ORGANIC LETTERS

2006
Vol. 8, No. 19
4271−4274

Synthesis and Light-Emitting Properties of Bipolar Oligofluorenes Containing Triarylamine and 1,2,4-Triazole Moieties

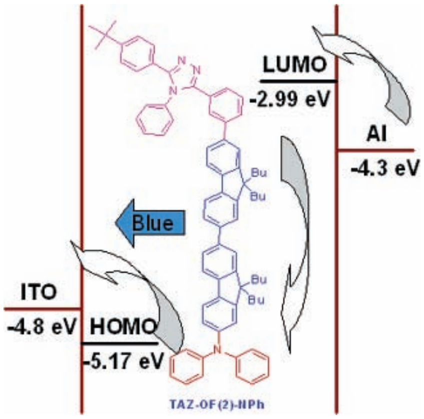
Zhong Hui Li,[†,§] Man Shing Wong,*[,†] Hiroshi Fukutani,[‡] and Ye Tao*[,‡]

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

mswong@hkbu.edu.hk; ye.tao@nrc.ca

Received June 22, 2006

ABSTRACT



A facile approach for synthesis of bipolar oligofluorenes, TAZ-OF(n)-NPh, $n = 2$ or 3 end-capped with hole-transporting diphenylamino and electron-transporting triazole moieties by Suzuki cross-coupling as the key reaction has been developed. This novel bipolar oligofluorenes exhibited blue-emission, high thermal and morphological stabilities. The single-layer OLED based on TAZ-OF(2)-NPh exhibited superior device performance with a maximum luminance of 1128 cd m^{-2} and luminance efficiency of up to 0.83 cd A^{-1}.

Maintaining the charge balance in an organic light-emitting diode (OLED) is considered to be an important issue for achieving high device performance[1,2] as it is a double-charge injection device, which requires the simultaneous supply of both electrons and holes to the electroluminescent (EL) material sandwiched between two electrodes. Two strategies have been developed to meet this demand which include the fabrication of multilayer configuration devices[2c] and an introduction of hole- and electron-transporting moieties into one single light-emitting molecular material.[3] The latter has been thought of as a promising approach to improve device performance because of the simplified device structure and fabrication procedure as well as the possibility of reducing

---

[†] Hong Kong Baptist University.

[‡] National Research Council of Canada.

[§] Present address: Department of Chemistry, Sichuan College of Education, Chengdu, 610041, Sichuan Province, China.

(1) (a) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Adachi, C.; Tokito, S.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1988**, *27*, L713.

