Full Emission Color Tuning in Bis-Dipolar Diphenylamino-Endcapped Oligoarylfluorenes

Zhong Hui Li,[†] Man Shing Wong,*[,†] Hiroshi Fukutani,[‡] and Ye Tao*[,‡]

Department of Chemistry and Center for Advanced Luminescence Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China, and Institute for Microstructural Sciences, National Research Council of Canada, M-50 Montreal Road, Ottawa, Ontario, Canada K1A 0R6

Received June 1, 2005. Revised Manuscript Received July 19, 2005

A novel series of monodisperse bis-dipolar emissive oligoarylfluorenes, OF(2)Ar-NPh, bearing an electron affinitive core, 9,9-dibutylfluorene as conjugated bridges, and diphenylamino as end-caps was successfully synthesized by a convergent approach using palladium catalyzed Suzuki cross-coupling. The results of optical and electrochemical investigations showed that the HOMO, LUMO, and energy gap of these diphenylamino endcapped oligoarylfluorenes can easily be modified or tuned by the use of various electron affinitive central aryl cores that included dibenzothiophene, phenylene, oligothiophenes, 2,1,3-benzothiadiazole, 4,7-dithien-2-yl-2,1,3-benzothiadiazole, thiophene *S*,*S*′-dioxide, and dibenzothiophene *S*,*S*′-dioxide as well as the extent of the π-conjugated core. As a result, their emission bands measured in chloroform can cover the full UV−vis spectrum (from 412 to 656 nm). In contrast to the common dipolar chromophores, most of OF(2)Ar-NPhs can form morphologically stable amorphous thin films ($T_g = 88-127$ °C) with a high decomposition temperature, $T_{dec} > 450$ °C. Remarkably, undoped OF(2)Ar-NPh-based multilayer OLEDs could exhibit good to excellent device performance with emission colors spanning the full UV−vis spectrum. OF(2)Ar-NPh bearing oligothiophene core based devices exhibit a maximum luminance of 5000−12500 cd m^{-2} and luminous efficiency up to 3.6−4.0 cd A^{-1}. Our findings provide a practical approach to design and tune the color emission of efficient and potentially useful light emitting materials.

Introduction

Despite the advent of a first generation organic light emitting diode (OLED) displays in consumer electronics (i.e., digital cameras and mobile phones), it is still of great interest to develop more efficient and stable multi-functional luminescent or phosphorescent materials to simplify/improve multilayer device fabrication processes and further enhance the device performance and stability.[1] The device performance of OLEDs depends on the charge balance of the injected holes and electrons as well as the exciton confinement in a device. As π-conjugated emissive materials often exhibit better hole injection and transport than electrons, the charge balance of an OLED device is often optimized by sequential deposition of functional layers to differentially perform the charge injection, charge transport, and light emission. Multifunctional emissive materials with a dipolar character, which transport holes and electrons more or less equally, may be used to simplify the fabrication and structure of a multilayer device. This approach has been widely investigated to correct the charge imbalance in molecular and polymeric emissive materials by means of incorporating electron affinitive substituents such as cyano, oxadiazole, triazole, and triazine moieties into the emissive π-conjugated core/main chains[2] or grafting them as side chains of a polymer[3] or attaching them onto the outer surface of dendritic wedges.[4]

Oligofluorenes, which constitute an important class of π-conjugated organic materials because of their excellent chemical, thermal, and photochemical stabilities as well as the ease of structural tuning to adjust the electronic and morphological properties, have been extensively investigated and explored for various functional properties including electroluminescence[5] and liquid crystalline[6] and two-photon

---

* Corresponding authors. E-mail: (M.S.W.) mswong@hkbu.edu.hk; (Y.T.) Ye.Tao@nrc.ca.

[†] Hong Kong Baptist University.

[‡] National Research Council of Canada.

(1) (a) 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. (b) Segura, J. L.; Martin, N. *J. Mater. Chem.* **2000**, *10*, 2403−2453. (c) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471−1507.

(2) (a) Yu, W.-L.; Meng, H.; Pei, J.; Huang, W. *J. Am. Chem. Soc.* **1998**, *120*, 11808−11809. (b) Peng, Z.; Zhang, J. *Chem. Mater.* **1999**, *11*, 1138−1143.

(3) (a) Lee, Y.-Z.; Chen, X.; Chen, S.-A.; Wei, P.-K.; Fann, W.-S. *J. Am. Chem. Soc.* **2001**, *123*, 2296−2307. (b) Jin, S.-H.; Kim, M.-Y.; Kim, J. Y., Lee, K.; Gal, Y.-S. *J. Am. Chem. Soc.* **2004**, *126*, 2474−2480.

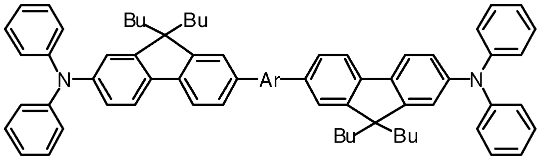
(4) (a) Kwok, C. C.; Wong, M. S. *Macromolecules* **2001**, *34*, 6821−6830. (b) Kwok, C. C.; Wong, M. S. *Chem. Mater.* **2002**, *14*, 3158−3166.

(5) (a) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 11576−11577. (b) Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332−1339. (c) Geng, Y.; Culligan, S. W.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 542−549. (d) Culligan, S. W.; Geng, Y.; Chen, S. H.; Klubek, K.; Vaeth, K. M.; Tang, C. W. *Adv. Mater.* **2003**, *15*, 1176−1179. (e) Wu, C.-C.; Lin, Y.-T.; Wong, K.-T.; Chen, R.-T.; Chien, Y.-Y. *Adv. Mater.* **2004**, *16*, 61−65.

(6) (a) Teetsov, J.; Fox, M. A. *J. Chem. Mater.* **1999**, *9*, 2117−2122. (b) Jo, J.; Chi, C.; Hoger, S.; Wegner, G.; Yoon, D. Y. *Chem. Eur. J.* **2004**, *10*, 2681−2688.

10.1021/cm051163v CCC: $30.25

absorption properties[7] for optoelectronic and photonic applications in the past few years. Recent studies have shown that fluorene-based materials[5,8,9] show great potential as highly stable and efficient blue emissive materials for OLEDs. Nevertheless, a large hole-injection barrier of fluorene-based materials often limits its device efficiency. On the other hand, we have recently shown that the end-capping of diphenylamino groups onto π-conjugated oligomers offers advantages of lowering the first ionization potential, enhancing thermal stability, and inducing good amorphous morphological stability of the oligomers. This has resulted in the development of a hole-transporting oligofluorene possessing optimal conjugated length for highly efficient and stable blue emission in nondoped multilayer OLED devices.[9] On the other hand, one of the major obstacles in the fabrication of a small-molecule based OLED full color display is the limited availability of efficient emissive materials that span the full visible spectrum.[10] Continuing our investigation on the structure−property correlations of functional materials[11] and elaborating our strategy further, we herein report an effective approach to tune the full color emission and functional properties of a novel series of bis-dipolar emissive oligoarylfluorenes that bears an electron affinitive core, dibutylfluorene as conjugated bridges, and diphenylamino as end-caps constituting D-π-A-π-D type bis-dipolar molecules. In fact, this type of molecular design or emissive materials applied in OLED applications is largely unexplored, even though these are typical structures for two-photon absorbing dyes.[12] Depending on the electronic nature of the central aryl moiety employed such as dibenzothiophene, phenylene, oligothiophenes, 2,1,3-benzothiadiazole, 4,7-dithien-2-yl-2,1,3-benzothiadiazole, thiophene *S*,*S*′-dioxide, and dibenzothiophene *S*,*S*′-dioxide, the emissive colors of these bis-dipolar oligoarylfluorenes can span almost the full UV−vis spectrum. In contrast to the diphenylamino end-capped oligofluorenes, simply extending the chain length of the fluorenyl backbone does not give rise to the full color tuning and LUMO adjustment as their energy gaps become saturated at terfluorene.[9] Another advantage of designing such bis-dipolar molecules as emissive materials is that they possess no or a very small net dipole moment; on the other hand, typical dipolar emissive molecules having a large dipole moment often tend to form aggregates or/and a crystalline state, which is detrimental to the device stability and efficiency.



