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Synthesis and Functional Properties of Strongly Luminescent Diphenylamino End-Capped Oligophenylenes

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Two novel homologous series of oligophenylenes (OPPs) symmetrically end-capped with diphenylamino groups and asymmetrically end-capped with anthryldiphenylamino groups were successfully synthesized by a convergent approach with use of palladium-catalyzed homo- and cross-coupling of arylboronic acids. The absorption maxima of both diphenylamino end-capped OPP series do not vary with the chain length although the molar absorptivities increase sequentially. On the other hand, the emission maxima slightly shift to longer wavelengths when the phenylene unit increases in the series. All the diphenylamino end-capped oligomers exhibit very large fluorescence quantum yields (81−89%). They also exhibit low first ionization potentials, corresponding to the oxidation of the triarylamino moiety, which are essentially unaffected by the oligomeric length extension. The good thermal stabilities of these oligomers allowed the fabrication of multilayer light-emitting devices and their investigations.

Introduction

Monodisperse π-conjugated oligomers and macromolecules with well-defined structure have drawn increasing interest[1] because of their unique functional properties that can be used for various electronic or optoelectronic applications such as field-effect transistors[2] and light-emitting diodes (LEDs).[3] They can also be used as model compounds for understanding chemical and physical properties of the related polymeric materials as well as for an investigation of structure−property correlation.[4] On the other hand, their rapid development has led to impressive progress on various practical strategies for their synthesis.[4,5] We are particularly interested in probing the structural features that would affect the technologically useful functional and material properties of oligomers and macromolecules as they are essential toward a rational design and an optimization of functional organic and polymeric materials. We have previously shown that the functional properties of the highly soluble and coplanar oligophenylenevinylenes such as light-emitting properties, photovoltaic effects, third-order nonlinear optical responses, and chemical sensing properties could be tuned and/or enhanced by end-substituent(s).[6] We have also found that an excess of the surface-functionalized dendritic wedges could have a detrimental effect on luminescence properties of dendrimers.[7]

Oligophenylenes (OPPs) are one of the important classes of π-conjugated oligomers that have been found useful as luminophores for light-emitting materials,[8] as semiconductors for field-effect transistors,[9] as rigid-rod cores for liquid crystalline materials,[10] and as biomimetic scaffolds for supramolecular assembly of nanosized barrels, ion channels and amphiphilic materials for biological applications,[11] as well as for biomembrane recognition and depolarization.[12] On the other hand, triphenylamines

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[1] (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537−553. (b) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377. (c) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747−1785. (d) Sheats, J. R.; Barbara, P. F. *Acc. Chem. Res.* **1999**, *32*, 191−192. (e) Segura, J. L.; Martin, N. *J. Mater. Chem.* **2000**, *10*, 2403−2453. (f) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644.

[2] (a) Garnier, F.; Hajlaoui, R.; Yassar, A. *Sciences* **1994**, *265*, 1684. (b) Katz, H. E. *J. Mater. Chem.* **1997**, *7*, 369−376. (c) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365−377. (d) Garnier, F. *Acc. Chem. Res.* **1999**, *32*, 209−215.

[3] (a) Kraft, A.; Grimsadle, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402−428. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121−128. (c) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471−1507.

[4] Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, Germany, 1998.

[5] (a) Robert, F.; Winum, J. Y.; Sakai, N.; Gerard, D.; Matile, S. *Org. Lett.* **1999**, *2*, 37−39. (b) Read, M. W.; Escobedo, J. O.; Willis, D. M.; Beck, P. A.; Strongin, R. M. *Org. Lett.* **2000**, *2*, 3201−3204. (c) Deng, X.; Mayeux, A.; Cai, C. *J. Org. Chem.* **2002**, *67*, 5279−5283.

[6] (a) Wong, M. S.; Li, Z. H.; Tao, Y.; D'Iorio, M. *Chem. Mater.* **2003**, *15*, 1198−1203. (b) Wong, M. S.; Li, Z. H.; Shek, M. F.; Samoc, M.; Samoc, A.; Luther-Davies, B. *Chem. Mater.* **2002**, *14*, 2999−3004. (c) Wong, M. S.; Li, Z. H.; Shek, M. F.; Chow, K. H.; Tao, Y.; D'Iorio, M. *J. Mater. Chem.* **2000**, *10*, 1805−1810. (d) Wong, M. S.; Chan, W. H.; Chan, W. Y.; Li, J.; Dan, X. *Tetrahedron Lett.* **2000**, *41*, 9293−9297.

[7] (a) Kwok, C. C.; Wong, M. S. *Macromolecules* **2001**, *34*, 6821−6830. (b) Kwok, C. C.; Wong, M. S. *Chem. Mater.* **2002**, *14*, 3158−3166.

[8] (a) Era, M.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1995**, *67*, 2436−2438. (b) Wang, Y. Z.; Sun, R. G.; Meghdadi, F.; Leising, G.; Epstein, A. J. *Appl. Phys. Lett.* **1999**, *74*, 3613−3615.

[9] Grundlach, D. J.; Lin, Y. Y.; Jackson, T. N.; Schlom, D. G. *Appl. Phys. Lett.* **1997**, *71*, 3853−3855.

[10] Deeg, O.; Kirsch, P.; Pauluth, D.; Bäuerle, P. *Chem. Commun.* **2002**, 2767−2763.

