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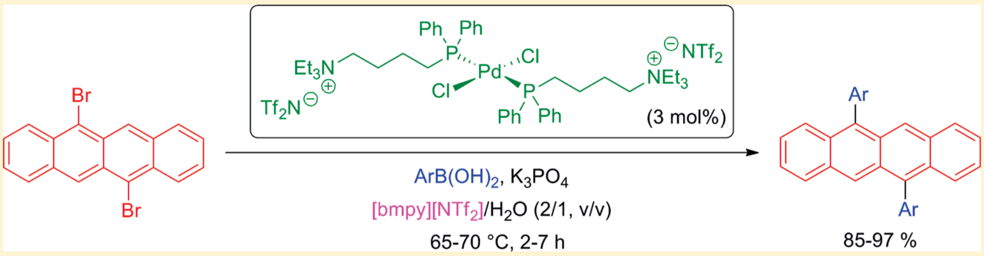
Cross-Coupling of 5,11-Dibromotetracene Catalyzed by a Triethylammonium Ion Tagged Diphenylphosphine Palladium Complex in Ionic Liquids

Antonio Papagni,[†] Claudio Trombini,[‡] Marco Lombardo,[*,‡] Stefano Bergantin,[†] Amani Chams,[§] Michel Chiarucci,[‡] Luciano Miozzo,[*,†,§] and Matteo Parravicini[†]

[†]Scienza dei Materiali, Università degli Studi di Milano Bicocca, Via R. Cozzi 53, 20125 Milano, Italy
[‡]Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna, via Selmi 2, 40126 Bologna, Italy
[§]ITODYS, Cnrs-Umr 7086, Université Paris Diderot, 15 rue Jean Antoine de Baïf, 75205 Paris Cedex 13, France

Supporting Information

ABSTRACT:



Suzuki–Miyaura cross-coupling reactions of 5,11-dibromotetracene with arylboronic acids, using a triethylammonium-tagged palladium(II) diphenylphosphine complex as catalyst in a pyrrolidinium-based ionic liquid (IL), allowed the preparation of new 5,11-diaryl-substituted tetracenes in good to excellent yields. The synthesis of the new 5,11-diboronic-tetracene bis-pinacolate ester and its use in Suzuki–Miyaura cross-coupling reaction with aryl bromides in IL are also reported.

Tetracene, pentacene, and their derivatives are among the most studied molecular organic semiconductors.[1] A large number of substituted acenes have been reported and used, for example, for organic light-emitting diodes, field-effect transistors, and solar cells.[2] Among them, substituted tetracenes, such as 5,6,11,12-tetraphenyltetracene (rubrene) and 5,11-dichlorotetracene,[3] show very high charge mobilities. Indeed, rubrene represents the state of the art in this field, showing exceptional charge carrier mobility values up to 20 cm^2/(V s). The origin of these outstanding mobility values has been ascribed to a favorable crystal packing,[4] even though deeper investigations, aimed at understanding the origin of the electronic properties of these organic semiconductors, are in progress. Within this framework, the improvement of mobility values is based on the tuning both of electronic properties at the molecular level and of the crystal packing, by acting on the nature of the substituents present on the tetracene backbone. Unfortunately, few protocols for the synthesis of substituted acenes are described in the literature. They are traditionally based on multistep aryllithium addition to naphthacenediones and Diels–Alder-based reactions, whose low yields and lack of generality are a limitation to the preparation of a wide spectrum of derivatives.[5] This is particularly true for 5,11-diaryl-substituted tetracenes, and to the best of our knowledge, only the syntheses of 5,11-diphenyl- and 5,11-ditolyltetracene are reported in the literature,[6] while the preparation of 5,11-dinaphthyltetracene is claimed in a recent patent.[7] Although cross-coupling procedures look very attractive as a general synthetic protocol for substituted tetracenes,[8] only recently the synthesis of substituted tetracenes has been reported via a Kumada–Corriu cross-coupling reaction between the 5,6,11,12-tetrachlorotetracene and methylmagnesium chloride,[9] and using a Suzuki–Miyaura cross-coupling reaction between the 5,11-dibromotetracene and a perylene-based boronic derivative.[10] This is quite surprising, since a Suzuki–Miyaura cross-coupling reaction is particularly appealing,[11] due to the wide commercial availability of stable boronic acids and esters, the mild conditions required, and the high tolerance toward functional groups. The difficulties related to the availability of iodo- and bromoacenes and their low reactivity for steric demands when the halides are at the 5-, 6-, 11-, and 12-positions partially justify the scarce use of these substrates in transition-metal-mediated cross-coupling reactions.

