Synthesis of Linearly Fused Benzodipyrrrole Based Organic Materials

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Abstract: The objective of this review is to give an overview of the synthetic methods to prepare different indolo[3,2-b]carbazoles and similar systems with a potential use in electro-optical devices such as OLEDs (organic light emitting diode), OPVs (organic photovoltaic) and OFETs (organic field effect transistor). Some further modifications to the core units and their implications for specific applications are also discussed.

Keywords: indolo[3,2-b]carbazole; organic electronics; pyrrolo[2,3-f]indole

1. Introduction

Polycyclic compounds containing two pyrrole rings have been widely studied because they possess many interesting properties. One of them is the good charge transfer properties these type of products possess [1,2], a second one is the feasibility to tune the electronic levels of these compounds for different applications. This causes these compounds to be excellent candidates for applications such as OPVs (organic photovoltaics) [3,4], DSSCs (dye-sensitized solar cell) [5], OLEDs (organic light emitting diodes) [6,7], and OFETs (organic field effect transistor, including thin film transistors) [8–10]. Advantages of organic materials for these applications are potentially low cost [11], lightweight and flexibility.

The main focus of this review will be the indolo[3,2-b]carbazoles, but also smaller benzodipyrrrole systems like pyrrolo[2,3-f]indole and pyrrolo[3,2-b]carbazoles (Figure 1), larger systems, and heterocyclic analogs of indolo[3,2-b]carbazole will be discussed.

Figure 1. Structure of indolo[3,2-b]carbazole, pyrrolo[2,3-f]indole and pyrrolo[3,2-b]carbazole.

The smaller systems can be considered as indolo[3,2-b]carbazoles with one or two of the outer benzo-rings missing. The larger systems have one or more extra rings compared to indolo[3,2-b]carbazole. We will only focus on the linear indolo[3,2-b]carbazole isomer, and its smaller and larger analogs in this review due to the more interesting spectroscopic properties [12].
In this review, we will discuss the synthesis of the parent indolo[3,2-b]carbazole scaffold and further functionalization and polymerization of this compound for applications such as OPVs, OLEDs and OFETs. However, the focus of the review is synthetic and we will not go in the details of the applications.

Another interesting application is the use of indolo[3,2-b]carbazole as anion sensor in aqueous environment [13] and the biological activity of indolo[3,2-b]carbazole [14–16]. In Figure 2, some examples of indolo[3,2-b]carbazoles tested in the above-mentioned applications are given.

Figure 2. Some examples of indolo[3,2-b]carbazole and their applications.

2. Indolo[3,2-b]carbazoles: Synthesis

2.1. Oxidative and Transition Metal Catalyzed Synthesis

The first synthesis of indolo[3,2-b]carbazole was reported by Grotta et al. They used N,N′-diphenyl-p-phenylenediamine 1 and platinum to perform a cyclodehydrogenation to obtain unsubstituted indolo[3,2-b]carbazole 2 in 10% yield (Scheme 1) [17]. Lamm et al. performed the same reaction on the dimethylated precursor, which was closed photochemical to indolo[3,2-b]carbazole in 10% yield. The electrochemical properties of this material were investigated [18,19]. Chakrabarty et al. used a similar method, but they started from 3-aminocarbazole to perform one photochemical cyclization to obtain indolo[3,2-b]carbazole [20].
Scheme 1. Cyclodehydrogenation of \( N,N' \)-diphenyl-\( p \)-phenylenediamine.

Bergman et al. used palladium acetate as an oxidizing agent to perform a similar ring closure to obtain indolo[3,2-\( b \)]carbazole 4 in much higher yield (83%) starting from disubstituted \( N,N' \)-diphenyl-\( p \)-phenylenediamine 3. The ester groups on indolo[3,2-\( b \)]carbazole 4 were further converted to di-aldehyde \( 5 \) in very good yield (Scheme 1) [21].

Nakano et al. started with 1,4-diiodo-2,5-methoxy-benzene 6 to perform a double Suzuki coupling with 2-chlorophenylboronic acid 7. The obtained product was demethylated and converted to the nonaflate ester 8 in two steps. This compound underwent two double Buchwald–Hartwig aminations with aniline to ultimately give the indolo[3,2-\( b \)]carbazole 9. It has also been proven possible to synthesize asymmetrical indolo[3,2-\( b \)]carbazoles by performing the Suzuki couplings in a stepwise manner (Scheme 2) [22].

Scheme 2. Pd-catalyzed quadruple \( N \)-arylation.

Chang et al. developed a general oxidative method starting from \( N \)-substituted amidobiphenyls to prepare carbazoles. In order to obtain a high yield, electron withdrawing groups such as acetyl or phenylsulfonyl should be placed on the amines. Alkyl substituted analogs seem to be disfavorable for the reaction.

\( \text{PhI(OAc)}_2 \) was shown to be the stoichiometric oxidant with the best results for the carbazole synthesis. Copper triflate was used as a catalyst and this improved the yield of the reaction going from 75% up to 93%. The optimized reaction conditions (for carbazole) were used on 2,2\(^{''}\)-bis(sulfonamide)-\( p \)-terphenyl 10 to afford indolo[3,2-\( b \)]carbazole 11 in 40% yield after a double cyclization (Scheme 3) [23].
2.2. Synthesis Starting from Indoles

Ishii et al. investigated the oligomerization of indole in acidic conditions. One of the compounds the authors found in the mixture obtained by combining indole 12 with p-toluenesulfonic acid in Dowtherm A (mixture of biphenyl (26.5%) and diphenyl ether (73.5%)) was indolo[3,2-b]carbazole 13, but only 6% yield was obtained under these conditions (Scheme 4) [24]. The generality of this method was not investigated. Korolev et al. treated 3-formylindole with acid and they detected several indolocarbazoles [25].