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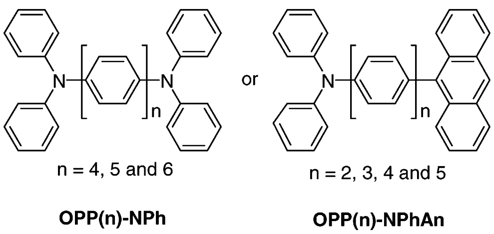
CHART 1. Molecular Structures of OPP(*n*)-NPh and OPP(*n*)-NPhAn



known to have a high hole transporting mobility and to form stable cation radicals have been widely used as hole transporting materials in LEDs[13] and shown potentials as molecular-based magnets.[14] It has been shown that light-emitting polymers grafted or end-capped with triphenylamine moieties exhibit improved LED device performance.[15]

To integrate the functional properties of the π-conjugated OPP system and the triphenylamine moiety, we herein report the first syntheses and investigation of the structure–functional property relationship of two novel series of blue-light-emitting π-conjugated OPPs bearing symmetrically end-capped diphenylamino moieties, **OPP(*n*)-NPh** where $n = 4$, 5, and 6, and asymmetrically end-capped anthryldiphenylamino moieties, **OPP(*n*)-NPhAn**, where $n = 2$, 3, 4, and 5 (Chart 1). In contrast to other soluble OPPs reported, to avoid severe reduction in the π-orbital overlap of the OPP backbone, which would affect the favorable functional properties, the functional substituents were incorporated at the end(s). Very recently, a series of diarylamino-capped oligothiophenes were synthesized and their optical and electrochemical properties were also investigated.[16]

Results and Discussion

It is important to note that palladium-catalyzed organoboronic acid coupling was more useful and versatile for diarylamino-substituted OPP synthesis than the organotin-coupling protocol. Syntheses of diarylamino end-capped OPPs were found to be nontrivial. The symmetrically diphenylamino-substituted OPP series, **OPP(*n*)-NPh**, was synthesized by a convergent approach with use of palladium-catalyzed homo-coupling[17] or cross-coupling[18] of 4-(diphenylamino)biphenyl-4′-boronic acid as a key step to construct the OPP skeleton. The synthetic route is summarized in Scheme 1.

Monoamination of 4,4′-dibromobiphenyl with diphenylamine catalyzed by palladium acetate/tri(*o*-tolyl)phosphine in the presence of sodium *tert*-butoxide[19] afforded 4-bromo-4′-(diphenylamino)biphenyl, **1**,[20] in 60% yield and disubstituted product in 36% yield. Attempts to improve the monoselectivity by means of chemoselective amination of 4,4′-bromoiodobiphenyl were not successful. Transformation of **1** to the corresponding boronic acid **2** was achieved by lithium-bromide exchange of **1** at −78 °C followed by the reaction with trimethyl borate at room temperature and subsequently acid hydrolysis. Ligand-promoted homo-coupling of boronic acid **2** carried out in toluene–methanol afforded **OPP(4)-NPh** in a moderate yield. On the other hand, double Suzuki cross-coupling of boronic acid **2** and 1,4-diiodobenzene afforded **OPP(5)-NPh** in a reasonably good yield under typical reaction conditions. It is important to note that the use of 1,4-dibromobenzene gave no desired cross-coupling product, which is attributed to the deactivation of the monosubstituted intermediate by the terminal amino group. With use of the same strategy, **OPP(6)-NPh** was synthesized by double Suzuki cross-coupling of boronic acid **2** and 4,4′-diiodobiphenyl,[21] which was prepared by the iodination of biphenyl with I_2/HIO_4 in acetic acid. It should also be stated that double cross-coupling of aryl bromide **1** with either 1,4-benzenediboronic acid or 4,4′-biphenyldiboronic acid afforded no desired oligomers.

The convergent synthesis of the asymmetrically diphenylaminoanthryl-substituted OPP series, **OPP(*n*)-NPhAn**, is outlined in Scheme 2. Chemoselective cross-coupling of 1-bromo-4-iodobenzene and boronic acid **2** with Suzuki's conditions afforded 4-bromo-4′-(diphenylamino)terphenyl, **3**, in an excellent yield. Conversion of bromide functionality to boronic acid functionality was achieved accordingly, using typical protocols yielding **4** in 90% yield. Cross-coupling of **2** with 9-bromoanthracene, **5**, and cross-coupling of aryl bromide **3** with 9-anthrancene-boronic acid, **6**, smoothly afforded **OPP(2)-NPhAn** and **OPP(3)-NPhAn**, respectively, in very good yields.

However, the use of other aryl bromides for the preparation of higher homologues of **OPP(*n*)-NPhAn** was not so satisfactory. To improve the odds, aryl iodide **7** was pursued and prepared by mono-cross-coupling of 4,4′-diiodobiphenyl and **6**, yielding **7** in 50% yield and dicoupled product in 35% yield. As anticipated, cross-coupling of **7** with boronic acid **2** as well as with boronic acid **4** afforded **OPP(4)-NPhAn** and **OPP(5)-NPhAn**, respectively, in satisfactory yields. All the newly synthesized oligomers were fully characterized with ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis and found to be in good agreement with the structures. In addition, all the oligomers show very good thermal stabilities as determined by thermal gravimetric analysis and their

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(11) (a) Baumeister, B.; Matile, S. *Chem. Commun.* **2000**, 913–914. (b) Baumeister, B.; Sakai, N.; Matile, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1955–1958. (c) Sidorov, V.; Douglas, T.; Dzekunov, S. M.; Abdallah, D.; Ghebremariam, B.; Roepe, P. D.; Matile, S. *Chem. Commun.* **1999**, 1429–1430.

(12) Winum, J. Y.; Matile, S. *J. Am. Chem. Soc.* **1999**, *121*, 7961–7962.

(13) (a) Adachi, C.; Nagai, K.; Tamoto, N. *Appl. Phys. Lett.* **1995**, *66*, 2679–2681. (b) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1–25. (c) Strohriegl, P.; Grazulevicius, J. V. *Adv. Mater.* **2002**, *14*, 1439–1452.