Ar = aromatic ring

OF(2)Ar-NPh

Results and Discussion

Synthesis. Syntheses of monodisperse bis-dipolar oligoarylfluorenes symmetrically end-capped with diphenylamino moieties, OF(2)Ar-NPh, are outlined in Scheme 1. 2,5-Dibromomothiophene *S*,*S*′-dioxide,[13] 4,7-dibromo-2,1,3-benzothiadiazole,[14] and 4,7-bis-(5-bromo-2-thienyl)-2,1,3-benzothiadiazole[15] were prepared according to the literature procedures. Dihalobithienyl was synthesized either by direct bromination of bithiophene with NBS or by lithiation with *n*BuLi followed by reaction with I_2. 3,6-Diiododibenzothiophene was prepared by double electrophilic iodination of dibenzothiophene in the presence of periodic acid/I_2. *m*CPBA oxidation of 3,6-diiododibenzothiophene afforded the corresponding dibenzothiophene *S*,*S*′-dioxide in excellent yield. 2,5‴-Diiodoterthiophene was prepared by lithiation with *n*BuLi followed by quenching with I_2 of terthiophene, which was obtained from the palladium catalyzed Kumada coupling of 2-thienylmagnesium bromide and 2,5-dibromothiophene. By adopting the convergent approach used previously, a double palladium catalyzed Suzuki cross-coupling reaction of 9,9-dibutyl-7-(diphenylamino)-2-fluorenylboronic acid,[9] as a key intermediate, with the corresponding dihaloarylene afforded the desired bis-dipolar oligoarylfluorenes in good to excellent yields (56−90%). It should be stated that the $Pd(OAc)_2$-2P(*o*-tol)$_3$ complex is found to be more efficient for the double cross-coupling reaction when the less reactive dihaloarylene such as 1,4-dibromobenzene is used. All the newly synthesized oligoarylfluorenes were fully characterized with ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis and found to be in good agreement with the structures.

Optical Properties. In view of the electronic absorption spectra obtained in chloroform, all oligoarylfluorenes show very similar spectral features, which are basically composed of two major absorption bands except OF(2)TBTD-NPh and OF(2)BTD-NPh, which have an additional band around

---

(7) Belfield, K. D.; Morales, A. R.; Hales, J. M.; Hagan, D. J.; VanStryland, E. W.; Chapela, V. M.; Percino, J. *Chem. Mater.* **2004**, *16*, 2267−2273.

(8) (a) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798−802. (b) Klärner, G.; Lee, J.-Y.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800−1805. (c) Donat-Bouillud, A.; Lévesque, I.; Tao, Y.; D'Iorio, M.; Beaupré, S.; Blondin, P.; Ranger, M.; Bouchard, J.; Leclerc, M. *Chem. Mater.* **2000**, *12*, 1931−1936. (d) Ego, C.; Marsitzky, D.; Becker, S.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Mackenzie, J. D.; Silva, C.; Friend, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 437−443.

(9) Li, Z. H.; Wong, M. S.; Tao, Y.; Lu, J. *Chem. Eur. J.* **2005**, *11*, 3285−3294.

(10) (a) Montes, V. A.; Li, G.; Radek, P.; Shinar, J.; Anzenbacher, P., Jr. *Adv. Mater.* **2004**, *16*, 2001−2003. (b) Radek, P.; Montes, V. A.; Shinar, J.; Anzenbacher, P., Jr. *J. Org. Chem.* **2004**, *69*, 1723−1725.

(11) (a) Wong, M. S.; Li, Z. H.; Shek, M. F.; Chow, K. H.; Tao, Y.; D'Iorio, M. *J. Mater. Chem.* **2000**, *10*, 1805−1810. (b) Wong, M. S.; Li, Z. H.; Tao, Y.; D'Iorio, M. *Chem. Mater.* **2003**, *15*, 1198−1203. (c) Li, Z. H.; Wong, M. S.; Tao, Y.; D'Iorio, M. *J. Org. Chem.* **2004**, *69*, 921−927. (d) Wong, M. S.; Li, Z. H. *Pure Appl. Chem.* **2004**, *76*, 1409−1419.

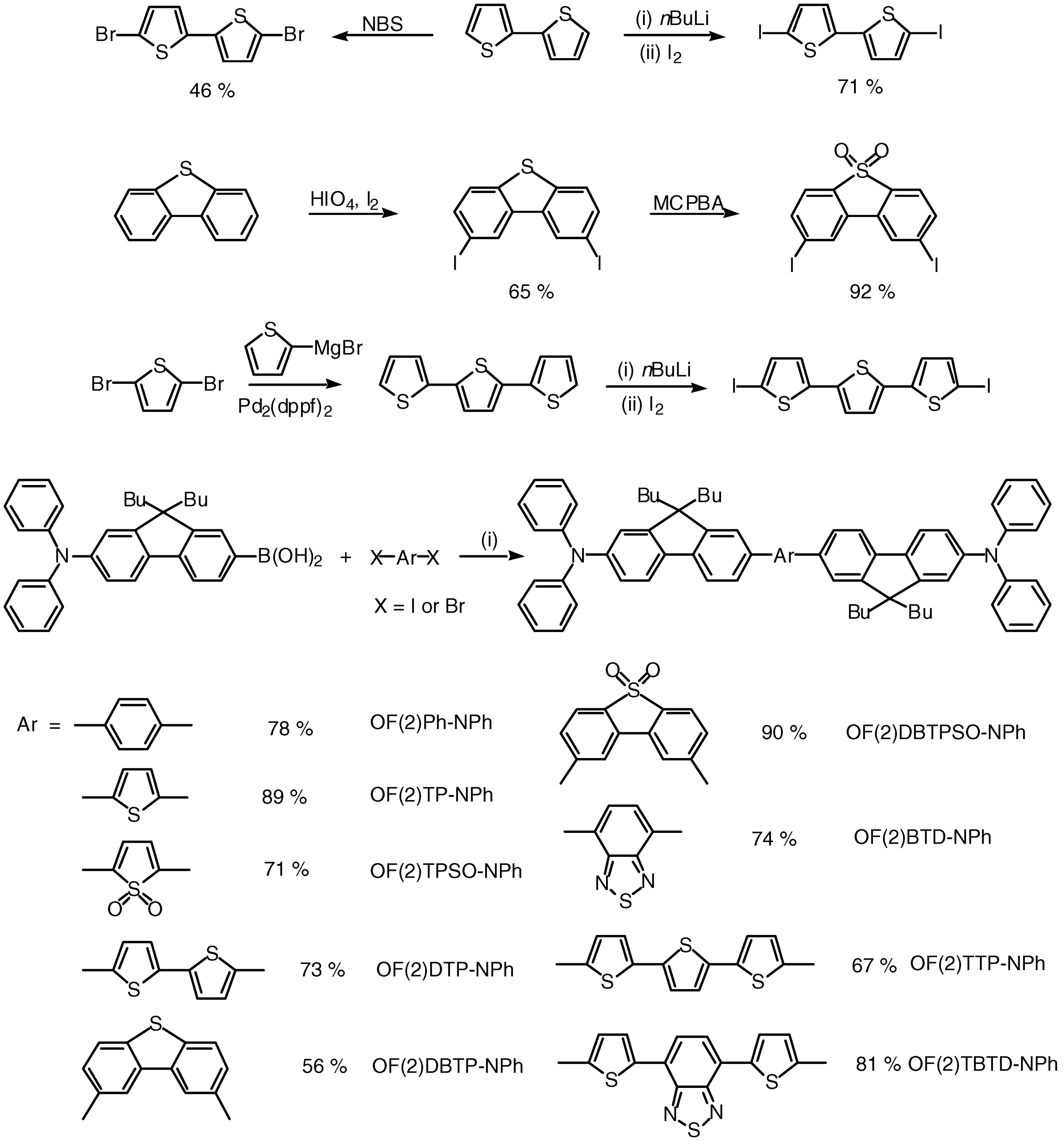
(12) (a) Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yan, L.; He, G. H.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863−1874. (b) Albota, M.; Beljonne, D.; Bredas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramanian, G.; Webb, W. W.; Wu, X. L.; Xu, C. *Science* **1998**, *281*, 1653−1656. (c) Mongin, O.; Porres, L.; Moreaux, L.; Mertz, J.; Blanchard-Desce, M. *Org. Lett.* **2002**, *4*, 719−722.