Recently, an effective protocol for the Suzuki–Miyaura cross coupling in ionic liquids (ILs) has been developed, where the ionic phosphine **1** (Scheme 1) acts as the palladium ligand (L).[12]

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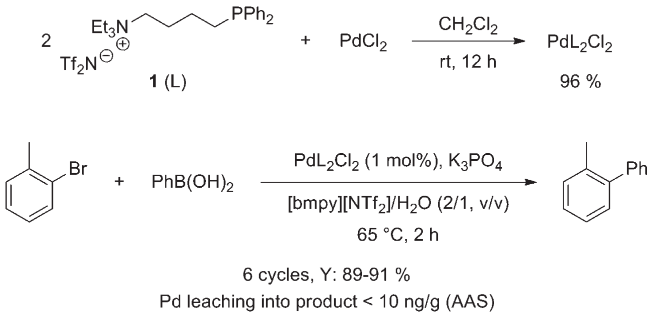
Scheme 1. Synthesis of the Ion-Tagged Palladium Complex PdL_2Cl_2 and Suzuki−Miyaura Cross-Coupling Reactions in 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethane)-sulfonamide ([bmpy][NTf_2])



The resulting ion-tagged palladium complex PdL_2Cl_2 proved to be suitable for Suzuki−Miyaura cross-coupling reactions under mild conditions, even using sterically hindered substrates. In addition, it is noteworthy that the ionic phase containing the catalytically active palladium species could be reused up to six times without loss of activity. The ability of the ionic ligand to stabilize the palladium catalyst, preventing precipitation of inactive "Pd black", is the key to success in catalyst recycling.

Here we report the application of this protocol to 5,11-dibromotetracene, which allows the preparation of a series of new 5,11-bis-aryl-substituted tetracenes in good to excellent chemical yields. In addition, we also describe the synthesis of the new 5,11-diboronic-tetracene bis-pinacolate ester and its use in Suzuki−Miyaura cross-coupling reactions with aryl bromides in ILs. Among the possible ILs, we decided to use those possessing a pyrrolidinium ion, since an enhanced reactivity had been previously observed with these ILs in palladium-mediated cross-coupling reactions.[13] On the other hand, imidazolium-based ILs, although almost as efficient as pyrrolidinium-based ILs, are known to afford N-heterocyclic carbene complexes (NHC) on prolonged heating in the presence of a base.

RESULTS AND DISCUSSION

We synthesized 5,11-dibromotetracene (**3a**) by electrophilic bromination with *N*-bromosuccinimide (NBS) in a $CHCl_3$−DMF mixture, as described by Müllen,[14] to overcome the low solubility of tetracene (**2**) in DMF, normally used in the bromination of polycyclic arenes.[15] Both 5,11- (**3a**) and 5,12-dibromotetracene (**3b**) are formed, but using the experimental conditions described by Müllen, the formation of **3b** is less than 10% (Scheme 2). Pure **3a** can be obtained by crystallization from toluene. The crude bromination mixture is also contaminated by some oxidation products (tetracene-quinone), which can be easily removed by filtration over a bed of SiO_2.

In a preliminary study, we tested the Suzuki coupling reaction of 5,11-dibromotetracene (**3a**) with aryl- or heteroarylboronic acids, using $Pd(PPh_3)_4$ as a catalyst in traditional toluene/water mixtures, but only traces of the desired diarylated tetracene derivatives were detected, in agreement with literature reports for similar reactions.[14] To overcome the reduced reactivity of **3a**, we carried out the Suzuki−Miyaura cross-coupling reaction in ILs, applying our original experimental conditions.[12a] 5,11-Dibromotetracene **3a** was allowed to react with differently substituted arylboronic acids (**a**−**d**) using the ligand **1** and [bmpy][NTf_2] as the IL at 60 °C. The reactions were very fast, and even though the starting dibromotetracene **3a** did not dissolve completely in the ionic liquid, it was completely consumed after 2 h at 60 °C. The reaction mixture turned from dark red to yellow when the starting material was consumed, and the course of the reaction can be easily monitored by TLC, since the formation of the products was accompanied by the appearance of a very characteristic bright yellow fluorescent spot. It is noteworthy that both the reaction workup and the purification of the products are very simple and fast, an important feature in order to limit the formation of endoperoxides by the reaction of products with oxygen (Scheme 3).