Cheng et al. started their synthesis from N-benzenesulfonylindole-2-carbaldehyde 14, which was subjected to a Horner–Wadsworth–Emmons reaction to obtain the corresponding cinnamate ester 15. This compound was then reacted with an excess of methylmagnesium iodide to obtain the tertiary alcohol 16. The protecting benzenesulfonyl group was removed and then the obtained compound 17 was treated with a catalytic amount of acid, which generated a stabilized cation that dimerized head-to-tail in acidic conditions. The resulting tetrahydro compound (structure not shown) was further oxidized with air oxygen to obtain the indolo[3,2-b]carbazole 18 (Scheme 5) [26].
Katritzky et al. prepared indolo[3,2-b]carbazoles starting from 2-[(benzotriazol-1-yl)methyl]indole 19, which was lithiated twice to form intermediate 20 and then C,N-dialkylated with 1-bromo-3-chloropropane. The resulting tricyclic compound 21 was then converted using ZnBr₂ as a catalyst into a cationic intermediate which dimerizes. The intermediate tetrahydroindolocarbazole (not shown) was oxidized with ambient oxygen to obtain the doubly fused indolo[3,2-b]carbazole 22 in 50% yield (Scheme 6) [27]. This synthesis is based on earlier work by Katritzky et al. in which benzotriazole was also used as a leaving group to perform a coupling reaction between indole and heteroaromatic structures. The overall yield of these reactions is however lower (22% starting from the corresponding benzotriazole compound) [28].

Bergman et al. prepared 6-formyl-indolo[3,2-b]carbazole 25 starting from 2,3′-diindolylmethane 23, which was prepared in several steps. This compound was then condensed with dichloroacetyl chloride in THF using pyridine as a base (84%) to form acylated compound 24. Acid catalyzed ring closure and hydrolysis of the dichloromethyl function at the meso position afforded the 6-formyl-indolo[3,2-b]carbazole 25 (80%) (Scheme 7) [29].

Ivonin and coworkers used indole and phenylglyoxal to prepare 2-hydroxy-2-indol-3-yl-acetophenone 26, which was then heated up to 200 °C. When the non-alkylated indole is used, only 10% of the dibenzoylated indolo[3,2-b]carbazole 27 is obtained. By using N-methylated indole for this reaction, the yield is increased up to 91% (Scheme 8) [30].
Dehaen et al. developed a strategy to prepare indolo[3,2-b]carbazoles starting from 3,3′-diindolylmethane 29. This diindolylmethane was obtained in situ by Bronsted- or Lewis acid-catalyzed condensation of indole 12 and an aliphatic aldehyde 28. The weak Lewis acid iodine was used in this case. In the second step, an orthoester and a strong Bronsted acid have been used to perform the ring closure (20%–50%). Previous to the ring closure, the 3,3′-connected diindolylmethane rearranged to a 2,3′-connected isomer to ultimately give indolo[3,2-b]carbazole 30 (Scheme 9) [31].

Another related method is the direct condensation of indole 12 with benzaldehyde 31 in the presence of hydrogen iodide to obtain 6,12-diphenyl-5,6,11,12-tetrahydroindolo[3,2-b]carbazole 32 in excellent yield in a single step. This compound then can further be functionalized and converted to the fully aromatic indolo[3,2-b]carbazole 33 (Scheme 9) [32].

Bhuyan et al. started their synthesis from isolated 3,3′-diindolylmethanes 29. The starting material was dimerized with iodine as a catalyst to achieve a symmetrical indolo[3,2-b]carbazole 34 in 50%–85% yield after 35 min. One equivalent of indole was left unreacted after elimination from the starting material. The final compound is symmetrical because the use of orthoformates is not required. The reaction however does not work with aliphatic and strong electron withdrawing aromatic R groups (Scheme 10) [33]. Another method by Bhuyan et al. is the three component reaction of indole with an aldehyde and N,N-dimethylbarbituric acid, which affords a 3-alkylindole that can dimerize to a symmetrical indolo[3,2-b]carbazole [34].
was used, in combination with ZnBr$_2$ as a Lewis acid catalyst, indolo[3,2-b]carbazole 38 in 55% yield after elimination of diethyl malonate [35].

Later, the aldehyde was converted to an acetal as an alternative to the condensation with diethylmalonate. Again, the methyl group was brominated. The obtained bis-electrophile compound can then be condensed with various electron rich (hetero)aromatic systems under the influence of a Lewis acid. N-alkyl-indole 37 has thus been used to obtain indolo[3,2-b]carbazole 38 in 55% yield after elimination of diethyl malonate [35].

Reddy et al. prepared functionalized indoles starting from N-Boc protected 2-aminobenzaldehyde 40. Nucleophilic attack of lithiated alkyne 41 and successive oxidation gave compound 42, which was converted by combination with 1-thio-2-ethoxyethyne 43, acidic deprotection and cyclization to 3-alkynylindole-2-carboxaldehyde 44. This compound was then condensed with 1-methyl-indole 45 in oxidative conditions, using copper(II) triflate, to obtain indolo[3,2-b]carbazole 46 in 60% yield (Scheme 12) [37].
2.3. Fischer Indole Synthesis

Robinson was the first to prepare the indolo[3,2-b]carbazole scaffold by performing a double Fischer indolization. He started from bishydrazone 47 to obtain the indolo[3,2-b]carbazole 2 in 27% yield, using a mixture of sulfuric acid and acetic acid (Scheme 13) [38].

Bergman et al. also exploited the Fischer indole synthesis to prepare functionalized indolo[3,2-b]carbazoles starting from 1,4-cyclohexanedione 48 and functionalized phenylhydrazines 49 (Scheme 14). The indolo[3,2-b]carbazoles 50 were prepared in 20%–50% yield, which is an improvement compared to the other synthesis described in the same paper using functionalized arylamines and Pd(OAc)$_2$ (10%) [39]. See Ong et al. for extra examples [40].
2.4. Cadogan Synthesis

Müllen et al. were the first to prepare indolo[3,2-b]carbazole via a Cadogan ring closure. First, they prepared terphenyl compound 53 by performing a double Suzuki coupling on 1,4-dibromo-2,5-dinitrobenzene 51 and phenylboronic acid 52 in 61% yield. Then, the double Cadogan ring closure was performed to obtain the final compound 54 (Scheme 15) [41]. For another example see Leclerc et al. [42].