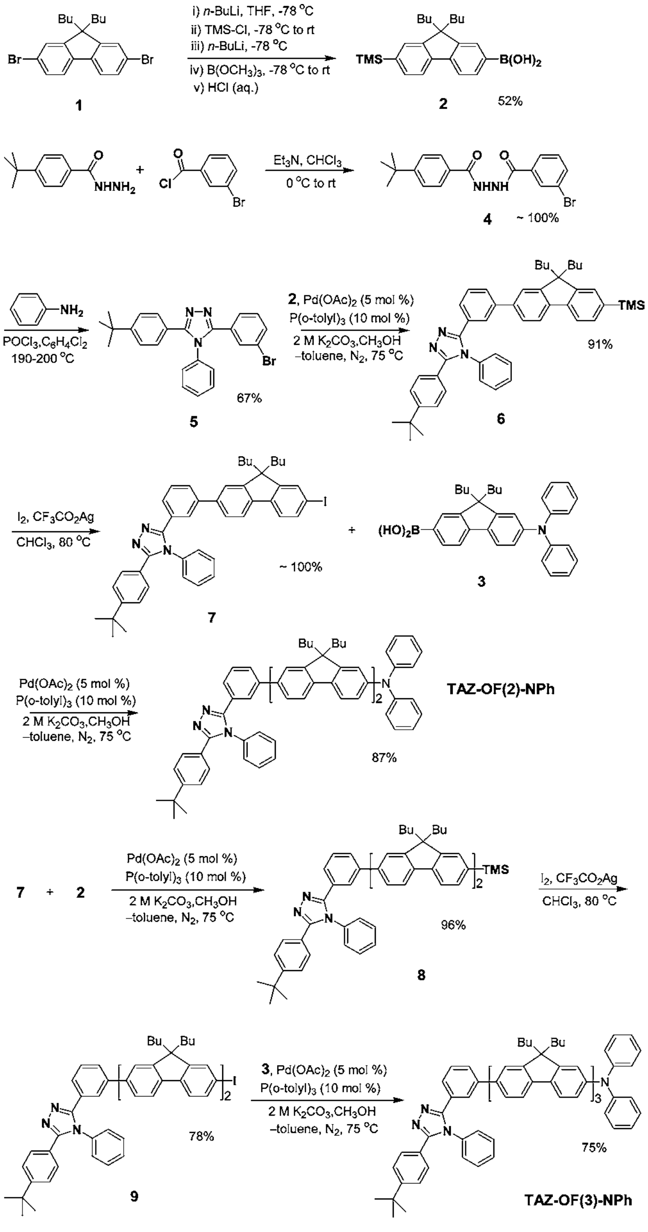
(2) (a) Adachi, C.; Nagai, K.; Tamoto, N. *Appl. Phys. Lett.* **1995**, *66*, 2679. (b) O'Brien, D. F.; Burrows, P. E.; Forrest, S. R.; Koene, B. E.; Loy, D. E.; Thompson, M. E. *Adv. Mater.* **1998**, *10*, 1108. (c) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1. (d) Loy, D. E.; Koene, B. E.; Thompson, M. E. *Adv. Funct. Mater.* **2002**, *12*, 245. (e) Hreha, R. D.; George, C. P.; Haldi, A.; Domercq, B.; Malagoli, M.; Barlow, S.; Bredas, J.-L.; Kippelen, B.; Marder, S. R. *Adv. Funct. Mater.* **2003**, *13*, 967. (f) Nomura, M.; Shibasaki, Y.; Ueda, M.; Tugita, K.; Ichikawa, M.; Taniguchi, Y. *Macromolecules* **2004**, *37*, 1204. (g) Domercq, B.; Grasso, C.; Maldonado, J.-L.; Halik, M.; Barlow, S.; Marder, S. R.; Kippelen, B. *J. Phys. Chem. B* **2004**, *108*, 8647. (h) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556.

10.1021/ol0615477 CCC: $33.50

or eliminating exciplex formation between layers.[4] Highly electron-rich triphenylamines known for their high hole mobility have been extensively used as hole-transporting materials in OLEDs.[5] It has been shown that light-emitting polymers grafted or end-capped with triphenylamine moieties exhibit improved OLED device performance.[6] Furthermore, highly electron-deficient triazole (TAZ) derivatives have been demonstrated to have more efficient electron-transport and hole-blocking characteristics and have a higher stability to high current density than the oxadiazole derivatives (e.g., PBD) in OLEDs.[7] Monodisperse oligofluorenes (OF) have recently attracted much attention because of their chemical and thermal stabilities and potential applications for optoelectronic molecular materials, especially for blue-emitting OLEDs devices.[8] As part of our efforts to investigate the structural factors of functional materials[9] that can enhance OLED performance and stability and toward the goal of integrating three active components including hole-transporting, electron-transporting, and light-emitting moieties into a single molecule to simplify device fabrication and to improve performance of resulting devices, we report herein the first synthesis of bipolar oligofluorenes, TAZ-OF(n)-NPhs, $n = 2$ or 3, in which the blue emitting bi- or terfluorene core is asymmetrically disubstituted with diphenylamino hole-transporting moiety and electron-transporting triazole derivative forming a multifunctional molecule and the investigation of their use in single-layer OLEDs. Meanwhile, to obtain blue light-emitting materials, the strongly electron-withdrawing triazole moiety must be decoupled with π-conjugated system of the oligofluorene core which was thus linked at the nonconjugated 3-position of the phenyl ring of the triazole moiety. Because of the bipolar character, good luminescence properties, high thermal stability, and good amorphous morphological stability, TAZ-OF(n)-NPhs show great potential for use as double charge carrier transport emitters in OLEDs

The synthetic strategy for asymmetrically disubstituted diphenylamine and triazole based bipolar oligofluorenes TAZ-OF(n)-NPhs, $n = 2$ or 3, is outlined in Scheme 1.

