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Ambipolar Diphenylamino End-Capped Oligofluorenylthiophenes as Excellent Electron-Transporting Emitters

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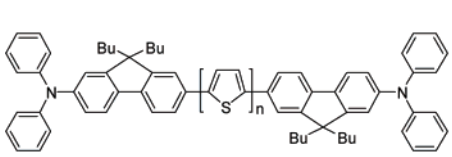
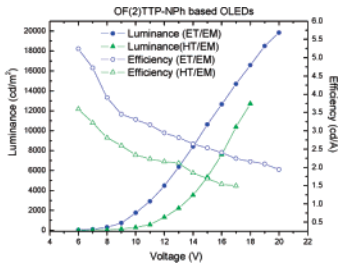
ABSTRACT



n = 3: **OF(2)TTP-NPh**; n = 4: **OF(2)QTP-NPh**



In addition to hole transport, diphenylamino-end-capped oligofluorenylthiophenes can exhibit efficient electron transport, in which the oligothiophene central core acts as an excellent electron-transporting moiety. The highly efficient undoped multilayer OLEDs using OF(2)-TTP-NPh and OF(2)QTP-NPh as an electron-transporting emitter exhibited a maximum luminance of 19 800 and 11 800 cd m^{-2} with a luminance efficiency up to 5.3 and 1.0 cd A^{-1}, respectively.

Thiophene-based materials have drawn considerable attention for their potential applications in the area of organic semiconductors because of their excellent chemical stability, high carrier mobility, and the ease of structural tuning to adjust the electronic, optical, and morphological properties.[1] A large number of oligothiophene and polythiophene derivatives have been synthesized and investigated as active compounds for field-effect transistors,[2] light emitting diodes (OLED),[3] photovoltaic cells,[4] and sensors.[5] Most of these thiophene-based materials play the functional role of hole-transport (p-type) in these devices. Although the electron-transporting (n-type) property is relatively rare in π-conjugated organic semiconductors, n-type activity can generally be introduced by incorporation of electron withdrawing groups such as fluoro, cyano, perfluoroalkyl, perfluoroaryl, and dicyanomethylene into the thiophene system.[6]

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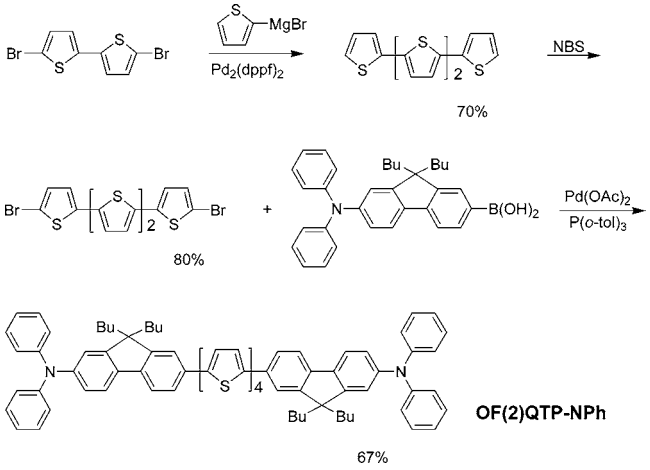
Multifunctional emissive materials with an ambipolar charge transporting character are of great interest for the development of highly efficient OLEDs. Such materials can provide better balanced transport for injected holes and electrons and thus could be used to simplify the structure and fabrication of a device. As π-conjugated emissive materials often exhibit better holes injection and transport than electrons, incorporation of electron affinitive moieties such as cyano, oxadiazole, triazole, and triazine functionalities into the emissive π-conjugated core/main chains or grafting them as side chains of a polymer or attaching them onto the outer surface of dendritic wedges is the commonly adopted approach to develop multifunctional emissive materials.[7]