![Scheme 15. Double Cadogan ring closure.](image)

Wrobel et al. exploited a microwave assisted Cadogan ring closure on terphenyl 55 to obtain 6,12-dialkoxy-indolo[3,2-b]carbazole 56 in reasonable yield (Scheme 16) [43].

![Scheme 16. 6,12-dialkoxy-indolo[3,2-b]carbazole.](image)

2.5. Oxidation of Indolo[3,2-b]carbazole

5,11-Dihydro-indolo[3,2-b]carbazole 2 can be oxidized to indolo[3,2-b]carbazole 57. This compound however is reactive towards nucleophiles and the reduction product of DDQ will do an addition on the oxidized indolo[3,2-b]carbazole to obtain the meso substituted compound 58 (Scheme 17) [44]. By putting t-butyl groups on the structure of 57, the oxidized molecule is stable and could be isolated and characterized by X-ray crystallography [45].

The Bergman group prepared the indolo[3,2-b]carbazole-6,12-dione 59 in fair yield by oxidizing indolo[3,2-b]carbazole 2 at the meso-positions with CrO₂ (34%) or H₂O₂ (30%).

The same compound 59 can be obtained by reaction of anhydride 60 with metallated indole 12, followed by acid-catalyzed ring closure of the bisindole ketoacid 61 in a polar solvent and deprotection of 62 (30% overall yield) (Scheme 17) [46]. Substituted derivates of 59 were prepared by Youssef et al. by reacting substituted anilines and tetrabromo-p-benzoquinone in a three step reaction. Also similar ring expanded systems were prepared by this method [47].
3. Indolo[3,2-b]carbazoles: Functionalization and Polymerization

Dehaen et al. functionalized non-alkylated indolo[3,2-b]carbazole 63 using FeCl₃. When using anhydrous FeCl₃, indolo[3,2-b]carbazole 63 was chlorinated at the 12 position to obtain 64. Another objective was to form dimer 65, which was also detected in the previous reaction (<5%). When the hydrated form, FeCl₃•H₂O, was used, dimer 65 was formed in 47% yield (Scheme 18) [48].

The indolo[3,2-b]carbazoles 63 obtained by Dehaen et al. with a free meso-position can be N-alkylated (83%) or -arylated (53%–70%) twice to obtain 66. Sulfonation only occurs one time, at the nitrogen next to the free meso-position (60%). The free nitrogen can then be arylated in 70% yield to form indolo[3,2-b]carbazole 67 [48].

A similar double N arylation was also performed by Hu et al. using 1-iodonaphtalene and substituted iodobenzenes, using even more drastic conditions [49,50].

When using non-alkylated indolo[3,2-b]carbazole 63, the free meso-position has been found to be the most reactive one for formylation (50%), bromination (96%), and diazotation (28%–42%) to get indolo[3,2-b]carbazole 68 (Scheme 19) [31,51]. Brominated compound 68 was alkylated and then converted to 6-(4′-formylphenyl)-5,11-dimethyl-12-pentyl-indolo[3,2-b]carbazole, which was then used by Maes et al. to prepare meso-substituted porphyrins [52].

The tetrahydroindolocarbazole 69 which was obtained when benzaldehyde and indole were used for the condensation, has phenyl groups as substituents at both meso position. The compound is however not yet fully aromatic. The tetrahydroindolocarbazole is first alkylated twice in 50%–67% yield to the more soluble indolo[3,2-b]carbazole 70 and then brominated with an excess of NBS, which at the same time aromatizes the middle ring, to obtain dihydroindolocarbazole 71. These bromine atoms can be converted to aldehydes and further to alkynes (Scheme 20) [32].
Grazulevicius et al. prepared indolo[3,2-b]carbazole polymers to be used as hole transporting materials and as emitting layer in OLEDs. The active material was prepared by alkylation of nitrogen and Buchwald–Hartwig amination of dibrominated indolo[3,2-b]carbazole 72 to prepare indolo[3,2-b]carbazole 73 which then was polymerized with acid catalysts.

**Scheme 18.** Chlorination and dimerization of indolo[3,2-b]carbazole.

**Scheme 19.** Functionalization of indolo[3,2-b]carbazole.
The tetrahydroindolocarbazole 69, which was obtained when benzaldehyde and indole were used for the condensation, has phenyl groups as substituents at both meso position. The compound is however not yet fully aromatic. The tetrahydroindolo[3,2-b]carbazole is first alkylated twice in 50%–67% yield to the more soluble indolo[3,2-b]carbazole 70 and then brominated with an excess of NBS, which at the same time aromatizes the middle ring, to obtain dihydroindolocarbazole 71. These bromine atoms can be converted to aldehydes and further to alkynes (Scheme 20) [32].

Indolo[3,2-b]carbazole 74 is functionalized at the free meso position with hydrazones to form 75. The alkyl and hydrazon functionalities contain reactive groups like oxetanes or vinyl groups. These are introduced in the molecules to enable self-polymerization at high temperatures (up to 180 °C) to obtain a more stable morphology (Scheme 21) [53,54]. Also epoxides were used to crosslink indolo[3,2-b]carbazoles under influence of aromatic dithiols [55]. A similar polymerization reaction with vinyl end-capped indolo[3,2-b]carbazoles was also performed by Nagase et al. after alkylation of one nitrogen atom of the indolo[3,2-b]carbazole scaffold [56]. Jiang et al. hypercrosslinked indolo[3,2-b]carbazoles using FeCl₃ as a catalyst and dimethylformamide dimethylacetal as the crosslinker [57].