(14) (a) Goodson, F. E.; Hauck, S. I.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 7527–7539. (b) Ito, A.; Ino, H.; Tanaka, K.; Kanemoto, K.; Kato, T. *J. Org. Chem.* **2002**, *67*, 491–498.

(15) (a) Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Müller, D. C.; Meerholz, K.; Yasuda, A.; Neher, D. *Adv. Mater.* **2001**, *13*, 565–570. (b) Pu, Y. J.; Soma, M.; Kido, J.; Nishide, H. *Chem. Mater.* **2001**, *13*, 3817–3819. (c) Shi, J.; Zheng, S. *Macromolecules* **2001**, *34*, 6571–6576.

(16) Tabet, A.; Schröder, A.; Hartmann, H.; Rohde, D.; Dunsch, L. *Org. Lett.* **2003**, *5*, 1817–1820.

(17) Wong, M. S.; Zhang, X. L. *Tetrahedron Lett.* **2001**, *42*, 4087–4089.

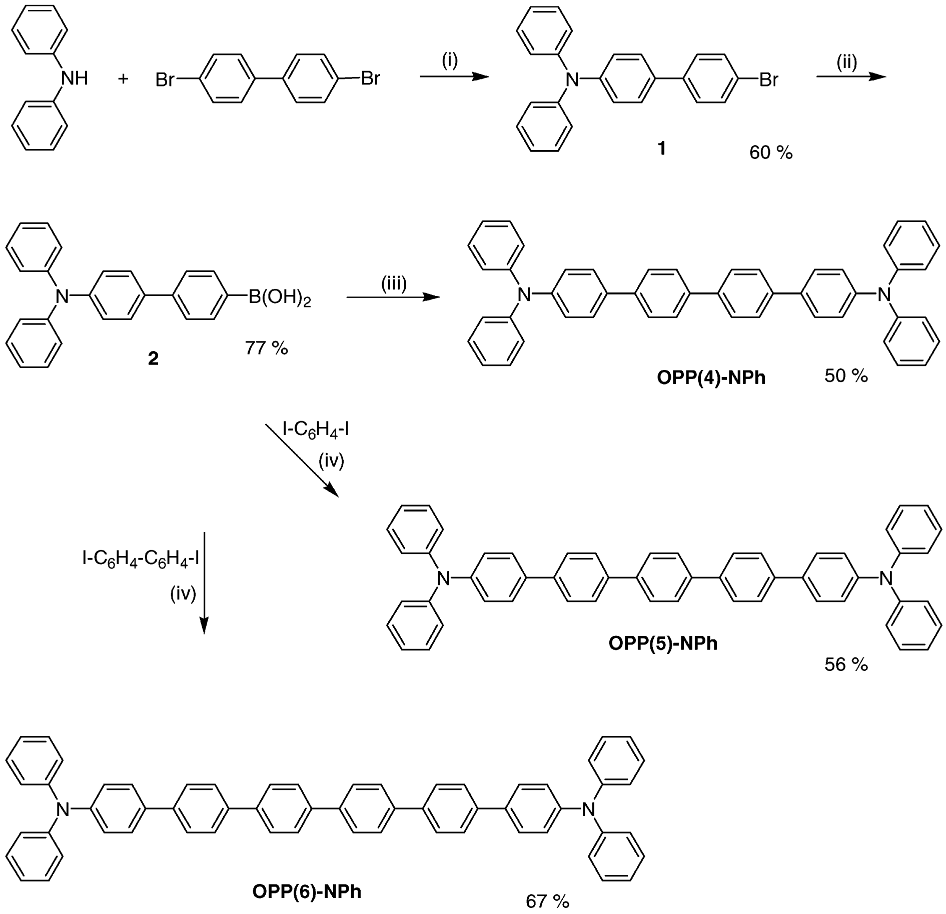
(18) (a) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147–168. (b) Suzuki, A. In *Metal-catalysed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(19) (a) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852–860. (b) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125–146.

(20) Bruce, A. R.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L.; He, G. S.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863–1874.

(21) Sekher, P.; Gano, J. E.; Luzik, E. D., Jr. *Synth. Commun.* **1997**, *27*, 3631–3636.

SCHEME 1. Synthesis of Symmetrically Diphenylamino-Disubstituted Oligophenylenes, OPP(*n*)-NPh (*n* = 4, 5, and 6)[a]