(13) Furukawa, N.; Hoshiai, H.; Shibutani, T.; Higaki, M.; Iwasaki, F.; Fujihara, H. *Heterocycles* **1992**, *34*, 1085−1088.

(14) Kurt, P.; Mike, Z.; Richard, S. *J. Heterocyclic Chem.* **1970**, *38*, 629−633.

(15) Yamashita, Y.; Suzuki, K.; Tomura, M. *Synth. Met.* **2003**, *133−134*, 341−343.

Scheme 1. Synthesis of Bis-dipolar Diphenylamino-substituted Oligoarylfluorenes, OF(2)Ar−NPh



Reagents and Conditions: (i) 5 mol % $Pd(OAc)_2$−2P(*o*-tol)$_3$, K_2CO_3, CH_3OH-Toluene, 75 °C or 5 mol % $Pd(PPh_3)_4$, K_2CO_3, THF, 80 °C.

350−390 nm contributed by benzothiadiazole or 4,7-dithien-2-yl-2,1,3-benzothiadiazole moieties (Figure 1). The absorption peak appears around 300−320 nm due to the $n \rightarrow \pi^*$ transition of triarylamine moieties and the absorption band contributed from the oligoarylfluorene core spanning from 368 to 526 nm corresponding to the $\pi \rightarrow \pi^*$ transition of

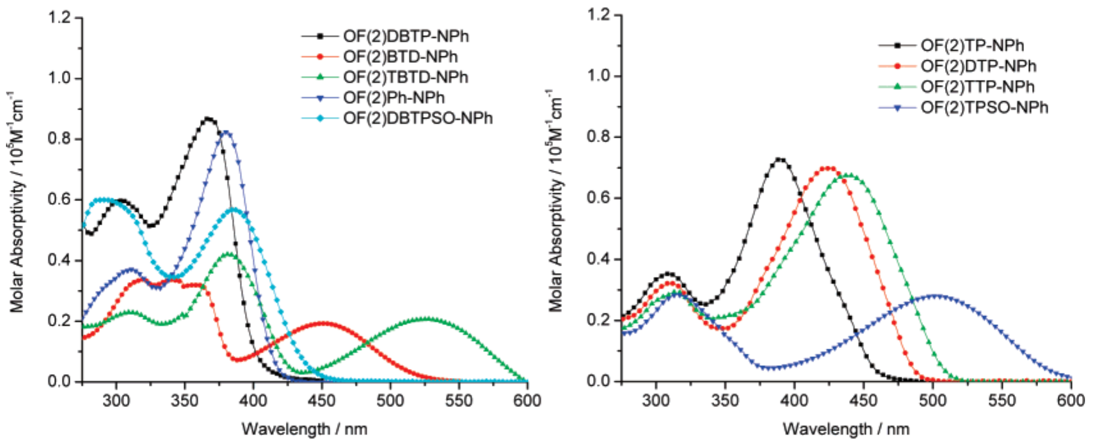


Figure 1. Absorption spectra of **OF(2)Ar−NPh**s measured in chloroform.

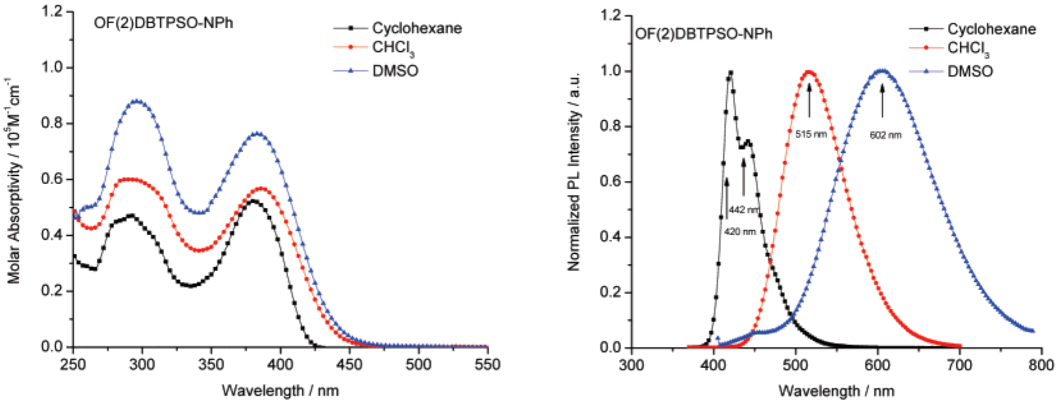


Figure 2. Absorption and emission spectra of **OF(2)DBTPSO−NPh** in different solvents.

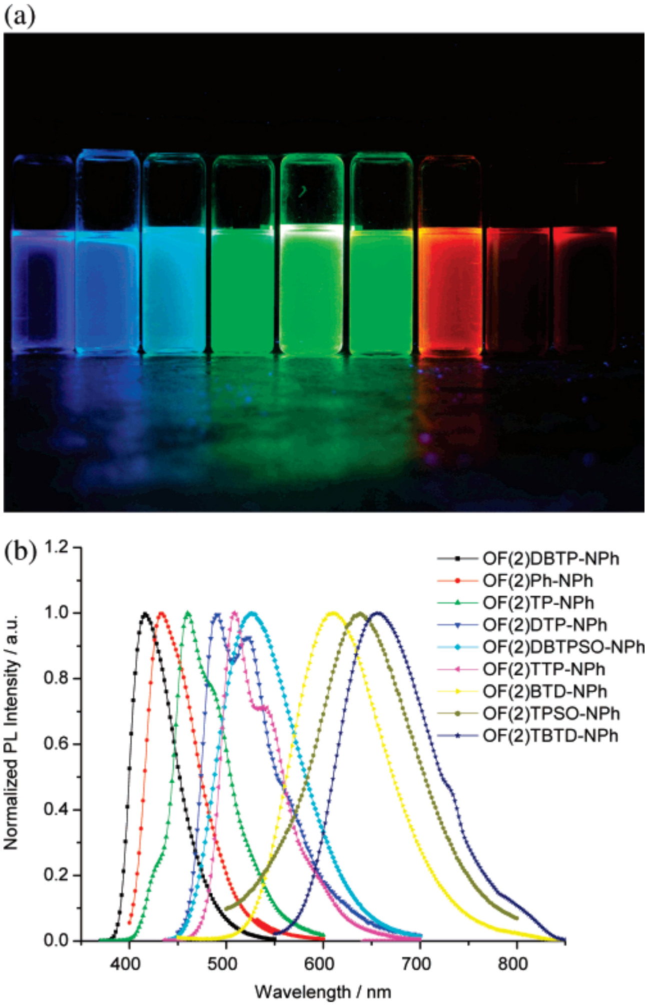


Figure 3. (a) Emission colors upon illumination and (b) Fluorescence spectra of **OF(2)Ar−NPh**s in chloroform.

oligofluorene core. In general, the absorption spectra of this series of bis-dipolar molecules do not exhibit significant solvatochromic effects. On the contrary, fluorescence spectra are solvent dependent, in which the spectra exhibit less or no vibronic structures and large red shifts with an increase in solvent polarity. The extent of the solvent induced spectral shift also depends on the electronic withdrawing property of the central aryl core. For instance, the emission maxima of OF(2)TBTD-NPh and OF(2)DBTPSO-NPh exhibit a solvatochromatic shift of 50 and 182 nm, respectively, changing from cyclohexane to DMSO (Figure 2). This suggests that the emission excited states of theses oligoarylfluorenes possess polar (charge-transfer) character. Furthermore, with the use of various electron affinitive aryl cores, the emission peaks measured in chloroform can span the full UV−vis spectrum (from 412 to 656 nm) (Figure 3). In general, the stronger the electron withdrawing strength of the central core, the longer the emission wavelength shifted is. The absorption and emission wavelengths can also be tuned/modified by the number of central aryl units (e.g., OF(2)TP-NPh, λ^{abs}_{max} = 390 nm and λ^{em} = 463, 489 nm; OF(2)DTP-NPh, λ^{abs}_{max} = 427 nm and λ^{em} = 490, 525 nm; and OF(2)TTP-NPh, λ^{abs}_{max} = 441 nm and λ^{em} = 507, 540 nm) On the other hand, the fluorescence spectra are excitation wavelength independent, in which because of excitation at either triarylamine moieties or oligoarylfluorene cores, the emission spectra obtained are identical. This suggests that energy or excitons can efficiently be transferred from the triarylamine moiety to the emissive oligoarylfluorene core. The fluorescence quantum yields (Φ_{FL}) measured in chloroform using 9,10-diphenylanthrancene or fluorescein as a standard are in the range of 11−99%, and the fluorescence lifetimes of all these oligoarylfluorenes are in the nanosecond time scale, suggesting that the emission originates from the singlet excited state to the ground state.