Scheme 20. Functionalization of indolo[3,2-b]carbazole.

Scheme 21. Synthesis of cross linkable indolo[3,2-b]carbazoles.
Irgashev et al. developed methods to introduce formyl and acyl groups on the 2- and 8-position of indolo[3,2-b]carbazole 76. The best results for the formylation reaction were obtained by using the “Rieche method”, using SnCl₄ and dichloromethylpentyl ether in excess. The di-formylated compound 77 was obtained in 80% yield [58].

Diacetylation of indolo[3,2-b]carbazole 76 was performed in 67%–90% yield, using BF₃•OEt₂ to obtain indolo[3,2-b]carbazole 79 [59]. The prepared aldehydes and acetyl groups were further used to couple indolo[3,2-b]carbazole with various electron withdrawing groups to get donor–acceptor systems 78 and 81 (Scheme 22). Compounds 78 showed a red shift in the absorption spectrum (onset around 470–550 nm) compared to the parent indolo[3,2-b]carbazole 76 (onset around 430–440 nm with low absorption). The (benzo[g])quinoxaliny substituted compounds 81, obtained after condensation with 80, showed an onset around 500–550 nm.

Scheme 22. Formylation and acetylation of indolo[3,2-b]carbazole.

Khodorkovsky and coworkers prepared a new fused indolocarbazole donor system 83, by two different approaches. The first is starting from 6,12-bis(2-chlorophenyl)-5,11- dihydroindolo[3,2-b]carbazole 82, which twice undergoes an intramolecular Buchwald–Hartwig amination. The second method begins with 5,11-bis(2-nitrophenyl)-5,11-dihydroindolo[3,2-b]carbazole 84, also obtained through Buchwald–Hartwig amination of the parent indolo[3,2-b]carbazole. Reduction, diazotation to 85 and insertion at the meso position gives the same ring closed product 83. The yield of the compound via this approach is however lower than for the previous method due to formation of other isomers (Scheme 23) [60,61].
Khodorkovsky and coworkers prepared a new fused indolocarbazole donor system [83], by two different approaches. The first is starting from 6,12-bis(2-chlorophenyl)-5,11-dihydroindolo[3,2-b]carbazole, which twice undergoes an intramolecular Buchwald–Hartwig amination. The second method begins with 5,11-bis(2-nitrophenyl)-5,11-dihydroindolo[3,2-b]carbazole. Reduction, diazotation to form indolo[3,2-b]carbazole-2,8-thiazole [90], also obtained by two variations, either directly or using various \( \pi \)-spacers (Scheme 25). The compound without spacer showed an onset in the absorption spectrum at 425 nm and a single peak at 352 nm in different solvents. For the compounds with the spacers the onset was around 475 nm and peaks at 370–420 nm (low energy) and 300–370 nm (high energy) [63].

Curiel et al. performed the condensation of indole with pyridine-2-carboxaldehyde to obtain indolo[3,2-b]carbazole [86]. This indolo[3,2-b]carbazole has then been converted into a complex with triphenylborane to obtain products 87 and 88 (Scheme 24). The maximum absorption peak in DCM shifted from 441 nm (no complexation), over 545 (once complexed) to 643 nm (double complexation) [62].

Shi et al. prepared a series of donor–acceptor systems starting from indolo[3,2-b]carbazole-2,8-dicarbaldehyde [89]. This compound was coupled with benzo[d]thiazole [90] to form 91, either directly or using various \( \pi \)-spacers (Scheme 25). The compound without spacer showed an onset in the absorption spectrum at 425 nm and a single peak at 352 nm in different solvents. For the compounds with the spacers the onset was around 475 nm and peaks at 370–420 nm (low energy) and 300–370 nm (high energy) [63].
Shi et al. introduced dimesitylboron-groups at various positions of the indolo[3,2-b]carbazole 92 to obtain compounds 93 with an absorption onset around 410–420 nm (Scheme 26). These compounds show quite high fluorescence quantum yields (up to 0.76) [64,65]. Shi et al. also prepared a combination of the above-mentioned systems, i.e., a benzothiazole moiety at one side and a dimesitylboron group at the other end of indolo[3,2-b]carbazole [66].

Ong and coworkers converted indolo[3,2-b]carbazoles to homopolymers. When they used N-alkylated parent indolo[3,2-b]carbazole 94 to undergo oxidative FeCl₃-mediated polymerization, they obtained the “para-polymer” 95. This means the indolo[3,2-b]carbazole is polymerized at the position para to the nitrogen atoms (2,8-positions).

They also performed a dehalogenative polymerisation on chlorinated indolo[3,2-b]carbazoles 96 and 97. The 2,8-dichloro-indolo[3,2-b]carbazole 96 gave the “para-polymer” 95; however the polydispersity index was lower with this method (1.16–1.20 instead of 2.08–2.63 for oxidative polymerization). The 3,9-dichloro-indolo[3,2-b]carbazole 97 on the other hand yielded the “meta-polymer” 98.
The absorption spectrum of the para-polymer was almost similar to the spectrum of the free indolo[3,2-b]carbazole (absorption onset at 370 nm in THF). The meta-polymer on the other hand showed an onset of absorption in THF at 450 nm. This shift in absorption is ascribed to the π-conjugation along the indolo[3,2-b]carbazole backbone (Scheme 27) [67]. Leclerc et al. prepared polyindolo[3,2-b]carbazoles with and without bithiophene spacers [68,69] by performing palladium catalyzed couplings.

Tao et al. prepared some indolo[3,2-b]carbazoles 100 and 102 with substitutions at the meso-positions, and at the 2,8-positions. The former have been obtained by Suzuki coupling of brominated indolo[3,2-b]carbazole 99 with the different boronic acids to obtain 100 (Scheme 28).