The photoluminescence efficiencies of poly- and oligothiophenes in the solid state are usually low due to the increased contribution of nonradiative decay via interchain interactions and intersystem crossing caused by the heavy-atom effect of sulfur.[3d,8] On the other hand, it has been shown that oligothiophenes end-capped with strong electron donating diphenylaminofluorenyl moieties have become highly efficient hole-transporting bis-dipolar emitters for OLEDs.[9] As a thiophene unit has an observed dipole moment of 0.52 D, oligothienyl moieties could act as electron accepting moieties,[10] in principle, to facilitate electron transports when they are coupled with a strong electron-donating group such as the diphenylamino group. Rather limited work has used oligothienyl moiety as an electron affinitive functional unit to modify the functional properties of a material[3d] or an electron-transporting moiety although regioregular poly(3-hexylthiophene) film has been shown to exhibit good electron transport.[11] To continue our effort on the investigation of structural factors that can enhance functional properties of a molecular material,[9,12] we herein report synthesis and light-emitting properties of ambipolar diphenylamino-end-capped oligofluorenylthiophenes, **OF(2)TTP-NPh** and **OF(2)QTP-NPh**, in which the oligothiophene central core acts as an excellent electron-transporting and light-emitting unit to enhance the performance of resulting devices. It is worth mentioning that an oxadiazole electron affinitive moiety end-capped with diphenylamino groups does not exhibit efficient electron-transporting and light-emitting properties in OLEDs.

OF(2)TTP-NPh was prepared according to the previously published procedure.[9] The synthesis of the ambipolar oligofluorenylthiophenes, **OF(2)QTP-NPh**, is outlined in Scheme 1. Double palladium-catalyzed Kumada cross-coupling of dibromobithienyl and freshly prepared thienylmagnesium bromide afforded quarterthiophene in good yield. Direct bromination of quarterthiophene with NBS in CH_2Cl_2 yielded the slightly soluble dibromoquarterthiophene, which was used without further purification. Double palladium-catalyzed Suzuki cross-coupling of 7-diphenylamino-9,9-di-*n*-butylfluorenyl-2-boronic acid[9] and dibromoquarterthiophene afforded ambipolar **OF(2)QTP-NPh** in a moderate yield (67%). The newly synthesized ambipolar oligofluorenylthiophenes were fully characterized with ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis and found to be in good agreement with their structures. (see the Supporting Information).

Scheme 1. Synthesis of Ambipolar Oligofluorenylthiophenes **OF(2)QTP-NPh**



The absorption maxima (λ_{max}^{abs}) red-shifts about 10 nm as the length of central oligothienyl core increases, with peaks at 441 and 451 nm for **OF(2)TTP-NPh** and **OF(2)QTP-NPh**, respectively. The emission spectra of these oligofluorenylthiophenes are mainly composed of two overlapped bands and the emission bands consistently red-shift about 16−20 nm as the thiophene unit increases from three to four (Figure 1 and Table 1). Upon excitation either at 324 nm attributed to the n → π* transition of end-capped triarylamine or at 441 or 451 nm corresponding to the π → π* transition of oligofluorenylthiophene backbone, the emission spectra are identical, suggesting that energy or exciton can efficiently transfer from the end-capped triarylamine to the oligofluorenylthiophene moiety. The fluorescence quantum yields (Φ_{PL}) of **OF(2)TTP-NPh** and **OF(2)QTP-NPh** measured in chloroform with fluorescein as a standard are 0.26 and

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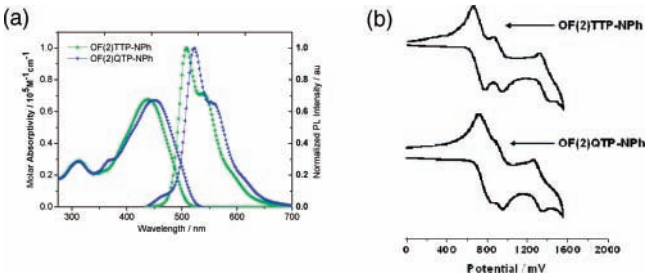

Figure 1. (a) Absorption spectra and emission spectra measured in $CHCl_3$. (b) Cyclic voltammogram measured in CH_2Cl_2 of **OF(2)TTP-NPh** and **OF(2)QTP-NPh**.

0.29, respectively. Furthermore, the fluorescence lifetimes of these oligofluorenylthiophenes are 1.19−1.21 ns, suggesting the emission originates from the decay of the singlet excited state to ground state.