Electrochemical Properties. To probe the redox properties of these diphenylamino endcapped oligoarylfluorenes, cyclic voltammetry performed in a three-electrode cell setup with 0.1 M Bu_4NPF_4 as a supporting electrolyte in CH_2Cl_2 was carried out (see Figure 4). The results are tabulated in Table 1. All the OF(2)Ar-NPhs exhibit a reversible two-electron oxidation wave with $E_{1/2}$ in the range of 0.31−0.42 V, corresponding to two arylamine oxidations as well as a (ir)reversible one-electron oxidation wave corresponding to the oxidation of the oligoarylfluorene π-conjugated core with $E_{1/2}$ or E_p in the range of 0.49−1.15 V. The highly extended oligoarylfluorenes OF(2)DBTP-NPh and OF(2)TTP-NPh even exhibit an additional (ir)reversible one-electron oxidation wave. In contrast to the D-π-D series,[9] both the arylamine and the oligoarylfluorene π-conjugated core oxidation potentials of OF(2)Ar-NPhs are significantly affected by the electronic withdrawing property and the conjugated length of the central aryl core. In general, the stronger the electronic withdrawing strength, which holds electrons more strongly, the higher the (first/second) oxidation potential is. On the other hand, the longer the conjugated

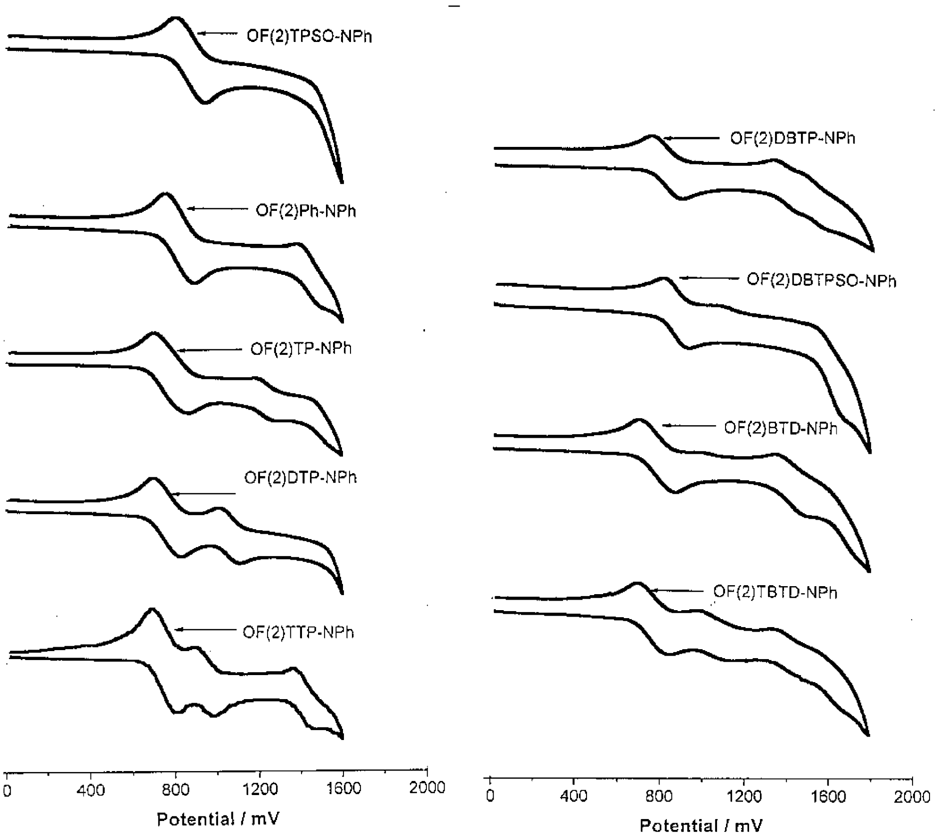


Figure 4. Traces of cyclic voltammetric measurements of **OF(2)Ar−NPh** series.

Table 1. Summaries of Physical Measurements of the OF(n)Ar-NPh Series

	λ^{abs}_{max}[a]/nm (ϵ_{max} 10^4/M^{-1} cm^{-1})	λ^{em}_{max}[a,b]/nm	Φ_{FL}[a]	τ[a,c]/ns	$E_{1/2}$[d]/V	HOMO[d]/eV	LUMO[e]/eV	energy gap[f]/eV	T_g[g](T_{dec}[h])/°C
OF(2)DBTP-NPh	368 (8.72)	412	0.77[i]	1.50	0.38, 0.94, 1.08	5.18	2.12	3.06	121 (466)
OF(2)Ph-NPh	381 (8.25)	433	0.99[i]	1.06	0.37, 0.98	5.17	2.15	3.02	101 (448)
OF(2)TP-NPh	390 (7.29)	463, 487	0.77[i]	1.14	0.34, 0.78	5.14	2.39	2.75	88 (459)
OF(2)DTP-NPh	424 (7.00)	490, 525	0.71[j]	0.71	0.32, 0.62	5.12	2.51	2.61	93 (461)
OF(2)TTP-NPh	441 (6.76)	507, 540	0.26[j]	1.19	0.31, 0.49, 0.98	5.11	2.60	2.51	105 (483)
OF(2)DBTPSO-NPh	386 (6.21)	530	0.56[j]	1.29	0.42, 1.15	5.22	2.43	2.79	127 (453)
OF(2)BTD-NPh	450 (6.70)	608	0.56[j]	1.63	0.34, 0.98	5.14	2.72	2.42	no (454)
OF(2)TPSO-NPh	503 (2.85)	644	0.11[j]	2.10	0.42, 1.00	5.22	3.12	2.10	97 (270)
OF(2)TBTD-NPh	526 (7.70)	656	0.29[j]	1.73	0.32, 0.97	5.12	3.06	2.06	110 (459)

[a] Measured in $CHCl_3$. [b] Excited at the absorption maxima. [c] Using a nitrogen laser as excitation source. [d] $E_{1/2}$ vs Fc^+/Fc estimated by CV method using a platinum disk electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution. Ferrocene was used as an external standard, $E_{1/2}$ (Fc/Fc^+) = 0.45 V vs SCE. [e] Energy gap was estimated from the absorption edge. [f] LUMO = HOMO − energy gap. [g] Determined by differential scanning calorimeter with a heating rate of 10 °C min^{-1} under N_2. [h] Determined by thermal gravimetric analysis with a heating rate of 10 °C min^{-1} under N_2. [i] Using 9,10-diphenylanthrancene (Φ_{360} = 0.9) as a standard. [j] Using fluorescein in 0.1 M NaOH (Φ_{435} = 0.92) as a standard.

aryl core, which can better stabilize the radical cation(s), the lower the oxidation potential is. The LUMO determined by the difference of HOMO and optical energy gap was tabulated in Table 1. Because of the electron withdrawing nature of the aryl central core, the LUMO of OF(2)Ar-NPhs is stabilized to various extents as compared to that of OF(3)-NPh, which contains a fluorenyl group as a core (LUMO = 2.11 eV). Consistently, the stronger the electron withdrawing strength, the more stabilized is the LUMO. These results further support that the LUMO, HOMO, and energy gap of these oligoarylfluorenes can easily be modified or tuned by the use of various central aryl cores.

Thermal Properties. The thermal properties of these oligoarylfluorenes were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 1). With the incorporation of diphenylamino endcaps, all the newly synthesized oligoarylfluorenes exhibit a high glass transition, T_g, from the remelt in the range of 88−127 °C except OF(2)BTD-NPh, indicating the ability of forming a morphologically stable amorphous thin film. They also show high thermal stabilities with a decomposition temperature of T_{dec} > 450 °C except for OF(2)TPSO-NPh.