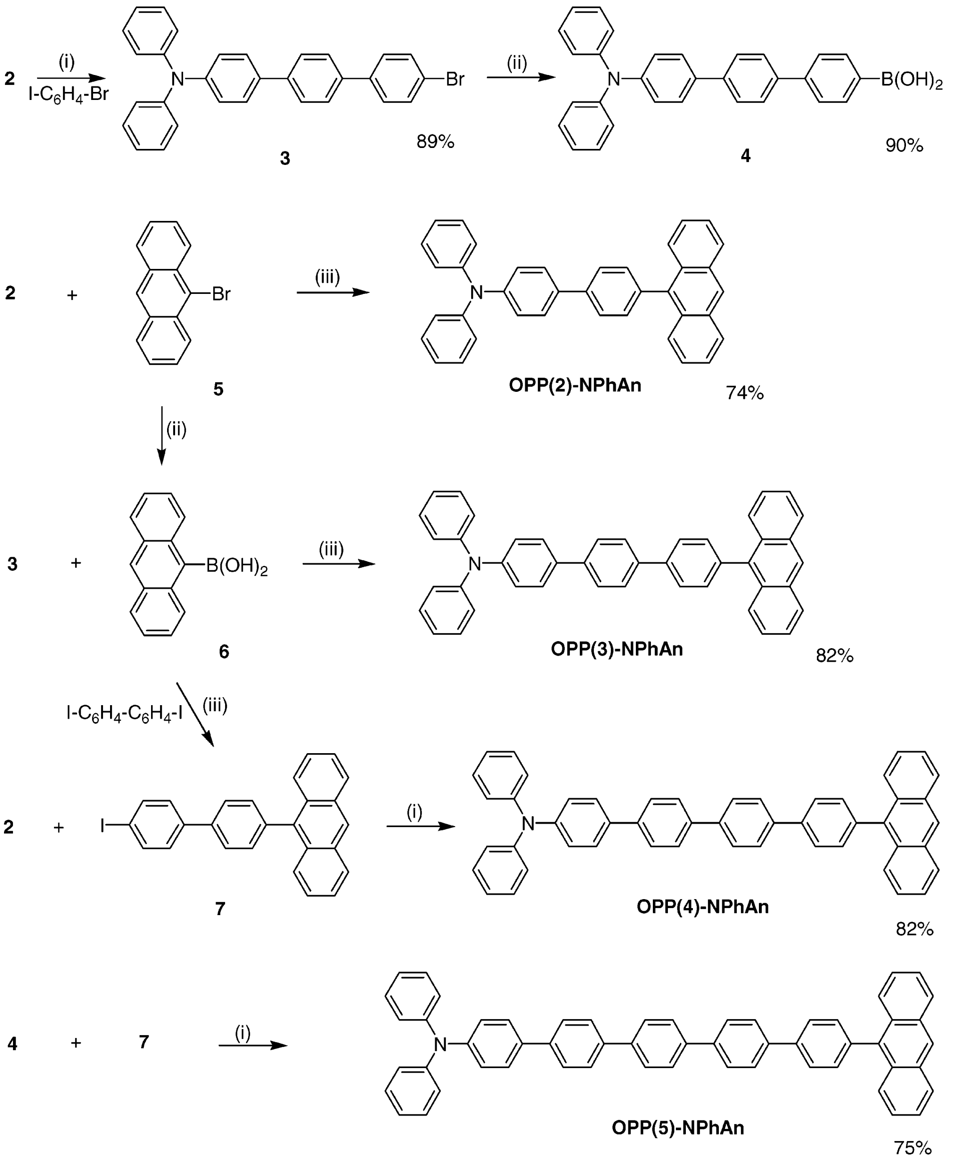
[a] Reagents and conditions: (i) 2 mol % of Pd(OAc)$_2$:2P(o-tol)$_3$, Na-*t*-BuO, toluene, 110 °C, overnight; (ii) (a) ^{n}BuLi, THF, −78 °C, 1 h, (b) B(OMe)$_3$, −78 °C to rt, 2 h, (c) H$^+$; (iii) 5 mol % of Pd(OAc)$_2$:2PPh$_3$, K$_2$CO$_3$, toluene−CH$_3$OH, 90 °C, 4 h; (iv) 2.5 mol % of Pd(PPh$_3$)$_4$, K$_2$CO$_3$, THF, 50 °C, overnight.

stabilities generally increase with the chain length (Table 1). In contrast to the asymmetrically anthryldiphenylamino-disubstituted OPPs, **OPP(*n*)-NPhAn**, the symmetrically diphenylamino-disubstituted OPPs, **OPP(*n*)-NPh**, exhibit high glass transition temperatures which also increase with the oligomeric length.

OPP(*n*)-NPhs show two overlapped absorption bands peaked at around 304 and 358 nm, which correspond to an n → π* transition of the triphenylamine moiety and a $\pi \rightarrow \pi$* transition of the OPP skeleton, respectively. In contrast to the unsubstituted OPPs,[1b] the absorption maxima (λ_{max}) of **OPP(*n*)-NPh**s remains essentially unchanged with an increase in chain length even though the molar absorptivities (ϵ) increase (Table 1). This suggests that chain length extension does not improve/enhance the π-orbital overlap further in the ground state. Upon irradiation at 304 nm, the emission spectra are identical with those excited at λ_{max}^{abs} = 358 nm. Nevertheless, the emission maxima sequentially shift to longer wavelengths and the fluorescence quantum yields enhance (81→95%) as the oligomeric length extends (Table 1). A similar trend is also present in the corresponding EL spectra (see the Supporting Information). This implies that in the excited state better or more π-orbital overlap is attained as the chain length increases.

On the contrary, the absorption spectra of the asymmetrically disubstituted **OPP(*n*)-NPhAn** series are consistently composed of several overlapped vibronic bands indicating restricted rotation of the π-conjugated system. Again, the λ_{max}^{abs} values remain fairly constant at 351 nm and the ϵ increase with an increase in phenylene unit (Table 1). Interestingly, **OPP(2)-NPhAn** exhibits an unexpectedly large Stoke shift (116 nm) as compared to the higher homologues (77−81 nm), which results in a significantly larger red shift in emission maximum (464 nm) than the other homologues (428−433 nm). Furthermore, the emission maximum of **OPP(2)-NPhAn** exhibits a larger solvatochromic effect ($\Delta\lambda_{max}^{em}$ = 146 nm, cyclohexane to DMSO) than those of higher homologues ($\Delta\lambda_{max}^{em}$ = 53−74 nm, cyclohexane to DMSO). This suggests that the emission (excited) state of **OPP(2)-NPhAn** possesses stronger polar (charge-transfer) character than higher homologues, which presumably gives rise to the anomalous shift. Similar to the **OPP(*n*)-NPh** series, the higher homologues of **OPP(*n*)-NPhAn**, $n \geq 3$, show a small red shift in emission maxima as the oligomeric length increases. Although the fluorescence quantum yields do not increase with chain length in this series, all the asymmetrically disubstituted oligomers exhibit very strong blue light emission (Φ > 85%). The fluores-

SCHEME 2. Synthesis of Asymmetrically Diphenylaminoanthryl-Substituted Oligophenylenes, OPP(n)-NPhAn (n = 2, 3, 4, and 5)[a]



[a] Reagents and conditions: (i) 2.5 mol % of $Pd(PPh_3)_4$, K_2CO_3,THF, 50 °C, overnight; (ii) (a) ^{n}BuLi, THF, −78 °C, 1 h, (b) $B(OMe)_3$, −78 °C to rt, 2 h, (c) H^+; (iii) 2.5 mol % of $Pd(PPh_3)_4$, K_2CO_3,THF, 80 °C, overnight.

