex\(^a\) as polymeric matrix. \(^c\) \( \phi_i \) determined by comparison with the emission area of PolyNP1 film, with the same absorption at the excitation wavelength.

### Table 4. Room temperature fluorescence quantum yields (\( \phi_i \)) and lifetimes (\( \tau_i \)) for Poly-t-bu in selected THF-water mixtures. Also present are the associated pre-exponential values (\( a_i \)) and fractional contribution of each decay time (\( \% C_i \)) and the chi-square values (\( \chi^2 \)) for the judgment of the quality of the fits. Radiative (k_\text{R}) and radiationless rate (k_\text{NR}) constants associated to the second decay component (\( k_2 \)) are also presented.

| Solvent     | \( a_1 \) | \( \tau_1 \) (ns) | \( a_2 \) | \( \tau_2 \) (ns) | \( \chi^2 \) | \( \phi_i \) | \%C_1 | \%C_2 | k_\text{R} (ns\(^{-1}\)) | k_\text{NR} (ns\(^{-1}\)) |
|-------------|---------|----------------|---------|----------------|-------------|------------|-------|-------|----------------|----------------|
| 100% THF: 0% Water | 0.947  | 0.23          | 0.053  | 1.45          | 1.01        | 0.046      | 73.9  | 26.1  | 0.032      | 0.658       |
| 80% THF: 20% Water | 0.768  | 0.5           | 0.232  | 1.87          | 1.29        | 0.161      | 47.0  | 53.0  | 0.086      | 0.449       |
| 50% THF: 50% Water | 0.692  | 0.78          | 0.308  | 2.36          | 1.27        | 0.332      | 42.6  | 57.4  | 0.141      | 0.283       |
| 30% THF: 70% Water | 0.627  | 0.98          | 0.373  | 2.74          | 1.35        | 0.485      | 37.5  | 62.5  | 0.177      | 0.188       |
| 10% THF: 90% Water | 0.601  | 1.23          | 0.399  | 3.3           | 1.05        | 0.612      | 36.0  | 64.0  | 0.185      | 0.118       |

\(^a\) Experimental conditions: nanoLed \( \lambda_\text{ex} = 339 \text{ nm} \); \( \lambda_\text{em} = 525 \text{ nm} \); 48.1 ps/ch, 3 kCounts.

\(^b\) \( k_\text{F} = \frac{\phi_i}{\tau_i} \)

\(^c\) \( k_\text{NR} = \frac{(1-\phi_i)}{\tau_2} \)
compound TPE in similar experimental conditions. Mono-t-Bu and Mono-Np, monomeric model compounds with p-position tert-butyl substituents and naphthalene-substituted ethenes, respectively, showed AIE active properties in the solid state and in THF:water mixtures. This behavior is attributed to RIR in the solid state and when the compounds aggregate with the addition of the "poor solvent" (water), which hinders the excited state radiationless channels. The polymer Poly-t-Bu, was found to be more fluorescent than its monomer Mono-t-Bu and to retain its AIE active properties. The $\Phi_e$ value of Poly-t-Bu is found one order of magnitude higher in the solid state than in solution ($\Phi_e = 64\%$ in film vs. 4.6% in THF). This is accompanied by a distinct microporosity in the solid state with a high $S_{\text{BET}}$ surface area of 417 m$^2$/g probably driven by the steric demand of the tert-butyl groups. Poly-t-Bu, therefore, represents a so-called conjugated polymer of intrinsic microporosity (cPIM) with an attractive combination of intrinsic microporosity and occurrence of distinct AIE effects, thus predestining further experiments into stimuli-responsive properties in contact with suited analytes. In contrast, the diphenyl-dinaphthylethylene derivative polymers, Poly-Np1 and Poly-Np2, are less emissive than Mono-Np and presented ACQ properties. These properties are assigned to the occurrence of strong $\pi$-$\pi$ interaction in these polymers, leading to the formation of non-fluorescent H-aggregates. The occurrence of $\pi$-$\pi$ interactions may also lead to a tight packing of Poly-Np1 and Poly-Np2, since these polymers do not show an intrinsic microporosity ($S_{\text{BET}}<17$ m$^2$/g).

Conflicts of interest

There are no conflicts to declare.

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