Thin Film Photoluminescence Properties. The thin film photoluminescence (PL) spectra of OF(2)Ar-NPhs retain most of the spectral features and exhibit a slight to moderate blue- or red-shift in emission maxima as compared to those obtained from chloroform. The most apparent difference in emission spectra comes from those bearing oligothiophene as a central core in which the red-shift is attributed to the improvement in the coplanarity of the thienyl moiety(ies) and the fluorenyl units in the solid state. Another example on the disparity in emission spectral characteristics comes from OF(2)DBTP-NPh. In contrast to the narrow emission band peaked at 412 nm measured in chloroform, the thin film PL

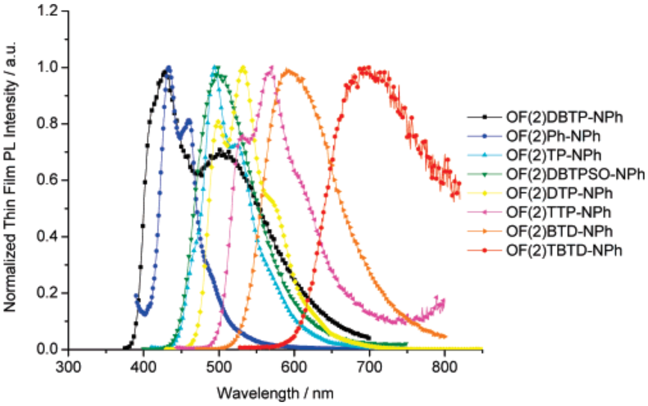


Figure 5. Thin film PL spectra of **OF(2)Ar−NPh**s.

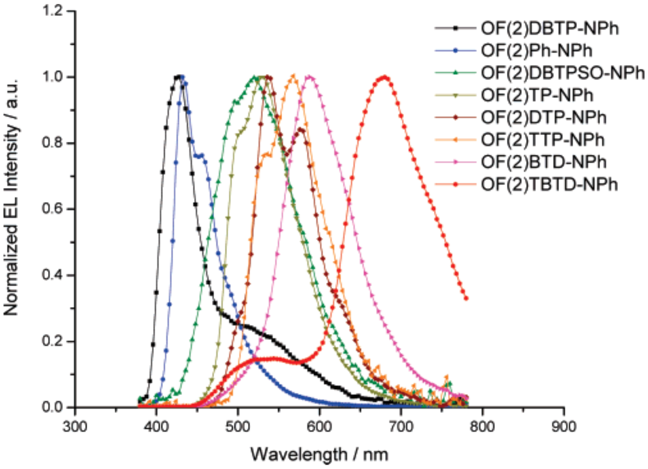


Figure 6. EL spectra of **OF(2)Ar−NPh**s.

Table 2. Summaries of PL and EL Results of OF(n)Ar-NPh Series

	$\lambda^{PL}{}_{max}{}^{a}$/nm	$\lambda^{EL}{}_{max}{}^{b}$/nm	$L_{max}{}^{c}$/cd m^{-2}	$\eta_c{}^{d}$/cd A^{-1}
OF(2)DBTP-NPh	430, 501	428, 500	2750	1.1[e]
OF(2)Ph-NPh	433, 457	433, 457	750	1.2[f]
OF(2)TP-NPh	494, 523	500, 530	5000	4.0[f]
OF(2)DTP-NPh	499, 532	536, 580	4000	1.8[f]
OF(2)TTP-NPh	532, 570	520, 570	12500	3.6[e]
OF(2)DBTPSO-NPh	500	520	6500	0.71[e]
OF(2)BTD-NPh	589	588	3600	0.61[g]
OF(2)TPSO-NPh		*h*	*h*	*h*
OF(2)TBTD-NPh	680	680	680	0.13[g]

[a] Emission peak(s) in thin film PL spectrum. [b] Emission peak(s) in EL spectrum. [c] Maximum luminance. [d] Current efficiency. [e] Structure of OLED: ITO/OF(*n*)-NPh (40 nm)/F-TBB (15 nm)/Alq$_3$ (20 nm)/LiF (1 nm)/Al (150 nm). [f] Structure of OLED: ITO/OF(2)Ar-NPh (40 nm)/PBD (40 nm)/LiF (1 nm)/Al (150 nm). [g] Structure of OLED: ITO/OF(*n*)-NPh (40 nm)/Alq$_3$ (20 nm)/LiF (1 nm)/Al (150 nm). [h] Unstable device.

exhibits two strong emission bands at 430 and 500 nm. The additional band could be due to aggregation; however, the contribution of the low energy emission decreases dramatically in the EL spectrum. Importantly, the emission colors of thin film PL of OF(2)Ar-NPhs also cover the full UV−vis spectrum (from 430 to 680 nm) as shown in Figure 5.

Electroluminescence Properties. Because of the low first ionization potential, good luminescence properties, high thermal stability, and good amorphous morphological stability, OF(2)Ar-NPhs show great potential for use as hole transport emitters in OLEDs (see Figure 6). The undoped multilayer OLEDs with the structure ITO/OF(2)Ar-NPh (40 nm)/PBD (40 nm)/LiF (1 nm)/Al (150 nm) was initially fabricated by the conventional vacuum deposition and investigated. To improve the performance of some devices, a highly morphologically stable, hole blocking amorphous material, 1,3,5-tris(4-fluorobiphenyl-4′-yl)benzene (F-TBB), either combined or not with an Alq$_3$ film as a hole-blocking/electron transport layer was used to replace the 2-biphenyl-4-yl-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD) layer. Results of the EL studies of OF(2)Ar-NPh based OLEDs are summarized in Table 2. The electroluminescence (EL) spectra of these OF(2)Ar-NPh-based devices did cover most of the UV−vis spectrum with emission peaks ranging from 428 nm for the OF(2)DBTP-NPh-based device to 680 nm for the OF(2)TBTD-NPh-based device (Figure 7). Generally, the EL spectra resemble well the PL spectra of thin films indicating that the EL purely originates from the oligomers. For oligoarylfluorenes bearing oligothiophene as a central core, there are significant differences in spectral features including emission maxima and vibronic structures in the EL spectra, which are voltage independent, when compared to thin film PL spectra. Such differences are likely due to the different contributions of vibronic states as the first derivatives of the EL and PL spectra overlap very well, indicating the emission of EL coming from the same emissive states of PL but with different intensities.

Although the electron transporting properties of these oligoarylfluorenes have been improved by the central electron affinitive moiety, an attempt to remove the hole-blocking layer in the OF(2)BTD-NPh and OF(2)TBTD-NPh based devices led to a relatively inferior efficiency and the leakage

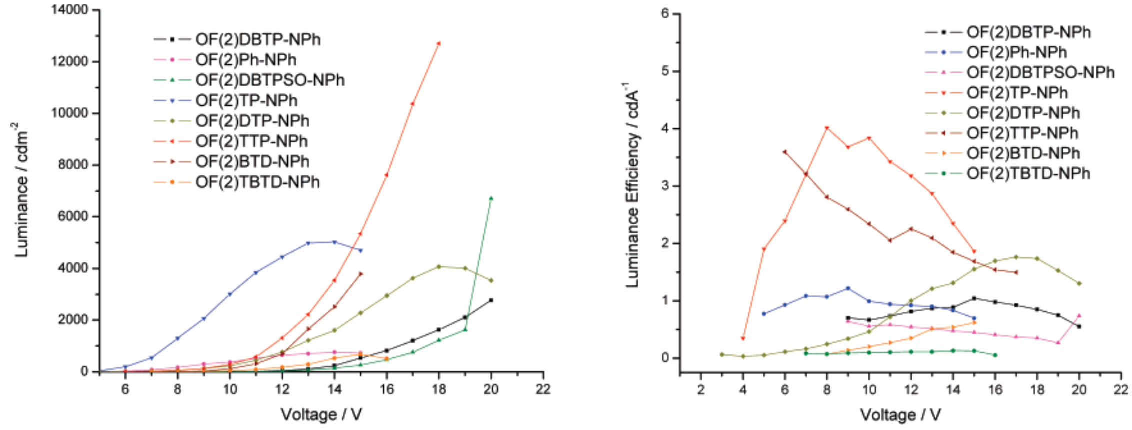


Figure 7. Plots of luminance-voltage and efficiency-voltage of **OF(2)Ar−NPh** based devices.

of Alq_3 emission in the OF(2)TBTD-NPh based device. However, with the use of a F-TBB hole-blocking layer, the OF(2)Ar-NPh-based devices could exhibit good to excellent device performance. Some of the particularly efficient devices, which could exhibit a maximum luminance of 5000−12500 cd m^{-2} and luminance efficiency up to 3.6−4.0 cd A^{-1} are fabricated from the oligoarylfluorenes bearing oligothiophene as a central core.