The electrochemical behavior of these two oligofluorenylthiophenes were investigated by cyclic voltammetry and the results are tabulated in Table 1 and shown in Figure 1. Both ambipolar **OF(2)TTP-NPh** and **OF(2)QTP-NPh** exhibit a low reversible two-electron oxidation wave with $E_{1/2}$ at 0.31 V, corresponding to two arylamine oxidations followed by a reversible one-electron oxidation wave, corresponding to the oxidation of the oligofluorenylthiophene π-conjugated core with $E_{1/2}$ at 0.49 and 0.45 V and a irreversible one-electron oxidation wave corresponding to the formation of radical tetracation on the π-conjugated core with $E_{1/2}$ at 0.98 and 0.82 V, respectively. It is worth mentioning that the longer the conjugated oligothienyl core, which can better stabilize the radical cation(s), the lower the (second/third) oxidation potential is. The LUMO determined by the difference of HOMO and optical absorption edge is tabulated in Table 1. Owing to the better effective conjugation between thienyl rings and the strong electron-withdrawing nature of the oligothienyl central core when coupled with a strong diphenylamino donating group, the LUMOs (LUMO = 2.60−2.73 eV) of these ambipolar oligofluorenylthiophenes are more stabilized as compared to that of **OF(3)-NPh**, which contains a fluorenyl group as a central core with a LUMO level of 2.11 eV.[9] The thermal behavior of these two oligofluorenylthiophenes were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 1). These two oligofluorenylthiophenes could form stable amorphous thin-films with glass transition temperature (T_g) above 104 °C. On the other hand, the decomposition temperatures (T_{dec}) of **OF(2)TTP-NPh** and **OF(2)QTP-NPh** are 483 and 464 °C, respectively, indicating that the two oligomers are highly thermally stable.

The potential of these diphenylamino-end-capped oligofluorenylthiophenes used as hole-transporting emitters (HT/EM) in OLEDs was first explored. The undoped multilayer OLEDs with device structures of ITO/**OF(2)TTP-NPh**[9] (40 nm) or **OF(2)QTP-NPh** (40 nm)/F-TBB (15 nm)/Alq3 (20 nm)/LiF (1 nm)/Al (150 nm) were fabricated by the conventional vacuum deposition and investigated. Their electroluminescence (EL) spectra with emission bands at 520/570 nm and 555/591 nm, respectively, compare well with the thin-film PL spectra indicating that the EL originates from the oligomers and showed 20−30 nm red-shifts relative to the solution PL due to the improved coplanarity of the oligothiophene core in the solid state. Despite the moderate solid-state PL efficiencies of **OF(2)TTP-NPh** (13%) and **OF(2)QTP-NPh** (17%), OLED devices based on these oligomers as hole-transporting emitters could exhibit excellent device performance with a maximum luminance of 6800−12500 cd/m^2 and luminance efficiency up to 2.8−3.6 cd/A (Figures 2 and 3). It is important to find that these

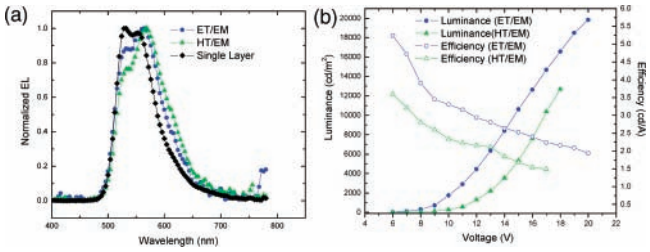

Figure 2. (a) EL spectra of **OF(2)TTP-NPh**-based OLEDs. (b) L−V−E plots of **OF(2)TTP-NPh**-based OLEDs.

oligomers could also act as efficient electron-transporting emitters (ET/EM) in OLEDs. The undoped multilayer OLEDs with device structure of ITO/NPB (40 nm)/**OF(2)-TTP-NPh** (35 nm) or **OF(2)QTP-NPh** (35 nm)/LiF (1 nm)/

Table 1. Summaries of Physical Measurements of **OF(2)TTP-NPh** and **OF(2)QTP-NPh**