TABLE 1. Summaries of Physical Measurements of OPP(n)-NPh and OPP(n)-NPhAn

	λ_{max}^{abs} ^{a}/nm (ϵ_{max} 10^4/M^{-1} cm^{-1})	λ_{max}^{em} ^{a,b}/nm	Φ_{FL} ^{a,c}	$\tau^{a,d}$/ns	$E_{1/2}$ ^{e}/V	T_g ^{f}/°C	T_m ^{f}/°C	T_{dec} ^{g}/°C
OPP(4)-NPh	358 (5.62)	425	0.81	1.15	0.48	99	252	497
OPP(5)-NPh	358 (6.38)	433	0.84	1.06	0.47	115	191	560
OPP(6)-NPh	358 (7.90)	436	0.95	1.20	0.47	125	319	590
OPP(2)-NPhAn	348 (2.30)	464	0.89	3.14	0.48, 0.84	no	267	446
OPP(3)-NPhAn	351 (2.87)	428	0.88	2.44	0.48, 0.84	no	284	470
OPP(4)-NPhAn	351 (3.41)	430	0.86	1.92	0.47, 0.81	no	273	519
OPP(5)-NPhAn	352 (5.92)	433	0.85	1.64	0.47, 0.80	no	271	533

[a] Measured in $CHCl_3$. [b] Excited at the absorption maxima. [c] Using 9,10-diphenylanthrancene ($\Phi_{360} = 0.9$) as a standard. [d] Using nitrogen laser as the excitation source. [e] $E_{1/2}$ vs Fc^+/Fc estimated by the CV method, using a platinum disk electrode as a working electrode, a platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution. All the potentials were calibrated with ferrocene, $E_{1/2}(Fc/Fc^+) = 0.45$ V vs SCE. [f] Determined by differential scanning calorimeter from remelt after cooling with a heating rate of 10 °C/min under N_2. [g] Determined by thermal gravimetric analyzer with a heating rate of 10 °C/min under N_2.

cence lifetimes of all these diphenylamino end-capped OPPs are in the order of a few nanoseconds, indicating that emission originates from the singlet excited state.

To examine the electrochemical properties of these oligomers, cyclic voltametry was carried out in a three-electrode cell setup with 0.1 M Bu_4NPF_4 as a supporting

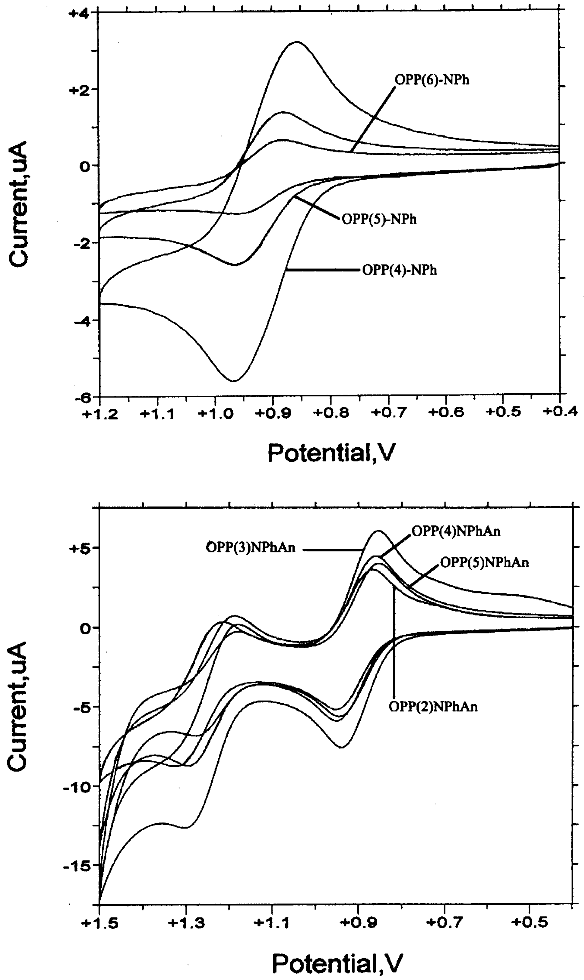


FIGURE 1. Cyclic voltamograms of the **OPP(*n*)-NPh** and **OPP(*n*)-NPhAn** series.

electrolyte in CH_2Cl_2. All the potentials reported are referenced to Fc/Fc^+ standard and the results are tabulated in Table 1. All the oligomers in the symmetrical series exhibit a reversible two-electron anodic redox couple (Figure 1). Similar to the absorption behavior, the oxidation potential, which corresponds to the arylamino oxidation, is essentially independent of the conjugated length of an oligomer even though the diarylamino functionality is fully conjugated to the oligophenylene backbone. One the other hand, the asymmetrically disubstituted oligomers exhibit two reversible one-electron anodic redox couples which correspond to the sequential removal of electrons from the arylamino group and anthrancene moiety forming radical cations and dications, respectively (Figure 1). Again, the first oxidation potential (or HOMO level) of the oligomers does not change significantly with the number of phenylene units. However, the removal of the second electron from the cation radical appears slightly easier as the chain length increases.