Conclusions

In summary, a novel series of monodisperse bis-dipolar emissive oligoarylfluorenes, OF(2)Ar-NPh, bearing an electron affinitive core, dibutylfluorene as conjugated bridges, and diphenylamino as end-caps has been synthesized by a convergent approach using palladium catalyzed Suzuki cross-coupling. We have shown that the absorption, emission, and electrochemical properties are significantly affected by the electronic nature of the electron affinitive central core of the bis-dipolar oligoarylfluorene, which provides an effective tool to tune/modify these functional properties leading to success in the full color emission tuning. Most of OF(2)Ar-NPhs show high thermal stabilities with a decomposition temperature of $T_{dec} > 450$ °C and form morphologically stable amorphous thin films ($T_g = 88-127$ °C). Highly efficient undoped multilayer OLED devices based on OF(2)TP-NPh and OF(2)TPP-NPh with a maximum luminance of 5000 and 12500 cd m^{-2} and luminance efficiency up to 4.0 and 3.6 cd A^{-1}, respectively, have been obtained. Our findings provide an effective approach to design and tune the color emission of efficient and potentially useful light emitting materials.

Experimental Procedures

The thin films for PL measurements were prepared by vacuum deposition. EL device fabrication and testing: ITO-glass substrates (15 Ω/□) were patterned using conventional photolithography and an acid mixture of HCl and HNO_3 as the etchant. The active area of each EL device was 1 × 5 mm^2. All organic layers were thermally deposited in a vacuum chamber at a base pressure of 2×10^{-7} Torr. The devices were tested in air under ambient conditions with no encapsulation. EL spectra, device luminances, and current−voltage characteristics were recorded using a combination of a Photo Research PR-650 SpectraScan and a Keithley 238 Source meter.

5,5′-Dibromo-2,2′-bithiophene. A mixture of bithiophene (1.66 g, 10 mmol) and NBS (3.74 g, 21 mmol) in DMF (10 mL) was stirred at room temperature for 8 h. The reaction mixture was poured into a large amount of water and extracted with dichloromethane (3 × 50 mL). The combined organic solution was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude product was further purified by recrystallization in *n*-hexane affording a brown crystal with an isolated yield of 46% (1.5 g). ^1H NMR (270 MHz, $CDCl_3$, δ) 6.94 (d, $J = 3.78$ Hz, 2H), 6.83 (d, $J = 3.78$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 137.6, 130.5, 124.0, 111.4. MS (FAB) *m/z* 324.1 (M^+).

5,5′-Diiodo-2,2′-bithiophene. To a 100 mL two-necked flask containing a solution of 2,2-bithiophene (1.66 g, 10 mmol) in dry THF (40 mL) equipped with a magnetic stirrer, a N_2 purge and a −78 °C acetone−dry ice bath was dropwise added 1.5 M *n*BuLi (16 mL, 24 mmol) while maintaining good stirring. After stirring for 1 h, iodine (6.10 g, 24 mmol) was added. After stirring for another 2 h at room temperature, a solution of sodium sulfite was added to decolorize the reaction mixture and extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude product was further purified by recrystallization in a mixture solvent of chloroform/methanol affording a brown crystal with an isolated yield of 71% (2.98 g). ^1H NMR (400 MHz, $CDCl_3$, δ) 7.13 (d, $J = 3.6$ Hz, 2H), 6.76 (d, $J = 3.6$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 142.0, 137.7, 125.5, 72.6. MS (FAB) *m/z* 419.5 ($M^+ + 1$).

3,6-Diiododibenzothiophene. A mixture of dibenzothiophene (1.84 g, 10 mmol), acetic acid (10 mL), water (1 mL), concentrated sulfuric acid (1 mL), iodine (2.54 g, 10 mmol), periodic acid (2.28 g, 10 mmol), and chloroform (10 mL) was heated at 50 °C overnight with good stirring. After cooling to room temperature, the product mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined dark purple organic layer was decolorized with sodium sulfite, washed with water, dried with anhydrous Na_2SO_4, filtered, and evaporated to dryness. Purification of the crude product by recrystallization in a mixture solvent of chloroform/ethanol (v/v = 4:1) afforded the title compound as a light-yellow crystal in 65% yield. ^1H NMR (270 MHz, $CDCl_3$, δ) 8.39 (s, $J = 1.35$ Hz, 2H), 7.71 (d, $J = 8.37$ Hz, 2H), 7.55 (d, $J = 8.37$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 139.0, 136.3, 135.8, 130.8, 124.4, 89.1. MS (FAB) *m/z* 436.2 (M^+).

3,6-Diiododibenzothiophene *S,S′*-Dioxide. To a solution of 3,6-diiododibenzothiophene (436 mg, 1 mmol) in dichloromethane (30 mL) stirred at 0 °C was added excess of 3-chloroperoxybenzoic acid. After being stirred for 4 h, the reaction mixture was quenched with a 2 M K_2CO_3 solution 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 using 1:1 petroleum ether/dichloromethane as an eluent affording 431 mg (92%) of a light yellow solid. ^1H NMR (270 MHz, $CDCl_3$, δ) 8.12 (d, $J = 1.35$ Hz, 2H), 7.90 (dd, $J = 8.10$ Hz, 2H), 7.54 (d, $J = 8.10$ Hz, 2H). ^{13}C NMR (66 MHz, $CDCl_3$, δ) 143.0, 138.3, 131.1, 130.3, 123.0, 95.5. MS (FAB) *m/z* 469.2 ($M^+ + 1$).

5,2′,5′,2″-Terthiophene. To a mixture of 2-bromothiophene (4.89 g, 30 mmol) and magnesium (0.86 g, 36 mmol) in 30 mL of THF was added a catalytic amount of iodine under a nitrogen atmosphere at room temperature with vigorous stirring. The reaction gradually took place and was allowed to proceed for about 1 h. After cooling to room temperature, 2,5-dibromothiophene (2.42 g, 10 mmol) and $Pd_2(dppf)_2$ (82 mg, 0.1 mmol) were added into the reaction mixture. After stirring for 2 h at room temperature, the reaction mixture was refluxed for another 4 h and then cooled to room temperature. Water was added to quench the reaction followed by diluted hydrochloric acid (6 M HCl) until a neutral solution was obtained. The reaction mixture was poured into a large amount of 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 using 4:1 petroleum ether/dichloromethane as eluent affording an orange solid product with an isolated yield of 99% (190 mg). ^1H NMR (270 MHz, $CDCl_3$, δ) 7.20 (dd, $J = 5.20$ Hz, 2H), 7.16 (dd, $J = 3.60$ Hz, 2H), 7.06 (s, 2H), 7.00 (dd, $J = 3.60$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 137.1, 136.2, 127.8, 124.5, 124.3, 123.7. MS (FAB) *m/z* 248.1 (M^+).

2,5″-Diiodo-5,2′,5′,2″-terthiophene. To a 100 mL two-necked round-bottomed flask containing 5,2′,5′,2″-terthiophene (2.44 g, 9.82 mmol) in 30 mL of dry THF equipped with a magnetic stirrer, a N_2 purge, and a −78 °C acetone−dry ice bath while maintaining good stirring was added 2.5 M *n*BuLi (11.8 mL, 29.5 mmol). After stirring for 1 h, iodine (6.35 g, 25 mmol) was added. After stirring for a further 2 h, water was added to the reaction mixture followed by diluted hydrochloric acid (6 M HCl) until a neutral solution mixture was obtained. The reaction mixture was poured into a large amount of water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The pure product was precipitated from a solution of dichloromethane by methanol affording an orange solid with an isolated yield of 81% (3.91 g). ^{1}H NMR (270 MHz, $CDCl_3$, δ) 7.14 (d, $J = 3.60$ Hz, 2H), 6.99 (d, $J = 8.40$ Hz, 2H), 6.82 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 137.8, 127.9, 125.2, 124.7, 124.3, 123.9. MS (FAB) *m*/*z* 500.4 (M^+).