Scheme 1. Synthesis of Asymmetric Bipolar Oligofluorenes TAZ-OF(n)-NPh



Transformation of the dibromide **1**[9b] into the corresponding 2-(trimethylsilyl)-7-fluorenylboronic acid **2** was carried out by a one-pot reaction affording a 52% overall yield. After first lithium bromide exchange at −78 °C followed by reaction with trimethylsilyl chloride at room temperature, second lithium bromide exchange at −78 °C was subsequently proceeded and followed by reaction with trimethyl borate and then acid hydrolysis. Reaction of 4-*tert*-butyl-

---

(3) (a) Tak, Y.-H.; Mang, S.; Greiner, A.; Bässler, H.; Pfeiffer, S.; Hörhold, H.-H. *Acta Polym.* **1997**, *48*, 450. (b) Li, X.-C.; Cacialli, F.; Giles, M.; Grüner, J.; Friend, R. H.; Holmes, A. B.; Moratti, S. C.; Yong, T. M. *Adv. Mater.* **1995**, *7*, 898. (c) Li, X.-C.; Yong, T. M.; Grüner, J.; Holmes, A. B.; Moratti, S. C.; Cacialli, F.; Friend, R. H. *Synth. Met.* **1997**, *84*, 437. (d) Chen, C.-T.; Lin, J.-S.; Moturu, M. V. R. K.; Lin, Y.-W.; Yi, W.; Tao, Y.-T.; Chen, C.-H. *Chem. Commun.* **2005**, *16*, 3980. (e) Haung, T.-H.; Lin, J.-T.; Chen, L.-Y.; Lin, Y.-T.; Wu, C.-C. *Adv. Mater.* **2006**, *18*, 602. (f) Kulkarni, A. P.; Kong, X.; Jenekhe, S. *Adv. Funct. Mater.* **2006**, *16*, 1057.

(4) (a) Zhang, H.-Y.; Huo, C.; Zhang, J.-G.; Zhang, P.; Tian, W.-J.; Wang, Y. *Chem. Commun.* **2006**, 281.

(5) (a) Adachi, C.; Nagai, K.; Tamoto, N. *Appl. Phys. Lett.* **1995**, *66*, 2679. (b) Strohriegl, P.; Grazulevicius, J. V. *Adv. Mater.* **2002**, *14*, 1439.

(6) (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. (b) Pu, Y. J.; Soma, M.; Kido, J.; Nishide, H. *Chem. Mater.* **2001**, *13*, 3817. (c) Shi, J.; Zheng, S. *Macromolecules* **2001**, *34*, 6571.

(7) (a) Kido, J.; Ohtaki, C.; Hongawa, K.; Okuyama, K.; Nagai, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L917. (b) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1993**, *63*, 2627. (c) Kido, J.; Kimura, M.; Nagai, K. *Science* **1995**, *267*, 1332. (d) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969. (e) Strukelj, M.; Miller, T. M.; Papadimitrakopoulos, F.; Son, S. *J. Am. Chem. Soc.* **1995**, *117*, 11976. (f) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, *77*, 904. (g) Yu, L.-S.; Chen, S.-A. *Adv. Mater.* **2004**, *16*, 744.

(8) (a) Pei, Q.; Yang, Y.*J. Am. Chem. Soc.* **1996**, *118*, 7416. (b) Marsitzky, D.; Klapper, M.; Müllen, K. *Macromolecules* **1999**, *32*, 8685. (c) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H. G.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671.

(9) (a) Li, Z. H.; Wong, M. S.; Tao, Y.; D'Iorio, M. *J. Org. Chem.* **2004**, *69*, 921. (b) Li, Z. H.; Wong, M. S.; Tao, Y.; Lu, J. P. *Chem.—Eur. J.* **2005**, *11*, 3285. (c) Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. *Chem. Mater.* **2005**, *17*, 5032. (d) Li, Z. H.; Wong, M. S. *Org. Lett.* **2006**, *8*, 1499.