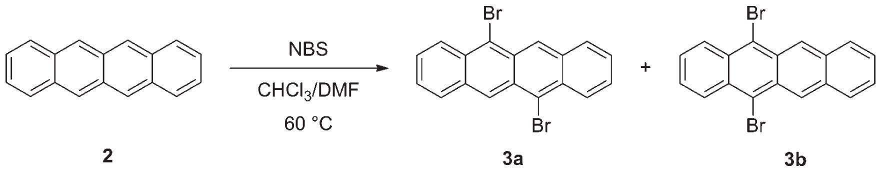
After purification by flash chromatography, 5,11-diaryltetracenes **4a**−**d** were collected in good to excellent chemical yields (Table 1). It is noteworthy that under our milder experimental conditions, in comparison to those reported by Müllen,[14] better yields and faster reactions are obtained.

With the aim of extending the potential and the scope of the Suzuki−Miyaura approach to disubstituted tetracenes, we also synthesized 5,11-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetracene (**6**). Thus, 5,11-dibromotetracene (**3a**) was reacted with bis(pinacolato)diboron **5** in the presence of $Pd(AcO)_2$ as catalyst at 80 °C in DMF, as described in the literature,[16] affording **6** in 87% chemical yield. The tetracene derivative **6**, in turn, has been used in Suzuki−Miyaura cross-coupling reactions with bromobenzene and 4-cyanobromobenzene, under the same experimental conditions used for **4a**−**d**, affording **4a**,**e** in 38% and 37% yields, respectively (Scheme 4).

Due to the peculiar polarity properties of ILs, the cross-coupling reactions performed in this medium seem to benefit from the effect of high ionic strength or high polarity, independent of the steric demand of the starting aryl halide. The high yield of **6**, synthesized in a high-polarity medium, seems to confirm this hypothesis. It is reasonable that the polarity of the medium plays an important role in the oxidative addition of Pd(0) into a C−Br bond: the Pd(II)−Br bond could have a higher ionic character or it could even be dissociated under these conditions, also favoring the transmetalation step in the catalytic cycle proposed for these reactions. The low yield in derivative **4** from **6** could be explained by the higher steric demands of **6** in comparison to the simpler boronic acids used in reaction with **3a**, which slow down the transmetalation step.

All the new compounds have been fully spectroscopically characterized (see the Experimental Section,) and their optical properties are reported in Table 2, together with the standard potential values as determined by electrochemical techniques using cyclic voltammetry. UV−visible absorption spectra of 5,11-disubstituted tetracenes closely resemble that of tetracene, with absorption maxima between 400 and 500 nm corresponding to the $\pi \rightarrow \pi^*$ transition in these compounds,[17] characterized by a series of vibronic replica, due to the coupling between the electronic transition and the 0.18 eV intramolecular vibration mode (due to C−C stretching of aromatic rings). Clearly the nature of the substituents does not affect the vibronic structure of the tetracene core, whereas the electronic interaction between them and the tetracene unit caused a small, systematic red shift of the band, with a maximum shift for the 5,11-dibromotetracene. The small red shift is due to the polarization of the electronic transition that originated this absorption band; the introduction of substituents in the 5,11- or 5,12-positions has a minor impact, while the introduction of substituents on the short edge (positions

Scheme 2. Synthesis of 5,11-Dibromotetracene



Scheme 3. Suzuki Cross-Couplings of 5,11-Dibromotetracene 3a in Ionic Liquids (L = 1)

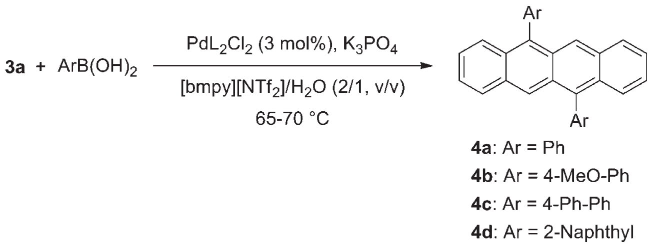


Table 1. Synthesis of 5,11-Diaryltetracenes 4a−d

entry[a]	product	reacn time (h)	yield (%)[b]
1	**4a**	2	97
2	**4b**	2	94
3	**4c**	4	93
4	**4d**	7	85

[a] Reaction conditions: PdL_2Cl_2 (3 mol %), [bmpy][NTf_2] (0.5 mL), arylboronic acid (3 equiv), K_3PO_4 (4 equiv), degassed water (0.25 mL), **3a** (0.065 mmol), 65−70 °C. [b] Yield of isolated product after flash chromatography.