Because of the strong fluorescence, low first ionization potential, and high thermal stabilities, these newly synthesized OPPs show potential for OLED applications. Multilayer OLEDs using the newly synthesized oligomers except **OPP(2)-NPhAn** as an emissive layer were initially fabricated by vacuum deposition with structure ITO/CuPc (10 nm)/oligomer (40 nm)/PBD (30 nm)/Al (150 nm). The EL spectra of these devices show almost identical spectral characteristics with blue emission maxima at around 436 nm and a shoulder peak at around 452 nm (see the Supporting Information). These emission maxima of EL spectra red shifted less than 10 nm as compared to those obtained from solution. Furthermore, the emission bands do not vary significantly with the chain length and/or the presence of the anthrancene moiety. The EL spectra features, which resemble the PL spectra of a thin film, are also independent of the applied voltage. These suggest that no exciplex formed in the device and the emissions originated from the oligomers. On the contrary, a very strong exciplex emission at around 490 nm was observed when NPB was used as the hole transporting layer, rather than CuPc. Our preliminary results indicate that **OPP(*n*)-NPh**-based OLEDs show better device performance than **OPP(*n*)-NPhAn**-based counterparts in terms of device stability. Among the devices fabricated, **OPP(5)-NPh**-based LED shows the most promising device properties for further optimization.

Conclusions

We have demonstrated an efficient method to synthesize two novel homologues series of OPPs bearing end-functionalized diphenylamino groups and anthryldiphenylamino groups by means of convergent approach using palladium-catalyzed homo- and cross-coupling of arylboronic acids. The functional properties of these diphenylamino end-capped oligomers including the absorption maxima and the first ionization potential are essentially unaffected by the chain length extension. On the other hand, the emission spectra slightly red shift when the phenylene unit increases. All these diphenylamino end-capped oligomers exhibit strong blue emission, low first ionization potential, and high thermal stabilities, making them suitable for luminescence applications.

Experimental Section

4-Bromo-4′-(diphenylamino)biphenyl (1). A single-necked 100-mL round-bottomed flask was charged with the diphenylamine (3.38 g, 20 mmol), sodium *tert*-butoxide (2.31 g, 24 mmol), palladium(II) acetate (0.11 g, 0.5 mmol), dry toluene (30 mL), 4,4′-dibromobiphenyl (6.24 g, 20 mmol), and tri-*o*-tolylphosphine (0.30 g, 1 mmol) and heated at 110 °C for 24 h under a nitrogen atmosphere. After cooling, the mixture was quenched with water and the solution extracted with dichloromethane (3 × 50 mL). The combined organic extract was washed with water and dried over anhydrous Na_2SO_4. Evaporation of volatiles left a dark solid, which was separated by column chromatography with petroleum ether (60−80 °C) as eluent affording the title compound in 60% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, $J = 8.64$ Hz, 2H), 7.39 (d, $J = 8.64$ Hz, 4H), 7.27 (s, 2H), 7.21 (s, 2H), 7.10 (d, $J = 7.56$ Hz, 6H), 7.01 (t, $J = 7.43$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 139.6, 133.6, 131.8, 129.3, 128.2, 127.5, 124.5, 123.7, 123.1, 120.9. MS (FAB) *m*/*z* 401.4 ($M^+ + 1$).

4-(Diphenylamino)biphenyl-4′-boronic Acid (2). To a 100-mL two-necked flask containing a solution of **1** (1.0 g, 2.5 mmol) in 20 mL of dry THF equipped with a magnetic stirrer, a N_2 purge, and a −78 °C acetone−dry ice bath was added 1.5 M *n*-butyllithium (2.5 mL, 3.75 mmol) with good stirring. After the mixture was stirred for 1 h, trimethyl borate (0.43 mL, 3.75 mmol) was added. After a further 2 h of stirring, water was first added to the reaction mixture and then HCl (6 M) was added in a dropwise fashion until an acidic mixture was obtained. The reaction mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. Petroleum ether was added to dissolve the starting raw material and to precipitate the product. The product boronic acid **2** was obtained as a white solid with an isolated yield of 77%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (s, 2H), 7.85 (d, J = 7.83 Hz, 2H), 7.61 (t, J = 7.29 Hz, 4H), 7.32 (t, J = 7.70 Hz, 4H), 7.06 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.8, 146.6, 140.8, 134.6, 133.8, 129.4, 127.5, 124.9, 124.0, 123.1. MS (FAB) m/z 365.3 (M^+).

4-Bromo-4′-(diphenylamino)terphenyl (3). A two-necked flask containing 1-bromo-4-iodobenzene (622 mg, 2.2 mmol), tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol), tetrahydrofuran (20 mL), **2** (730 mg, 2 mmol), and 2 M K_2CO_3 (5 mL) equipped with a magnetic stirrer, a N_2 purge, and a reflux condenser was heated at 50 °C overnight. The reaction mixture was then poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography with petroleum ether as eluent affording the title compound as a pale yellow solid with an isolated yield of 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.00 Hz, 2H), 7.60 (d, J = 8.00 Hz, 2H), 7.56 (d, J = 8.40 Hz, 2H), 7.49 (m, 4H), 7.27 (d, J = 8.00 Hz, 4H), 7.13 (d, J = 7.20 Hz, 6H), 7.03 (t, J = 7.60 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.4, 139.9, 139.6, 138.2, 134.2, 131.9, 129.3, 128.5, 127.6, 127.2, 127.1, 124.5, 123.7, 123.0, 121.5. MS (FAB) m/z 477 (M^+). Anal. Calcd for $C_{30}H_{22}BrN$: C, 75.63; H, 4.65; N, 2.93. Found: C, 75.60; H, 5.05; N, 3.23.