Table 1. Summaries of Measurements of TAZ-OF(n)-NPhs

	$\lambda^{abs}_{max}{}^{a}$/nm ($\epsilon \times 10^4$/M^{-1} cm^{-1})	$\lambda^{em}_{max}{}^{a,b}$/nm	$\Phi^{a,c}$	$E_{1/2oxd}{}^{d}$/V	HOMO^{e}/eV	$E_{1/2\ red}{}^{d}$/V	LUMO^{e}/eV	$T_g{}^{f}$/°C	$T_{dec}{}^{g}$/°C
TAZ-OF(2)-NPh	375 (4.38)	435	0.52	0.37, 0.91	−5.17	−1.38	−2.99	127	448
TAZ-OF(3)-NPh	374 (4.76)	435	0.52	0.35, 0.82	−5.15	−1.38	−2.99	126	452

[a] Measured in $CHCl_3$. [b] Excited at the absorption maxima. [c] Using quinine sulfate monohydrate ($\Phi_{313} = 0.48$) in 1.0 M H_2SO_4 as a standard. [d] $E_{1/2}$ vs Fc^+/Fc estimated by CV method using 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 and all the potentials were calibrated with ferrocene, $E_{1/2}$ (Fc/Fc^+) = 0.43 V vs SCE. [e] Estimated from CV measurements. [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.

benzoyl hydrazide and 3-bromobenzoyl chloride in the presence of triethylamine at room temperature afforded the disubstituted hydrazine **4** in a quantitative yield. Condensation of **4** and aniline in the presence of $POCl_3$ at 195 °C afforded 1,2,4-triazole derivative **5** in 67% yield. Palladium-catalyzed Suzuki cross-coupling of the bromide **5** and boronic acid **2** using $Pd(OAc)_2/2P(o\text{-tolyl})_3$ as a catalyst afforded the desired trimethylsilylfluorene derivative **6** in an excellent yield. Iododesilylation of **6** was carried out in the presence of silver trifluoroacetate at 80 °C affording the corresponding iodide **7** in quantitative yield.[10] Palladium-catalyzed Suzuki cross-coupling of iodide **7** and 7-diphenylamino-2-fluorenylboronic acid, **3**, which was prepared according to the literature procedure,[9b] afforded TAZ-OF(2)-NPh in 87% yield. On the other hand, cross coupling of **7** and boronic acid **2** afforded the trimethylsilylbifluorene derivative **8** in an excellent isolated yield of 96%. Iododesilylation of **8** gave the corresponding bifluorene iodide **9**. Palladium-catalyzed Suzuki cross-coupling of **9** and boronic acid **3** afforded the target compound TAZ-OF(3)-NPh in a good yield. All the newly synthesized asymmetrically disubstituted bipolar oligofluorenes were fully characterized with ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis and found to be in good agreement with their structures.

These bipolar oligofluorenesTAZ-OF(n)-NPhs show distinct glass transition temperatures (T_g's ~ 126 °C) as determined by differential scanning calorimetry (DSC), which remain fairly constant despite an increase in fluorenyl unit, suggesting that these oligofluorenes could form morphologically stable amorphous thin film. Furthermore, TAZ-OF(n)-NPhs show high thermal stabilities with decomposition temperatures (T_{dec}'s) of ~450 °C which slightly increase as the oligofluorene chain length increases as determined by thermal gravimetric analyzer (TGA) (Table 1)

The absorption maxima (λ^{abs}_{max}) of these bipolar oligofluorenes TAZ-OF(n)-NPhs peaked at 375 nm and are relatively blue shifted (~10 nm) as compared to the symmetrically diphenylamino-disubstituted analogues, indicating the nonconjugated nature of the oligofluorene core and triazole moiety.[9b] In addition, the incorporation of triazole moiety onto the nonconjugated position of the oligofluorene backbone may cause the resulting molecule to be less coplanar than the analogues end-capped with diphenylamino groups in their ground state leading to a blue shift in λ^{abs}_{max}.[11] Although the λ^{abs}_{max} of TAZ-OF(n)-NPhs remain fairly constant, their molar absorptivities (ϵ_{max}) increase slightly as the oligofluorene chain length increases (Figure 1a and Table 1). On the other hand, their emission spectra are structureless, indicating noncoplanar excited state with slightly red-shifted (Δ 3−10 nm) emission maxima (λ^{em}_{max} = 435 nm) when compared to those of the corresponding symmetrically diphenylamino-disubstituted oligofluorenes.