The latter have been obtained by incorporating the substituent in the starting aldehyde 101, which is condensed with indole 12 to form indolo[3,2-b]carbazole 102.

The absorption spectrum of these compounds showed peaks at 288–354 nm (dichloromethane solution) and 302–356 nm (in films). The compounds showed emission peaks (in dichloromethane)
at 435–444 nm and at 436–450 nm (in films) [6,70]. Some other interesting similar structures of this kind were prepared by Leclerc et al. Here the indolo[3,2-b]carbazoles were end-capped with thiophene, benzene and styrene moieties [71]. Grazulevicius et al. expanded the scope of the reaction with various aromatic systems [72]. Liu et al. performed a double Heck reaction on dibromoindolo[3,2-b]carbazole to connect triphenylamine with the use of an alkene spacer [73].

Chen et al. copolymerized both 2,8-dibromo-indolo[3,2-b]carbazole 103 and 3,9-dibromoindolo[3,2-b]carbazole 103 with 9,9-dibutyl-fluorene 104 to obtain copolymers 105 (Scheme 29) with absorption peaks (in THF) at 357 nm (2,8-isomer) and 392 nm (3,9-isomer). Photoluminescence was at 437 nm and 457 nm respectively (in THF) [74].

Fan et al. and Lu et al. both prepared copolymers consisting of indolo[3,2-b]carbazole 106 as the donor-system and benzothiadiazole 107 as the acceptor part. Fan used a thieno[3,2-b]thiophene spacer 108, while Lu inserted an alkylated thiophene spacer 109 (Scheme 30). The polymer 110 with the thiophene spacers showed an absorption peak (in chloroform) at 538 nm and showed a weak absorption up to 650 nm. The one with the thieno[3,2-b]thiophene spacer showed two peaks, one at 420 nm and one at 570 nm (in dichlorobenzene solution and in thin film) and had absorption up to 675 nm [75,76]. For another example, see Hashimoto et al. [77].
Chen et al. prepared several donor–acceptor alternating copolymers 116 starting from 2,8- and 3,9-diboronate esters 111 as the indolo[3,2-b]carbazole donorsystem. These indolo[3,2-b]carbazoles are coupled with four different dibrominated acceptorsystems 112, 113, 114 and 115 by performing a Suzuki coupling (Scheme 31) [78].

Peng et al. prepared copolymers of indolo[3,2-b]carbazole 117 with pyrazino[2,3-g]quinoxaline 118 by realizing a Stille coupling with the dibrominated compounds mentioned above and bis-(tributylstannyl)thiophene 119 (Scheme 32). The polymers 120 showed an absorption onset from 800 nm (in THF) [79].

Grigoras et al. prepared polymers starting from brominated indolo[3,2-b]carbazoles 121 and 1,4-diethynylbenzene 122 by performing a Sonogashira coupling (Scheme 33). All polymers 123 show an absorption onset around 470 nm (in chloroform and thin film). The peaks of the absorption spectrum...
Grigoras et al. prepared polymers starting from brominated indolo[3,2-b]carbazoles 121 and 1,4-diethynylbenzene 122 by performing a Sonogashira coupling (Scheme 33). All polymers 123 show an absorption onset around 470 nm (in chloroform and thin film). The peaks of the absorption spectrum are located at 350 nm for the para- and the meso-polymer. The meta-polymer had a peak at 400 nm. We can again conclude that polymerization is best performed at the 3,9-positions and that the spacer used will cause a higher effective conjugation length [80].

![Scheme 33. Polymerization of indolo[3,2-b]carbazole with π-spacer.](image)

Dehaen et al. prepared polymers 127 by performing Sonogashira couplings on 2,8-dialkynyl-indolo[3,2-b]carbazole 124 and halogenated acceptor systems like BODIPY 125 or DPP (diketopyrrolo[3,4-c]pyrrole) 126 (Scheme 34). The polymer with the DPP functionality shows a peak in the absorption spectrum at 505 nm and an onset around 600 nm. The polymer with the BODIPY core on the other hand has a peak at 536 nm and an onset around 700 nm (all in chloroform solution) [81]. Yagai et al. synthesized similar indolo[3,2-b]carbazoles, end-capped with a DPP functionality connected to the indolo[3,2-b]carbazole without an alkyn spacer. These molecules showed an onset in the absorption spectrum at 650 nm (in chloroform) [82].

![Scheme 34. Donor–acceptor polymers.](image)
4. Smaller Organic Donor Systems

4.1. Pyrrolo[2,3-f]indole

The earliest synthesis of pyrrolo[2,3-f]indole was reported by Kingsley and Plant by condensing benzoin 128 with either 1,4-phenylenediamine 129 or 5-amino-indole 130 in a two-step procedure (Scheme 35). The synthesis starting from 1,4-phenylenediamine 129 gave the desired compound 131 in 20% yield. Starting from 5-aminoindole 130, the yield was only 6%.

![Scheme 35. Synthesis of pyrrolo[2,3-f]indole.](image)

The angular isomer (pyrrolo[3,2-e]indole) was also formed during the reaction, the yield however was even lower for this compound. They showed an onset in the absorption spectrum at lower wavelengths, which makes the linear systems (pyrrolo[2,3-f]indole) more interesting for long wavelength absorption [12].

Samsoniya et al. reported the synthesis of the parent pyrrolo[2,3-f]indole 137 in 1977, starting from 5-amino-indoline 132 which first undergoes diazo coupling, reduction and condensation with ethylpyruvate to form intermediate 133. Fischer indolization in acidic medium affords tetrahydropyrrolo[2,3-f]indole 134, followed by oxidation to afford pyrrolo[2,3-f]indole 135. Deprotection and saponification of 135 gives compound 136, which is decarboxylated to the parent pyrrolo[2,3-f]indole 137 (Scheme 36) [83,84].