1,4-Bis[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]benzene [OF(2)Ph-NPh]. To a mixture of 1,4-dibromobenzene (94 mg, 0.40 mmol), 9,9-bis(*n*-butyl)-2-diphenyl-amino-7-fluorenylboronic acid (470 mg, 0.96 mmol), palladium (II) acetate (11 mg, 5 mol %), and tri(*o*-tolyl)phosphine (30 mg, 10 mol %) in a 100 mL round-bottomed flask was added toluene (20 mL), methanol (10 mL), and a 2 M aqueous solution of K_2CO_3 (2 mL). The reaction mixture was stirred under an atmosphere of nitrogen at 75 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into cool 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 then purified by silica gel column chromatography using petroleum ether/dichloromethane (v/v = 6:1) as eluent affording the desired product as a light yellow solid (301 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.75 (s, 4H), 7.67 (d, $J = 7.6$ Hz, 2H), 7.55−7.61 (m, 6H), 7.24 (t, $J = 7.8$ Hz, 8H), 7.13 (d, $J = 7.6$ Hz, 10H), 7.01 (dd, $J = 7.6$ Hz, 6H), 1.86−1.94 (m, 8H), 1.06−1.11 (m, 8H), 0.70 (t, $J = 7.6$ Hz, 20H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 152.4, 151.3, 148.0, 147.1, 140.3, 140.3, 138.7, 135.9, 129.1, 127.4, 125.8, 123.8, 123.4, 122.5, 121.2, 120.4, 119.4, 119.3, 55.0, 40.0, 26.1, 23.0, 13.9. MS (FAB) *m*/*z* 965.2 (M^+). Anal. Calcd for $C_{72}H_{72}N_2$ (%): C, 89.58; H, 7.52; N, 2.90. Found: C, 89.38; H, 7.45; N, 3.08.

2,5-Bis[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]thiophene [OF(2)TP-NPh]. The previous procedure was followed using 2,5-dibromothiophene (67 mg, 0.25 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (367 mg, 0.75 mmol), palladium (II) acetate (5.6 mg), tri(*o*-tolyl)phosphine (15 mg), 2 M K_2CO_3 (3.0 mL), toluene (10 mL), and methanol (5 mL). The pure product was separated by silica gel column chromatography using 4:1 petroleum ether/dichloromethane as eluent affording 216 mg (89%) of a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.60 (s, 4H), 7.54−7.55 (m, 4H), 7.35 (s, 2H), 7.22−7.26 (m, 8H), 7.11−7.14 (m, 10H), 6.98−7.03 (m, 6H), 1.86−1.94 (m, 8H), 1.05−1.12 (m, 8H), 0.64−0.78 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 152.3, 151.4, 147.9, 147.2, 144.0, 140.5, 135.7, 132.4, 129.1, 124.5, 123.9, 123.6, 123.4, 122.5, 120.3, 119.6, 119.4, 119.2, 55.0, 40.0, 26.0, 23.0, 13.9. MS (FAB) *m*/*z* 971.0 (M^+). Anal. Calcd for $C_{70}H_{70}N_2S$ (%): C, 86.55; H, 7.26; N, 2.88; S, 3.31. Found: C, 86.35; H, 7.41; N, 3.09; S, 3.25.

5,5′-Bis[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]-2,2′-bithiophene [OF(2)DTP-NPh]. The previous procedure was followed using 5,5′-dibromo-2,2′-bithiophene (81 mg, 0.25 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (367 mg, 0.75 mmol), palladium (II) acetate (5.6 mg), tri(*o*-tolyl)phosphine (15 mg), 2 M K_2CO_3 (3 mL), toluene (10 mL), and methanol (5 mL). The pure product was separated by silica column chromatography using 4:1 petroleum ether/dichloromethane as eluent affording 192 mg (73%) of an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.58 (d, $J = 7.60$ Hz, 2H), 7.55 (dd, $J = 8.00$ Hz, 4H), 7.50 (s, 2H), 7.29 (d, $J = 4.00$ Hz, 2H), 7.22−7.26 (m, 8H), 7.20 (d, $J = 3.60$ Hz, 2H), 7.12 (d, $J = 8.40$ Hz, 10H), 7.00 (dd, $J = 7.60$ Hz, 6H), 1.85−1.92 (m, 8H), 1.05−1.11 (m, 8H), 0.66−0.72 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 152.3, 151.4, 147.9, 147.3, 143.9, 140.7, 136.3, 135.6, 132.0, 129.2, 124.5, 124.3, 123.9, 123.4, 122.6, 120.4, 119.6, 119.5, 119.1, 55.0, 40.0, 26.0, 23.0, 13.9. MS (FAB) *m*/*z* 1053.3 (M^+). Anal. Calcd for $C_{74}H_{72}N_2S_2$ (%): C, 84.37; H, 6.89; N, 2.66; S, 6.09. Found: C, 84.27; H, 7.05; N, 2.84; S, 6.05.

3,6-Bis[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]-dibenzothiophene *S*,*S*′-Dioxide [OF(2)DBTPSO-NPh]. The previous procedure was followed using 3,6-diiododibenzothiophene *S*,*S*′-dioxide (121 mg, 0.26 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (304 mg, 0.62 mmol), palladium (II) acetate (7 mg), tri(*o*-tolyl)phosphine (19 mg), 2 M K_2CO_3 (2 mL), toluene (20 mL), and methanol (10 mL). The pure product was separated by silica gel column chromatography using 1:1 petroleum ether/dichloromethane as eluent affording 253 mg (90%) of a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.11 (s, 2H), 7.91 (d, $J = 8.00$ Hz, 2H), 7.79 (d, $J = 8.00$ Hz, 2H), 7.72 (d, $J = 8.00$ Hz, 2H), 7.60 (dd, $J = 7.20$ Hz, 4H), 7.54 (s, 2H), 7.25 (dd, $J = 7.80$ Hz, 8H), 7.13 (d, $J = 6.80$ Hz, 10H), 7.00−7.05 (m, 6H), 1.88−1.96 (m, 8H), 1.08−1.25 (m, 8H), 0.65−0.73 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 152.4, 151.7, 147.8, 147.7, 141.8, 137.2, 136.4, 135.1, 132.3, 129.3, 129.2, 126.4, 124.0, 123.3, 122.7, 122.5, 121.4, 120.7, 120.1, 119.6, 119.0, 55.2, 40.0, 26.1, 23.0, 13.9. MS (FAB) *m*/*z* 1104.2 ($M^+ + 1$). Anal. Calcd for $C_{78}H_{74}N_2O_2S_2$ (%): C, 84.90; H, 6.76; N, 2.54; S, 2.91. Found: C, 84.58; H, 6.93; N, 2.78; S, 2.94.

4,7-Bis[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]-2,1,3-benzothiadiazole [OF(2)BTD-NPh]. A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (147 mg, 0.5 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (587 mg, 1.2 mmol), tetrakis(triphenylphosphine)palladium (58 mg, 0.05 mmol), THF (20 mL), and 2 M K_2CO_3 (3 mL) was stirred under an atmosphere of nitrogen at 80 °C overnight. After cooling to room temperature, the reaction mixture was poured into a large amount of cool water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was then purified by silica gel column chromatography with petroleum ether/dichloromethane (v/v = 3:1) as eluent affording the desired product as a orange solid (380 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.01 (d, $J = 7.60$ Hz, 2H), 7.88 (d, $J = 10.00$ Hz, 4H), 7.77 (d, $J = 8.40$ Hz, 2H), 7.62 (d, $J = 8.40$ Hz, 2H), 7.24−7.28 (m, 8H), 7.15 (d, $J = 7.60$ Hz, 10H), 7.03 (dd, $J = 7.80$ Hz, 6H), 1.95−1.99 (m, 4H), 1.88−1.92 (m, 4H), 1.07−1.14 (m, 8H), 0.73 (t, $J = 7.40$ Hz, 20H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 154.3, 152.7, 151.0, 147.9, 147.3, 141.1, 135.7, 135.4, 133.4, 129.2, 128.2, 127.8, 123.9, 123.6, 123.3, 122.6, 120.6, 119.2, 119.1, 55.1, 39.9, 26.1, 23.0, 13.9. MS (FAB) *m*/*z* 1023.8 (M^+). Anal. Calcd for $C_{72}H_{70}N_4S$ (%): C, 84.50; H, 6.89; N, 5.47. Found: C, 84.44; H, 6.86; N, 5.64.