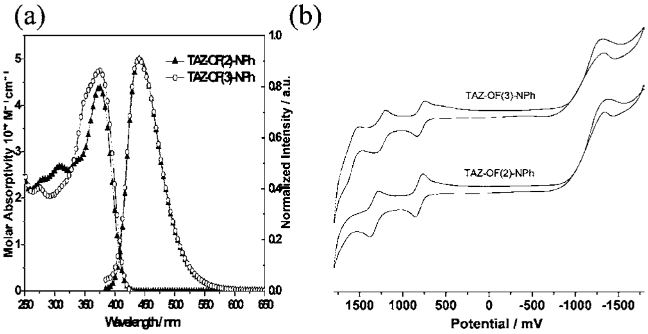


Figure 1. (a) Absorption and emission spectra measured in $CHCl_3$ and (b) cyclic voltammogram measured in CH_2Cl_2 of TAZ-OF(n)-NPh, n = 2 and 3.

Upon excitation either at 269 nm corresponding to the λ^{abs}_{max} of triazole moiety or at 314 nm attributed to the n→π* transition of triarylamine or at 375 nm corresponding to the π→π* transition of oligofluorene backbone, the emission spectra obtained are almost identical, suggesting that energy or exciton can efficiently transfer from the end-substituent to the oligofluorene core. The fluorescence quantum yields (Φ_{PL}) of TAZ-OF(n)-NPhs measured in chloroform using quinine sulfate monohydrate in 1.0 M H_2SO_4 as a standard[12] are 0.52 which does not increase with an extension of chain length, indicating the longer homologue does not improve coplanarity of the π-conjugated system. These Φ_{PL} values

---

(10) Wilson, S. R.; Jacob, L. A. *J. Org. Chem.* **1986**, *51*, 4833.

(11) (a) Berlman, I. B. *J. Phys. Chem.* **1970**, *74*, 3085. (b) Nijegorodov, N. I.; Downey, W. S. *J. Phys. Chem.* **1994**, *98*, 5639. As revealed from the MM2-optimized geometries, TAZ-OF(2)-NPh showed a slightly greater twisting between the two fluorene units than the symmetrically diphenylamino end-capped analogoues (~1°). The twisting between bifluorene skeleton and phenyl ring of the traizole moiety is ~35.8°. These twistings may be the cause of blue shift.

(12) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

are slightly smaller than those of the corresponding symmetrically diphenylamino-disubstituted analogous,[9c] consistently indicating that introduction of triazole moiety onto the oligofluorene skeleton might perturb the coplanarity altering the fluorescent nature of oligofluorene core.

Cyclic voltammetry was carried out in a three-electrode cell setup with 0.1 M of Bu_4NPF_6 as a supporting electrolyte in CH_2Cl_2 to examine the electrochemical properties of the oligofluorenes. The results are tabulated in Table 1. The asymmetrically substituted oligofluorenes TAZ-OF(*n*)-NPhs exhibited two reversible one-electron anodic redox couples which correspond to the sequential removal of electrons from the arylamino group and oligofluorene core forming radical cations and dications, respectively. (Figure 1b) Both the arylamine oxidation and the oligofluorene core oxidation proceed more easily with an increase in conjugated length as this electrochemically formed radical cation can be efficiently delocalized and hence stabilized. Importantly, TAZ-OF(*n*)-NPhs also exhibited a quasi-reversible reduction at −1.38 V under the same CV conditions corresponding to the one-electron reduction of the triazole moiety which does not affect by the conjugated length of oligofluorene due to the nonconjugated linking. The advantages of incorporation of diphenylamino endcap leading to the HOMO level of 5.15 eV to reduce the energy barrier for the hole injection from ITO to the emissive oligofluorene core[9] and incorporation of triazole moiety resulting in the LUMO level of 2.99 eV to facilitate electron injection and electron transport (Table 1) of this oligofluorene are apparent. As a result, TAZ-OF-(*n*)-NPhs can also be used as double charge carrier transport/injection materials (Figure 2).