![Scheme 36. Alternative synthesis of pyrrolo[2,3-f]indole.](image)

Berlin et al. prepared pyrrolo[2,3-f]indoles and other isomers from dinitroxylenes in a two-step procedure. Condensation of the methyl group of dinitroxylene 138 with dimethylformamide
diethylacetal and successive reduction of the obtained compound 139 gave pyrrolo[2,3-f]indole 140 in 40% overall yield (Scheme 37) [85].

**Scheme 37.** Berlin pyrrolo[2,3-f]indole synthesis.

Dmitrienko et al. condensed 5-amino-indoline 141 with 3-bromo-2-butanone 142 to get the linear substituted tetrahydropyrrolo[2,3-f]indole 143, which is oxidized with DDQ to pyrrolo[2,3-f]indole 144 (42% overall), whereas the angular isomer was obtained when using 5-amino-indole. The same researchers also demonstrated that it was possible to get the unsubstituted pyrrolo[2,3-f]indole in a multistep procedure by condensing indoline 141 with bromoacetaldehyde diethyl acetal to form 145. This compound was ring closed to 146, oxidized to 147 and deprotected to 148 in 25% overall yield (Scheme 38) [86].

**Scheme 38.** Condensation reactions of 5-amino-indoline.

Chunchatprasert et al. have prepared pyrrolo[2,3-f]indole 151 (24%) by condensing biselectrophilic 5-acetoxy-4-acetylpyrrole 149 with 2,3-unsubstituted pyrrole 150 under the influence of montmorillonite clay in 1,2-dichloroethane solvent (Scheme 39) [87].

**Scheme 39.** Condensation reaction of pyrroles to form pyrrolo[2,3-f]indoles.
Both Field et al. and Tsuji et al. have prepared pyrrolo[2,3-f]indoles from 2,5-dialkynyl-1,4-phenylenediamine 152 via transition metal catalyzed reactions. Tsuji used phenyl substituted alkynes and benzyl substituted amines to afford the pyrrolo[2,3-f]indole 153 in 79% yield [88]. Field however employed substituted alkynes and unprotected amine groups on the starting material to get around 20% yield of the non-substituted pyrrolo[2,3-f]indole 153 by using a rhodium catalyst 154 (Scheme 40) [89].

![Scheme 40. Pyrrolo[2,3-f]indole synthesis starting from 1,4-di-amino-2,5-di-alkynylbenzene.](image)

In 2011, Miura et al. improved the method of Field by carrying out a one pot double cyclisation-N-arylation on 155 to obtain pyrrolo[2,3-f]indole 156 in 43% yield [90].

Sperry et al. have shown that it was possible to further improve the reaction by using a gold catalyst 157 to realize the double cyclisation starting from free amino groups and substituted alkynes on starting material 155 in 76% yield (Scheme 41) [91].

![Scheme 41. Improved synthesis of pyrrolo[2,3-f]indole starting from 2,4-dialkynyl-1,3-diaminobenzene.](image)

Cho et al. started their synthesis from 1,4-phenylene bishydrazide 158 to perform a double Fischer indolization using various ketones 159. The linear pyrrolo[2,3-f]indole 160 was the major product of this reaction (up to 60%), accompanied by the angular by-product which is not shown here (Scheme 42) [92].
Yoshikai et al. optimized the reaction of anilines with ketones to oxidatively form indoles via an N-aryl imine intermediate. These optimized conditions were used to perform a double indole formation starting from 1,4-phenylenediamine 129 and acetophenone 161. Pyrrolo[2,3-f]indole 163 is formed in 29% yield via intermediate 162 (Scheme 43) [93].

Liotta et al. prepared the pyrrolo[2,3-f]indole scaffold starting from terephthaldehyde 164. This compound is condensed with two equivalents of ethyl-2-azidoacetate 165, after which the obtained compound 166 is thermally closed by nitrene insertion to obtain the final pyrrolo[2,3-f]indole 167 in 72% yield (Scheme 44) [94].

Tokoro et al. developed a transition metal-catalyzed C-H activation to convert \(N,N'-(1,4\)-phenylene)diacetamide 168 and an arylalkyne 169 into substituted pyrrolo[2,3-f]indole 170 (Scheme 45). The reaction works well with simple aryls (8%–63%) as well as with electron deficient systems (benzothiadiazole (76%), fluorenone (80%)) and electron rich systems (carbazole (64%)) [95].
4.2. Pyrrolo[3,2-b]carbazole

Chunchatprasert et al. used the method as described earlier to prepare pyrrolo[3,2-b]carbazoles starting from the same biselectrophilic pyrrole 149. In this case, 2,3-unsubstituted indole 12 was used to obtain pyrrolo[3,2-b]carbazole 171 in 65% yield (Scheme 46) [96].

Van der Eycken et al. performed a microwave assisted Cadogan ring closure on the Suzuki coupled product 174 of 6-bromo-indole 172 and 2-nitro-phenylboronic acid 173, using triethyl phosphite to obtain pyrrolo[3,2-b]carbazole 175 (Scheme 47) [97].

Nagarajan et al. used 3-amino-carbazoles 176, ethylene glycol 177 and a ruthenium catalyst to prepare pyrrolo[2,3-c]carbazoles 179 in good yield (73%), however this affords the angular isomer instead of the linear [98].

When Nagarajan et al. applied their procedure, using 3-amino-carbazoles 176 and propargyl alcohol 178, catalyzed by Zn(OTf)2, they again obtained the angular isomer, pyrrolo[2,3-c]carbazole 179 (75%) instead of the linear isomer [99].