4-(Diphenylamino)terphenyl-4′-boronic Acid (4). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (s, 2H), 7.89 (d, J = 8.10 Hz, 2H), 7.74 (t, J = 3.10 Hz, 4H), 7.67 (t, J = 8.10 Hz, 4H), 7.33 (t, J = 7.83 Hz, 4H), 7.08 (dd, J = 6.21 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.0, 146.8, 141.0, 138.7, 138.5, 134.8, 133.4, 129.6, 127.5, 127.1, 126.6, 126.5, 125.4, 124.2, 123.3, 123.2.

9-Anthrylboronic Acid (6). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 2H), 8.53 (s, 1H), 8.04 (m, 4H), 7.51 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 132.6, 130.6, 128.9, 128.3, 125.8, 125.0, 124.9, 67.0. MS (FAB) m/z 222.0 (M^+).

4,4′-Diiodobiphenyl. A mixture of biphenyl (1.54 g, 10 mmol), acetic acid (10 mL), water (1 mL), concentrated sulfuric acid (1 mL), iodine (2.79 g, 11 mmol), periodic acid (1.25 g, 5.5 mmol), and carbon tetrachloride (2 mL) was maintained at 80 °C for 4 h with magnetic stirring. After the slurry product was cooled to room temperature, it was poured into water and extracted the solution with dichloromethane (3 × 50 mL). After the combined dark purple organic layer was decolorized with sodium sulfite it was washed with water, dried with anhydrous Na_2SO_4, filtered, and evaporated to dryness, which afforded the pure title compound as a white solid in almost 100% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.37 Hz, 4H), 7.22 (d, J = 8.64 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 137.9, 128.6, 93.5. MS (FAB) m/z 406.2 (M^+).

4-(9′-Anthryl)-4′-iodobiphenyl (7). A mixture of 4,4′-diiodobiphenyl (1.62 g, 4 mmol), tetrakis(triphenylphosphine)-palladium(0) (116 mg, 0.1 mmol), **6** (888 mg, 4 mmol), 2 M K_2CO_3 (8 mL), and THF (40 mL) under nitrogen atmosphere was heated at 80 °C overnight with magnetic stirring. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel (70−230 mesh) column chromatography with petroleum ether as eluent affording the title compound as a yellow solid with an isolated yield of 50% and dicoupling product of 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.05 (d, J = 8.37 Hz, 2H), 7.77 (m, 6H), 7.43 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.1, 138.0, 136.7, 131.7, 129.0, 128.9, 128.4, 127.4, 127.0, 126.8, 126.7, 125.4, 125.4, 125.1, 93.2. MS (FAB) m/z 456.7 (M^+). Anal. Calcd for $C_{26}H_{17}I$: C, 68.43; H, 3.75. Found: C, 68.13; H, 4.12.

4,4′-Bis(diphenylamino)quaterphenyl (OPP(4)-NPh). A mixture of **2** (183.0 mg, 0.50 mmol), 1:2 palladium(II) acetate: triphenylphosphine (5 mol %), toluene (10 mL), methanol (5 mL), and 2 M K_2CO_3 (1 mL) was heated at 90 °C for 4 h. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was further purified by silica gel column chromatography with 4:1 petroleum ether:dichloromethane as eluent. The product was a white solid with an isolated yield of 49%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.40 Hz, 4H), 7.64 (d, J = 8.40 Hz, 4H), 7.51 (d, J = 8.40 Hz, 4H), 7.26 (t, J = 8.00 Hz, 8H), 7.14 (m, 12H), 7.03 (t, J = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.2, 139.5, 139.0, 134.5, 129.3, 127.6, 127.2, 127.0, 124.4, 123.8, 123.0. MS (FAB) m/z 640.5 (M^+). Anal. Calcd for $C_{48}H_{36}N_2$: C, 89.96; H, 5.66; N, 4.37. Found: C, 89.80; H, 5.90; N, 4.24.

4,4′-Bis(diphenylamino)quinquephenyl (OPP(5)-NPh). A mixture of 1,4-diiodobenzene (164 mg, 0.5 mmol), tetrakis-(triphenylphosphine)palladium(0) (58 mg, 0.04 mmol), boronic acid **2** (400 mg, 1.10 mmol), tetrahydrofuran (20 mL), and 2 M K_2CO_3 (2.5 mL) was heated at 50 °C overnight with magnetic stirring under a nitrogen atmosphere. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel (70−230 mesh) column chromatography with petroleum ether/dichloromethane (v/v 4:1) as eluent to give the title compound as a white solid with an isolated yield of 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 8H), 7.65 (d, J = 8.40 Hz, 4H), 7.52 (d, J = 8.40 Hz, 4H), 7.27 (t, J = 7.80 Hz, 8H), 7.14 (m, 12H), 7.03 (t, J = 7.40 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.3, 139.6, 139.6, 139.0, 134.4, 129.3, 127.6, 127.4, 127.3, 127.0, 124.5, 123.8, 123.0. MS (FAB) m/z 716.3 (M^+). Anal. Calcd for $C_{54}H_{40}N_2$: C, 90.47; H, 5.62; N, 3.91. Found: C, 90.39; H, 5.68; N, 3.91.

4,4′-Bis(diphenylamino)sexiphenyl (OPP(6)-NPh). A white solid with isolated yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 8H), 7.71 (d, J = 8.40 Hz, 4H), 7.66 (d, J = 8.40 Hz, 4H), 7.52 (d, J = 8.40 Hz, 4H), 7.27 (d, J = 8.40 Hz, 8H), 7.14 (m, 12H), 7.03 (t, J = 7.40 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 147.6, 147.3, 145.6, 139.7, 137.1, 129.3, 128.6, 127.6, 127.4, 127.0, 126.5, 124.5, 123.8, 123.3, 123.0, 121.9. MS (FAB) m/z 793.5 (M^+). Anal. Calcd for $C_{60}H_{44}N_2$: C, 90.87; H, 5.59; N, 3.53. Found: C, 90.65; H, 5.76; N, 3.66.