4,7-Bis{5′′-[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]-2′′-thienyl}-2,1,3-benzothiadiazole [OF(2)TBTD-NPh]. The previous procedure was followed using 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (229 mg, 0.5 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (734 mg, 1.5 mmol), tetrakis(triphenyl-phosphine)palladium (58 mg, 0.05 mmol), 2 M K_2CO_3 (3 mL), and tetrahydrofuran (20 mL). The pure product was separated by silica gel column chromatography using 2:1 petroleum ether/dichloromethane as eluent affording 480 mg (81%) of a deep red solid. ^{1}H NMR (270 MHz, $CDCl_3$, δ) 8.13 (d, $J = 4.05$ Hz, 2H), 7.92 (s, 2H), 7.54−7.66 (m, 8H), 7.46 (d, $J = 4.05$ Hz, 2H), 7.21−7.27 (m, 8H), 7.12 (d, $J = 7.29$ Hz, 10H), 7.00 (t, $J = 7.56$ Hz, 6H), 1.87−1.93 (m, 8H), 1.06−1.13 (m, 8H), 0.71

(t, $J = 7.29$ Hz, 20H). ^{13}C NMR (66 MHz, CDCl$_3$, δ) 152.5, 152.2, 151.3, 147.8, 147.2, 146.4, 140.9, 138.0, 135.5, 132.0, 129.1, 128.5, 125.6, 125.2, 124.7, 123.8, 123.6, 123.3, 122.5, 120.4, 119.8, 119.4, 119.1, 55.2, 40.1, 26.1, 23.1, 14.0. MS (FAB) *m*/*z*: 1187.8 (M$^+$). Anal. Calcd for $C_{80}H_{74}N_4S_3$ (%): C, 80.90; H, 6.28; N, 4.72. Found: C, 80.66; H, 6.36; N, 4.72.

2,5-Bis[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]-thiophene *S,S*′-Dioxide [OF(2)TPSO-NPh]. The previous procedure was followed using 2,5-dibromothiophene *S*,*S*′-dioxide (137 mg, 0.5 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (587 mg, 1.2 mmol), tetrakis(triphenylphosphine)palladium (58 mg, 0.05 mmol), 2 M K_2CO_3 (3 mL), and THF (30 mL). The pure product was separated by silica gel column chromatography using 2:1 petroleum ether/dichloromethane as eluent affording 358 mg (71%) of a deep red solid. ^{1}H NMR (400 MHz, CDCl$_3$, δ) 7.79 (d, $J = 8.00$ Hz, 2H), 7.65 (d, $J = 10.00$ Hz, 4H), 7.56 (d, $J = 8.40$ Hz, 2H), 7.24 (t, $J = 7.8$ Hz, 8H), 7.09−7.13 (m, 10H), 7.06 (s, 2H), 7.00−7.03 (m, 6H), 1.84−1.92 (m, 8H), 1.03−1.11 (m, 8H), 0.69 (t, $J = 7.20$ Hz, 20H). ^{13}C NMR (100 MHz, CDCl$_3$, δ) 152.8, 151.6, 148.1, 147.8, 143.2, 141.8, 134.9, 129.2, 125.5, 125.1, 124.2, 123.1, 122.9, 121.0, 120.1, 119.7, 119.3, 118.7, 55.2, 39.8, 26.0, 23.0, 13.9. MS (FAB) *m*/*z* 1003.1 (M$^+$). Anal. Calcd for $C_{70}H_{70}N_2O_2S$ (%): C, 83.79; H, 7.03; N, 2.79; S, 3.19. Found: C, 83.89; H, 6.78; N, 2.93; S, 3.16.

3,6-Bis[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]-dibenzothiophene [OF(2) DBTP-NPh]. The synthetic procedure of OF-(2)Ph-NPh was followed using 3,6-diiododibenzothiophene (218 mg, 0.5 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (734 mg, 1.5 mmol), palladium (II) acetate (17 mg), tri(*o*-tolyl)-phosphine (46 mg), 2 M K_2CO_3 (4 mL), toluene (20 mL), and methanol (10 mL). The pure product was separated by silica gel column chromatography using 4:1 petroleum ether/dichloromethane as eluent affording 300 mg (56%) of a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$, δ) 8.51 (s, 2H), 7.95 (d, $J = 8.40$ Hz, 2H), 7.79 (d, $J = 8.00$ Hz, 2H), 7.64 (s, 2H), 7.69−7.74 (m, 4H), 7.61 (d, $J = 8.00$ Hz, 2H), 7.26 (t, $J = 8.40$ Hz, 8H), 7.15 (d, $J = 7.20$ Hz, 10H), 7.05 (d, $J = 8.00$ Hz, 2H), 7.02 (t, $J = 7.20$ Hz, 4H), 1.91−2.00 (m, 8H), 1.08−1.13 (m, 8H), 0.73 (t, $J = 7.40$ Hz, 20H). ^{13}C NMR (100 MHz, CDCl$_3$, δ) 152.3, 151.5, 148.0, 147.2, 140.3, 139.2, 138.7, 138.5, 136.2, 135.9, 129.2, 126.4, 126.3, 123.8, 123.5, 123.1, 122.5, 121.5, 120.4, 120.0, 119.5, 119.3, 55.1, 40.0, 26.1, 23.0, 13.9. MS (FAB) *m*/*z* 1071.2 (M$^+$). Anal. Calcd for $C_{78}H_{74}N_2S$ (%): C, 87.43; H, 6.96; N, 2.61; S, 2.99. Found: C, 87.31; H, 6.80; N, 2.83; S, 3.10.

5,5′′-Bis[2′-diphenylamino-9′,9′-bis(*n*-butyl)-7′-fluorenyl]-2,2′,5′,2′′-terthiophene [OF(2)TTP-NPh]. The previous procedure was followed using 2,5′′-diiodo-5,2′,5′,2′′-terthiophene (125 mg, 0.25 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (367 mg, 0.75 mmol), palladium (II) acetate (5.6 mg), tri(*o*-tolyl)phosphine (15 mg), 2 M K_2CO_3 (2 mL), toluene (10 mL), and methanol (5 mL). The pure product was separated by silica gel column chromatography using 4:1 petroleum ether/dichloromethane as eluent affording 190 mg (67%) of an orange solid. ^{1}H NMR (400 MHz, CDCl$_3$, δ) 7.53−7.60 (m, 6H), 7.49 (s, 2H), 7.22−7.28 (m, 6H), 7.16 (d, $J = 4.00$ Hz, 2H), 7.09−7.13 (m, 12H), 7.00 (dd, $J = 7.60$ Hz, 6H), 1.84−1.91 (m, 8H), 1.05−1.11 (m, 8H), 0.66−0.71 (m, 20H). ^{13}C NMR (100 MHz, CDCl$_3$, δ) 152.3, 151.5, 147.9, 147.3, 144.2, 140.8, 136.2, 135.9, 135.6, 132.0, 129.2, 124.6, 124.1, 123.9, 124.6, 124.1, 123.9, 123.4, 122.6, 120.4, 119.7, 119.5, 119.2, 55.1, 40.0, 26.0, 23.0, 13.9. MS (FAB) *m*/*z* 1135.6 (M$^+$). Anal. Calcd for $C_{78}H_{74}N_2S_3$ (%): C, 82.50; H, 6.57; N, 2.47. Found: C, 82.74; H, 6.56; N, 2.88.

Acknowledgment. This work was supported by an Earmarked Research Grant (HKBU2051/01P) from Research Grants Council, Hong Kong SAR, China.

CM051163V