By blocking the 4-position with a methyl group, both methods were suitable to prepare the linear isomer instead of the angular one that is normally formed. The yield of pyrrolo[2,3-b]carbazole 180 formation is 72% and 67%, respectively (Scheme 48).
5. Heterocyclic Analogs

Wang et al. prepared several tetracyclic indolonaphthyridines 190 starting from methyl 2-iodobenzoate 186. The first step is a Sonogashira coupling (88%–99%), followed by a saponification of the ester to get the corresponding carboxylic acid (61%–94%). Then a Curtius rearrangement is performed (73%–78%) and the obtained isocyanate 187 is subjected to an aza-Wittig reaction with 188, immediately followed by thermal ring closure of the carbodiimide intermediate 189 to form the final product 190 (Scheme 50). When a pyridine analog of 188 is used, multiple isomers are possible [101].

Donaghey et al. obtained a heterocyclic analog of indolo[3,2-b]carbazole where the outer benzo rings are replaced by thieno rings. The reaction starts from tetrabrominated 2,2′-(2,5-dibromo-1,4-phenylene)-bis-(3-bromothiophene) 191, which undergoes a quadruple Buchwald-Hartwig amination to obtain the pentacyclic pyrroloindacenodithiophene (thieno[2′,3′:4,5]pyrrolo[2,3-f]thieno[3,2-b]indole) 192 (40%) (Scheme 51) [102]. This building block will be used further on in the section about polymers and properties (vide infra).
Mo et al. synthesized an indolo[3,2-b]carbazole analog in which the middle aromatic ring is replaced by a pyrrole ring to form a pyrrolo[3,2-b:4,5-b']diindole 197. The synthesis starts from N-alkylated or N-arylated pyrrole 193 that is coupled with two molecules of 2-bromo-nitrobenzene 194 to form 195 in moderate yield (38%–50%). Then, a double Cadogan ring closure (48%–53%) is performed to obtain 196, which is alkylated twice in 65%–87% yield to obtain the final compound 197 (Scheme 52) [103].

The reaction is also possible starting from 2,4-dibromo-nitrobenzene or 2,5-dibromo-nitrobenzene 198 (38%–61%) to obtain dibrominated compounds 199. These compounds are further functionalized by Suzuki, Stille and Yamamoto coupling. The non-functionalized compound shows an absorption onset at 385–390 nm. The compounds with functionalization at the 2- and 9-position (X1 = Ar or CN) do not
show different properties. The 3,8-functionalized isomer \((X^2 = \text{Ar or CN})\) show a slight red-shift in the absorption spectrum (30–50 nm).

6. Larger Systems

Earlier we mentioned a method to prepare indolonaphthyridines from methyl 2-iodo-benzoate (Scheme 50) [67]. The authors started from diethyl 2,5-dihydroxyterephthalate to quantitatively convert this compound to diethyl 2,5-dialkynylterephthalate in two steps, which now was used as a substrate for a double cyclization reaction. After saponification to diethyl 2,5-dialkynylterephthalate, Curtius rearrangement to form iminophosphoranes was obtained. The final step of the reaction however only worked with phenyl substituted toxylylene as a substrate for a double cyclization reaction. After saponification to convert this compound to diethyl 2,5-dialkynylterephthalate, aza-Wittig reaction with isobenzofuran and heating for 15 h, a heptacyclic polyheteroaromatic system was obtained. The final step of the reaction however only worked with phenyl substituted iminophosphoranes and not with the pyridine analogs (Scheme 53) [101].

![Scheme 53. Synthesis of heptacyclic system.](image1)

Turner et al. prepared dibenzoindolo[3,2-b]carbazoles in 10%–17% overall yield using a multistep procedure involving the condensation of pyrroloindole intermediate and ortho-xylylene derivative. The intermediate was prepared from a 1,4-disubstituted benzenebisamide (Scheme 54) [104].

![Scheme 54. Dibenzoindolo[3,2-b]carbazole synthesis.](image2)
Yorimitsu et al. started from dibenzothiophene, which was oxidized to sulfone 210 by using aqueous hydrogen peroxide. In the next step, an aniline 211 is used to perform a nucleophilic aromatic substitution to obtain the corresponding carbazole 212 in 94% yield (Scheme 55).

On yet another substrate, benzothiophenesulfone, the authors first performed a Diels–Alder reaction with isobenzofuran 214 to afford the expanded benzonaphthothiophene sulfone, which can be converted to benzo[b]carbazole (not shown, 62%).

When using the bifunctional benzodithiophenedisulfone 213, and applying the same methodology, dibenzoindolo[3,2-b]carbazole 215 can be obtained in 22%–38% overall yield (Scheme 55) [105].

Sung et al. performed a double Fischer indolization on 1,4-phenylene bishydrazide 147 and 3,4-dihydronaphthalen-1(2H)-one to obtain another isomer of dibenzoindolo[3,2-b]carbazole [106] (not shown).

Hsu et al. prepared three heptacyclic carbazole derivatives 219, 222 and 223 by different annelation reactions to a carbazole precursor 216. The first one contains an sp3 center between the carbazole moieties and the two thiophene rings. The two thiophene rings 217 were linked by a Suzuki reaction with carbazole 216, followed by Grignard addition of four aryl groups to the two ester groups to obtain 218. Acid catalyzed ring closure of the intermediate biscarbinol gave the final heptacyclic compound 219 (Scheme 56) [107].

For the two other analogs, the ester functionality in the thiophene starting material 220 was replaced by a bromine atom and additionally carbazole was dibrominated after protection of the α-positions of thiophene to get 221.

To obtain the bis(silacyclopentadiene) compound, the four bromine atoms are lithiated and the end product 222 is formed by addition of SiCl₂Oct₂ (94%).

The pyrrole analog did not require protection of thiophene. The tetrabrominated product was subjected to Buchwald–Hartwig amination to obtain the heptacyclic pyrrole analog 223 (90%) (Scheme 56) [108].
Sung et al. performed a double Fischer indolization on 1,4-phenylene bishydrazide and 3,4-dihydronaphthalen-1(2H)-one to obtain another isomer of dibenzoindolo[3,2-b]carbazole [106] (not shown).