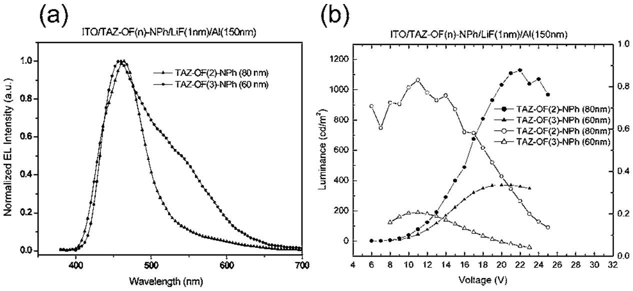


Figure 2. (a) Electroluminescence spectra and (b) luminance−voltage and efficiency−voltage plots of TAZ-OF(*n*)-NPh-based OLED devices.

The undoped single-layer OLEDs with the structure of ITO/TAZ-OF(*n*)-NPh (40−80 nm)/LiF (1 nm)/Al (150 nm) were fabricated by the conventional vacuum deposition and subsequently investigated for their electroluminescent (EL) properties. The EL spectra of the TAZ-OF(2)-NPh-based devices compare very well with the solution and thin film photoluminescence (PL) spectra indicating the blue emission originate from the oligofluorenes and showed some red-shifts relative to the solution and thin film PL spectra. The EL emission maxima (λ^{EL}_{max}) of these devices also showed a red-shift with an increase in the thickness of the emitting layer. For TAZ-OF(2)-NPh-based devices, λ^{EL}_{max} shift from 436 to 464 nm and the 1976 CIE coordinates shift from (u', v' = 0.165, 0.262) to (u', v' = 0.149, 0.296) with a layer thickness increasing from 40 to 80 nm. Such a small red shift might be caused by the microcavity effect in these devices.[13] However, TAZ-OF(3)-NPh-based devices showed much larger thickness-dependent red shift of λ^{EL}_{max} (from 436 to 500 nm and the 1976 CIE coordinates from (u', v' = 0.153, 0.313) to (u', v' = 0.193, 0.502)) with spectral broadening. In addition to the possible microcavity effect, the presence of molecular aggregation as inferred from the red-shift and band broadening of the thin-film PL spectrum of TAZ-OF(3)-NPh would further aggravate the adverse situation. Importantly, the single-layer TAZ-OF(2)-NPh-based device exhibited superior device performance with a maximum luminance of 1128 cd m^{-2} and a luminance efficiency of up to 0.83 cd A^{-1}, whereas the TAZ-OF(3)-NPh-based devices exhibited a maximum luminance of 370 cd m^{-2} and a luminance efficiency of up to 0.20 cd A^{-1}.

In summary, a facile approach for the synthesis of the asymmetrically disubstituted bipolar oligofluorenes containing hole-transporting and electron-transporting moieties using Suzuki cross-coupling as the key reaction has been presented. This approach could also be applicable for the construction of other structurally uniform and well-defined π-conjugated functional bipolar oligomers. The newly synthesized bipolar oligofluorenes, TAZ-OF(*n*)-NPhs exhibited desirable luminescence and material properties. The single-layer TAZ-OF-(2)-NPh-based OLED exhibited a blue emission with a maximum luminance of 1128 cd m^{-2} and a luminance efficiency of up to 0.83 cd A^{-1}.

Acknowledgment. We are grateful to the Hong Kong Research Grants Council (HKBU 2018/05P) for financial support of this work.

Supporting Information Available: The synthetic procedures and physical data of intermediates and **TAZ-OF-(*n*)-NPh**, n = 1−2 and their device data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0615477

---

[13] Bulović, V.; Khalfin, V. B.; Gu, G.; Burrows, P. E.Garbuzov, D. Z.; Forrest, S. R. *Phys. Rev. B* **1998**, *58*, 3730.