2 and 3) has a greater impact on the position of this band. In the same way, the introduction of substituents in the 5,11-positions has a minor impact also on fluorescence spectra. Notably, compounds **3a** and **4e** are not fluorescent, due to the heavy-atom effect of bromine (**3a**) or to the presence of electron acceptors (**4e**). The standard potentials of compounds **4a**−**e**, **6**, and rubrene have been determined using cyclic voltammetry (CV). Rubrene is considered as the reference molecule. Voltammograms are presented in the Supporting Information. All these molecules exhibit a reversible one-electron redox process with a standard potential value in the range 0.810−1.24 V (Table 2). As expected, rubrene shows the lowest standard potential, due to the presence of four phenyl groups on the tetracene structure, whereas higher standard potentials are measured for molecules **4a**−**e** and **6**, depending on the nature and structure of the 5,11-substituents. The electron-withdrawing character of the cyano groups induces the greater increase in the standard potential; in contrast, the methoxyphenyl groups, known as electron donors, induce a slight increase of the standard potential, in comparison to that of rubrene. The HOMO−LUMO gap is slightly modified by the different substituents, as confirmed by the positions of the absorption and fluorescence spectra. Moreover, the significant anodic shifts measured by electrochemistry indicate that substituents cause a rigid shift of the position of the HOMO and LUMO levels.

Scheme 4. Synthesis and Suzuki Cross-Couplings of 5,11-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetracene 6 in Ionic Liquids (L = 1)

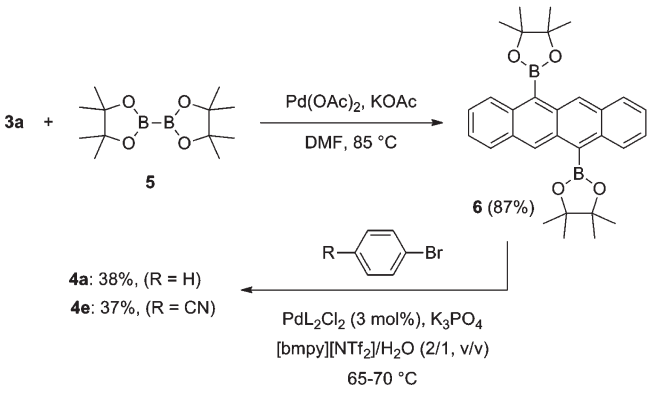


Table 2. Optical Properties and Electrochemistry Data for 5,11-Diaryltetracenes 4a−e

entry	product	absorption max (nm)[a]	fluorescence max (nm)[b]	std potential (V)[c]
1	**4a**	493	502	0.887
2	**4b**	495	510	0.827
3	**4c**	495	499	1.034
4	**4d**	495	509	1.045
5	**4e**	493	n.d.[d]	1.195
6	**3a**	501	n.d.[d]	
7	**6**	488	509	0.973
8	rubrene			0.810

[a] Position of the lowest energy absorption maximum, in 10^{-5} M CH_2Cl_2 solution. See the Supporting Information for full absorption spectra. [b] In 10^{-5} M CH_2Cl_2 solution. [c] Standard potential in V vs SCE. [d] Compound is not fluorescent.

■ CONCLUSIONS

We have reported here a palladium cross-coupling protocol in ionic liquids for the synthesis of 5,11-diaryltetracenes **4a**−**e** starting from 5,11-dibromotetracene (**3a**). The use of both ionic liquids and ionic ligands turned out to be useful for the synthesis of these challenging substrates in high chemical yields and under very mild conditions. The synthesis of the 5,11-diboronyl-tetracene **6** derivative has been also described together with a preliminary study on its reactivity in Suzuki−Miyaura cross-coupling reactions. The physicochemical characterization of the products synthesized showed that the physical properties of the tetracene can indeed be tuned by installing different substituents onto its skeleton.