Hsu et al. prepared three heptacyclic carbazole derivatives 219, 222, and 223 by different annelation reactions to a carbazole precursor 216. The first one contains an sp3 center between the carbazole moieties and the two thiophene rings. The two thiophene rings 217 were linked by a Suzuki reaction with carbazole 216, followed by Grignard addition of four aryl groups to the two ester groups to obtain 218. Acid catalyzed ring closure of the intermediate biscarbinol gave the final heptacyclic compound 219 (Scheme 56) [107].

For the two other analogs, the ester functionality in the thiophene starting material 220 was replaced by a bromine atom and additionally carbazole was dibrominated after protection of the α-positions of thiophene to get 221.

To obtain the bis(silacyclopentadiene) compound, the four bromine atoms are lithiated and the end product 222 is formed by addition of SiCl2Oct2 (94%).

The pyrrole analog did not require protection of thiophene. The tetrabrominated product was subjected to Buchwald–Hartwig amination to obtain the heptacyclic pyrrole analog 223 (90%) (Scheme 56) [108].

Scheme 56. Synthesis of heptacyclic carbazole analogs.

7. Polymerization and Applications

The pyrroloindacenodithiophenes 192 (thieno[2′,3′:4,5]pyrrolo[2,3-f]thieno[3,2-b]indole) prepared by Donaghey et al. (Scheme 51) were connected with different acceptors by Stille coupling with the stannylated compound 224 to obtain an alternating copolymer (Scheme 57). When using benzothiadiazole 225 or difluorbenzothiadiazole 226, absorption spectra (in chloroform) showed peaks up to 900 and 850 nm for polymers 227 and 228, respectively.

The authors also used two different acceptors to copolymerize with their donor systems: 1,3-dibromo-5-octylthieno[3,4-c]pyrrole-4,6-dione 229 and 3,3′-dibromo-5,5′-di-2-ethylhexyl 1,1′-bi(thieno[3,4-c]pyrrole)-4,4′,6,6′(5H,5′H)-tetrone 230.

These polymers (231 and 232 respectively) showed less red shifted absorption (up to 750 nm) in comparison to the two previous systems [102].

The silicon 222, carbon 219 and nitrogen 223 bridged heptacyclic systems described by Hsu (Scheme 56) were co-polymerized with benzothiadiazole 225 or 233 (Scheme 58). An alternating co-polymer was obtained after Stille or Suzuki coupling [107,108].

While the monomers show absorption up to 400 and 460 nm in toluene, the polymers show absorption up to 700 nm (carbon 234 and silicon 235 bridge) and 840 nm (nitrogen 236 bridge) [108].

Tokoro et al. prepared interesting alternating co-polymers 238 with pyrrolo[2,3-f]indole and aryl building blocks. The one-step reaction starts from N,N′-diacetyl-p-phenylenediamine 168 and 1,4-dialkynyl-benzene 237 (Scheme 59). It was also proven that the benzene core of the di-alkynyl could be replaced by either electron-rich as electron-poor aryls to obtain various donor–acceptor...
systems. The absorption spectrum of the polymer with a benzene moiety in the backbone showed a maximum at 365 nm (in DCM solution). When electron withdrawing systems like benzothiadiazole \(239\) or fluorenonyl \(240\) were used instead of benzene, the absorption peak shifted to 442–453 nm [95].

Scheme 57. Polymer synthesis with heterocyclic indolo[3,2-b]carbazole analog.
8. Conclusions

The past two decades have seen a large activity in the domain of indolo[3,2-b]carbazoles and the related smaller and larger benzodipyrrrole analogs. New synthetic methods were reported, leading to superior materials. Certainly, the full potential of this work has not been realized. It is expected that we will see further development in this area.

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Abbreviations

The following abbreviations are used in this manuscript:

| Abbreviation | Definition                              |
|--------------|-----------------------------------------|
| Ac           | Acetyl                                  |
| Ac$_2$O      | Acetic anhydride                        |
| AcOH         | Acetic acid                             |
| BHT          | 3,5-dibutyl-4-hydroxytoluene            |
| BINAP        | 2,2′-bis(diphenylphosphino)-1,1′-binaphtyl |
| Bz           | Benzoyl                                 |
| Cbz          | Carboxybenzyl                           |
| dba          | dibenzylideneacetone                    |
| DCE          | 1,2-dichloroethane                      |
| DCM          | dichloromethane                         |
| DDO          | 2,3-dichloro-5,6-dicyano-1,4-benquinone |
| DMA          | Dimethylacetamide                       |
| DMF          | Dimethylformamide                       |
| DMFDEA       | Dimethylformamidediethylacetal          |
| DMSO         | Dimethylsulfoxide                       |
| DPP          | Diketopyrrolo[3,4-c]pyrrole             |
| DSSC         | Dye sensitized solar cell               |
| EtOH         | Ethanol                                 |
| HMFA         | Hexamethylphosphoramide                 |
| LDA          | Lithium disopropylamide                |
| MeOH         | Methanol                                |
| NBS          | N-bromo-succinimide                     |
| Nf           | Nonanoyl                                |
| NMP          | N-methyl-2-pyrrolidone                  |
| OFET         | Organic field effect transistor         |
| OLED         | Organic light emitting diode            |
| OPV          | Organic photovoltaic                    |
| Ph           | Phenyl                                  |
| PPA          | Polyphosphoric acid                     |
| PPSE         | Polyphosphoric acid trimethylsilyl ester|
| p-TSA        | Para toluenesulphonic acid              |
| t-AmOH       | tertiary amylicoloh                     |
| TEA          | Triethylamine                           |
| TFFA         | Trifluoroacetic anhydride               |
| Tf           | Triflate                                |
| THF          | Tetrahydrofuran                         |
| THP          | Tetrahydropryan                         |
| TIPS         | Triisopropylsilyl                       |
| TMSCl        | Trimethylsilylchloride                  |
| Ts           | Tosyl                                   |

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