9-[4-(4′-Diphenylamino)biphenyl]anthracene (OPP(2)-NPhAn). A mixture of 9-bromoanthracene (257.3 mg, 1.00 mmol), tetrakis(triphenylphosphine)palladium(0) (58.5 mg, 0.05 mmol), boronic acid **2** (365.8 mg, 1.00 mmol), 2 M K_2CO_3, and (2 mL) tetrahydrofuran (20 mL) under nitrogen atmosphere was heated at 80 °C overnight with magnetic stirring. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel (70−230 mesh) column chromatography with 4:1 petroleum ether:dichloromethane as eluent affording the title compound as a yellow solid with an isolated yield of 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.04 (d, J = 8.37 Hz, 2H), 7.76 (t, J = 8.64 Hz, 4H), 7.63 (d, J = 8.91 Hz, 2H), 7.46 (t, J = 8.24 Hz, 4H), 7.28 (m, 12H), 7.04 (t, J = 7.16 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.2, 139.5, 137.1, 136.6, 134.6, 131.6, 131.3, 130.1, 129.2, 128.2, 127.7, 126.8, 126.5, 126.4, 125.2, 125.0, 124.4, 123.9, 122.9. MS (FAB) m/z 498.3 ($M^+ + 1$). Anal. Calcd for $C_{38}H_{27}N$: C, 91.72; H, 5.47; N, 2.81. Found: C, 91.64; H, 5.70; N, 3.03.

9-[4-(4′-Diphenylamino)terphenyl]anthracene (OPP(3)-NPhAn). A light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.06 (d, J = 8.00 Hz, 2H), 7.85 (d, J = 8.00 Hz, 2H), 7.81 (d, J = 8.00 Hz, 2H), 7.76 (d, J = 8.40 Hz, 2H), 7.72 (d, J = 8.00 Hz, 2H), 7.56 (d, J = 8.40 Hz, 2H), 7.51 (d, J = 8.00 Hz, 2H), 7.46 (dd, J = 7.6 Hz, 2H), 7.37 (t, J = 8.80 Hz, 2H), 7.26 (m, 4H), 7.17 (m, 6H), 7.04 (t, J = 7.20 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.3, 139.7, 139.6, 139.1, 137.7, 136.6, 134.4, 131.7, 131.3, 130.2, 129.3, 128.4, 127.6, 127.4, 127.0, 126.8, 126.6, 125.4, 125.1, 124.5, 123.9, 123.0. MS (FAB) m/z 573.5 (M^+). Anal. Calcd for $C_{44}H_{31}N$: C, 92.11; H, 5.45; N, 2.44. Found: C, 91.80; H, 5.53; N, 2.55.

9-[4-(4′-Diphenylamino)quaterphenyl]anthracene (OPP(4)-NPhAn). A mixture of **7** (214 mg, 0.47 mmol), tetrakis(triphenylphosphine)palladium(0) (27 mg, 0.02 mmol), boronic acid **2** (257 mg, 0.70 mmol), tetrahydrofuran (20 mL), and 2 M K_2CO_3 (2 mL) was heated at 50 °C overnight with magnetic stirring under nitrogen atmosphere. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel (70−230 mesh) column chromatography with 8:1 petroleum ether:dichloromethane as eluent affording the title compound as a light yellow solid with an isolated yield of 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.06 (d, J = 8.40 Hz, 2H), 7.85 (dd, J = 6.00 Hz, 4H), 7.77 (m, 6H), 7.68 (d, J = 8.40 Hz, 2H), 7.53 (dd, J = 6.80 Hz, 4H), 7.47 (dd, J = 7.60 Hz, 2H), 7.37 (dd, J = 8.00 Hz, 2H), 7.27 (m, 4H), 7.15 (m, 6H), 7.04 (t, J = 7.40 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.2, 139.6, 138.9, 137.7, 136.5, 134.3, 131.7, 131.3, 130.1, 129.2, 128.7, 128.3, 127.5, 127.3, 127.2, 127.2, 126.9, 126.9, 126.8, 126.7, 126.6, 125.3, 125.0, 124.4, 123.8, 122.9. MS (FAB) m/z 649.4 (M^+). Anal. Calcd for $C_{50}H_{35}N$: C, 92.42; H, 5.43; N, 2.16. Found: C, 92.25; H, 5.41; N, 2.39.

9-[4-(4′-Diphenylamino)quinquephenyl]anthracene (OPP(5)-NPhAn). A light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.06 (d, J = 8.40 Hz, 2H), 7.77 (m, 16H), 7.53 (dd, J = 8.20 Hz, 4H), 7.47 (t, J = 7.20 Hz, 2H), 7.37 (t, J = 7.20 Hz, 2H), 7.27 (m, 4H), 7.15 (m, 6H), 7.03 (t, J = 7.40 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 147.3, 139.8, 139.7, 139.7, 139.5, 139.0, 137.9, 136.6, 134.4, 131.8, 131.4, 130.2, 129.3, 128.4, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 127.0, 126.9, 126.8, 126.7, 125.4, 125.1, 124.5, 123.8, 123.0. MS (FAB) m/z 725.5 (M^+). Anal. Calcd for $C_{56}H_{39}N$: C, 92.66; H, 5.41; N, 1.93. Found: C, 92.46; H, 5.60; N, 2.25.

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Supporting Information Available: General experimental details, absorption and emissive spectra of the newly synthesized oligomers, EL spectra and plots of external efficiency of OLEDs, and ^{1}H NMR spectra of all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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