■ EXPERIMENTAL SECTION

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Varian Inova spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS. HPLC studies were carried out with a reverse-phase column (ZORBAX-Eclipse XDB-C8 Agilent Technologies) using the following conditions. *Method A*: H_2O/MeCN from 90/10 to 0/100 in 20 min, flow 0.5 mL/min, T = 30 °C. *Method B*: H_2O/MeCN from 70/30 to 20/80 in 8 min, flow 0.4 mL/min, T = 30 °C. All starting materials were purchased from Aldrich, Acros, or ABCR and used as received. Electrochemical analyses were carried out in a one-compartment three-electrode cell using a Biologic VSP Potentiostat (Grenoble, France). Dichloromethane (SDS, ProLabo, HPLC grade) and the supporting electrolyte, tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Aldrich, electrochemical grade), were used without further purification. EC-Lab Express software supplied by BioLogic was used for data acquisition. Electrochemical analyses were performed using a platinum disk (outer diameter 1.6 mm) as the working electrode, a stainless steel grid as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Prior to each analysis, the working electrode was carefully polished with diamond paste (1 μm), rinsed with ethanol, and then air-dried. Cyclic voltammetry (CV) was carried out in dichloromethane containing the monomer (5×10^{-4} M) and tetrabutylammonium hexafluorophosphate electrolyte salt (10^{-1} M), by varying the potential between 0 and 1.3 V at a potential scan rate of 50 mV s^{-1}. Absorption and fluorescence spectra were measured on 10^{-5} M CH_2Cl_2 solutions. UV–vis absorption spectra were measured with a Varian CARY 500 spectrophotometer. Fluorescence spectra were measured on a SPEX Fluorolog-3 instrument (Jobin-Yvon). Compounds **4a**–**e** were characterized by NMR and mass spectroscopy and judged >95% pure, but no satisfying elemental analyses could be obtained, due to their instability toward air oxidation.

General Procedure for the Synthesis of 5,11-Diaryltetracene. In an oven-dried Schlenk tube, under an argon atmosphere, the Pd complex $PdCl_2L_2$ (2.8 mg, 0.002 mmol, 3 mol %) was dissolved in 0.5 mL of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([bmpy][NTf_2]) and the yellow, clear solution was stirred under vacuum for a few minutes. Arylboronic acid (0.194 mmol, 3 equiv), K_3PO_4 (0.260 mmol, 4 equiv), and 0.25 mL of degassed water were added to the solution, and the reaction mixture was heated at 65–70 °C. After a few minutes an orange homogeneous solution was formed. 5,11-Dibromotetracene (**3a**; 25 mg, 0.065 mmol, 1 equiv) was added to the reaction mixture, which was vigorously stirred at 65–70 °C until complete consumption of the starting material (monitored by TLC). After it was cooled to room temperature, the reaction mixture was taken up with CH_2Cl_2, adsorbed on silica, and directly charged onto a silica gel column. The desired product was isolated by elution with cyclohexane/CH_2Cl_2 mixtures. During the whole process exposure to light and air should be minimized in order to avoid the possible formation of oxidized side products.

*5,11-Diphenyltetracene (**4a**).* Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.36 (s, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.71–7.61 (m, 8H), 7.59–7.53 (m, 4H), 7.35–7.29 (m, 2H), 7.28–7.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.1, 136.8, 131.5, 131.0, 129.4, 129.04, 128.96, 128.5, 127.6, 126.6, 125.9, 125.3, 124.7. MS (EI): m/z 380 [M^+]. HPLC (λ = 280 nm, method A): t_R = 23.7 min.

*5,11-Bis(4-methoxyphenyl)tetracene (**4b**).* Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.40 (s, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 4H), 7.34–7.24 (m, 4H), 7.21 (d, J = 8.4 Hz, 4H), 4.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.1, 136.6, 132.6, 131.2, 131.0, 129.7, 129.5, 129.0, 126.7, 125.9, 125.2, 124.6, 114.0, 55.4. MS (EI): m/z 441 [M^+]. HPLC (λ = 280 nm, method A): t_R = 23.0 min.

*5,11-Bis(biphenyl-4-yl)tetracene (**4c**).* Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.48 (s, 2H), 7.94–7.91 (m, 4H), 7.88–7.79 (m, 4H), 7.73 (d, J = 7.8 Hz, 4H), 7.65 (d, J = 7.7 Hz, 4H), 7.60–7.52 (m, 4H), 7.45 (t J = 7.4 Hz, 2H), 7.36–7.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.9, 140.3, 138.1, 136.7, 136.5, 132.0, 131.1, 129.4, 129.1, 129.0, 128.9, 128.5, 128.2, 127.5, 127.2, 125.4, 124.8. MS (EI): m/z 532 [M^+]. HPLC (λ = 280 nm, method A): t_R = 26.7 min.

*5,11-Bis(naphthalen-2-yl)tetracene (**4d**).* Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of two atropoisomers): δ (ppm) 8.43 (s, 2 H), 8.14 (s, 1.2 H), 8.18–8.14 (m, 2H), 8.09 (d, J = 10.5 Hz, 4H), 7.98 (d, J = 7.1 Hz, 2H), 7.80 (d, J = 8.5 Hz, 1H), 7.73–7.62 (m, 9H), 7.32–7.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, mixture of two atropoisomers): δ (ppm) 137.0, 136.9, 136.70, 136.69, 133.5, 132.9, 131.10, 131.06, 130.5, 130.43, 130.40, 129.8, 129.60, 129.57, 129.3, 129.2, 129.02, 128.97, 128.4, 128.2, 128.12, 128.09, 128.07, 128.0, 127.1, 126.6, 126.5, 126.34, 126.28, 126.1, 126.0, 125.8, 125.4, 125.2, 124.9, 124.8. MS (EI): m/z 480 [M^+]. HPLC (λ = 280 nm, method A): t_R = 25.3 min.

Synthesis of 5,11-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetracene (6). In an oven-dried round-bottom flask equipped with a reflux condenser, under an argon atmosphere, Pd(OAc)$_2$ (4.4 mg, 0.019 mmol), bis(pinacolato)diboron (**5**; 148 mg, 0.582 mmol), KOAc (86 mg, 0.873 mmol), and 5,11-dibromotetracene (**3a**; 75 mg, 0.194 mmol) were dissolved in 15 mL of anhydrous DMF and heated at 80 °C for 7 h. The red solution turned yellow-green during the reaction. The reaction mixture was then cooled to 0 °C, and 30 mL of water was added. The aqueous layer was extracted twice with ethyl acetate (30 mL). The collected organic phases were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by flash chromatography using cyclohexane/CH_2Cl_2 (80/20) as the eluent (yellow solid, yield 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.21 (s, 2H), 8.42 (d, 2H, J = 9.2 Hz), 7.97 (d, 2H, J = 8.0 Hz), 7.45–7.36 (m, 4H), 1.66 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.8, 133.4, 131.0, 130.4, 129.6, 128.1, 125.7, 124.5, 84.5, 25.2 (carbon attached to boron was not observed).[18] MS (EI): m/z 481 [M^+]. HPLC (λ = 280 nm, method B): t_R = 21.3 min.

Suzuki Reaction with 5,11-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetracene (6). In an oven-dried Schlenk tube, under an argon atmosphere, the Pd complex $PdCl_2L_2$ (1.9 mg, 0.0013 mmol, 3 mol %) was dissolved in 0.5 mL of [bmpy][NTf_2] and the yellow, clear solution was stirred under vacuum for a few minutes. **6** (21 mg, 0.044 mmol, 1 equiv), K_3PO_4 (0.176 mmol, 4 equiv), and 0.25 mL of degassed water were added to the solution, which was heated at 65–70 °C. The aryl bromide (0.132 mmol, 3 equiv) was added to the reaction mixture, which was vigorously stirred at 65–70 °C until complete consumption of the diboronic ester (monitored by TLC). After it was cooled to room temperature, the reaction mixture was taken up with CH_2Cl_2, adsorbed on silica, and directly charged onto a silica gel column. The desired product was isolated by elution with cyclohexane/CH_2Cl_2 mixtures. During the whole process exposure to light and air should be minimized in order to avoid the possible formation of oxidized side products.

*5,11-Bis(4-cyanophenyl)tetracene (**4e**).* Yield: 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.25 (s, 2H), 7.99 (d, J = 8.4 Hz, 4H), 7.86 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 4H), 7.49 (d, J = 9.2 Hz, 2H), 7.40–7.32 (m, 4H). MS (EI): m/z 430 [M^+].

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Figures giving absorption and fluorescence spectra, cyclic voltammograms, and ^{1}H and ^{13}C NMR and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: marco.lombardo@unibo.it (M.L.); luciano.miozzo@unimib.it (L.M.).

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