	λ_{max}^{abs} [a]/nm ($10^4\epsilon$/M^{-1} cm^{-1})	λ_{max}^{em} [a,b]/nm	Φ[a,c]	τ[a,d]/ns	$E_{1/2}$[e]/eV	HOMO[e]/eV	E_g[f]/eV	LUMO[g]/eV	T_g[h]/°C	T_{dec}[i]/°C
OF(2)TPP-NPh	441 (6.76)	507, 540	0.26	1.19	0.31, 0.49, 0.98	5.11	2.51	2.60	105	483
OF(2)QTP-NPh	451 (6.74)	523, 560	0.29	1.21	0.31, 0.45, 0.82	5.11	2.39	2.73	104	464

[a] Measured in $CHCl_3$. [b] Excited at the absorption maxima. [c] Using fluorescein in 0.1 M NaOH (Φ_{435} = 0.96) as a standard. [d] Using nitrogen laser as excitation source. [e] $E_{1/2}$ vs Fc^+/Fc estimated by the CV method using platinum disc 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; all the potentials were calibrated with ferrocene, $E_{1/2}$(Fc/Fc^+) = 0.45 V vs SCE. [f] Estimated from the edge of electronic absorption spectra. [g] Estimated from the difference of HOMO and optical absorption edge. [h] Determined by differential scanning calorimeter from remelt after cooling with a heating rate of 10 deg/min under N_2. [i] Determined by thermal gravimetric analyzer with a heating rate of 10 deg/min under N_2.

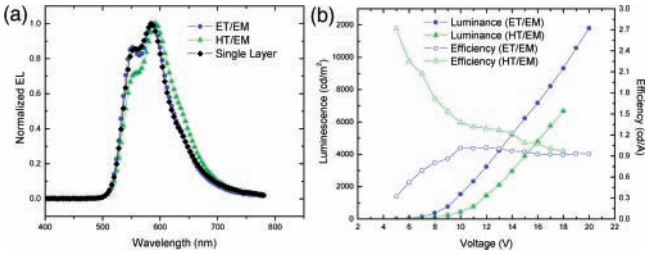

Figure 3. (a) EL spectra of **OF(2)QTP-NPh**-based OLEDs. (b) L−V−E plots of **OF(2)QTP-NPh**-based OLEDs.

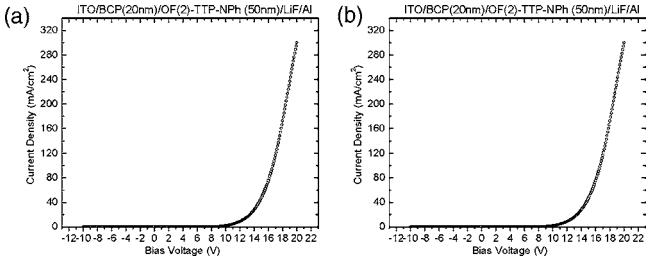

Figure 4. The I−V plots of the (a) **OF(2)TTP-NPh**-based and (b) **OF(2)QTP-NPh**-based electron-only devices.

Al (150 nm) exhibited superior device performance to those using these oligomers as hole-transporting emitters with a maximum luminance of 11800−19800 cd/m^2 and a luminance efficiency up to 1.0−5.3 cd/A. The EL spectra obtained from both types of devices were very similar indicating that the emission comes from the oligomers. These results confirmed the electron affinitive functional role of the central oligothienyl moiety in this class of materials. As these oligofluorenylthiophenes are ambipolar, they can also be used as double charge carrier transport/injection materials. The undoped single-layer OLEDs with structure of ITO/**OF(2)TTP-NPh** (40 nm) or **OF(2)QTP-NPh** (40 nm)/LiF (1 nm)/Al (150 nm) were also fabricated and investigated. The EL spectra of these single-layer devices compare very well with those multilayer devices (Figures 2a and 3a). As the single layer structure does not provide proper charge carriers and exciton confinement, excitions can quench at the electrodes without undergoing a radiative recombination process, and charge carriers can reach the opposite electrodes without forming excitons, the performance of these single-layer devices was far from satisfactory with maximum luminance of 330−1400 cd/m^2 and a luminance efficiency up to 0.04−0.1 cd/A.

To further affirm the electron transport abilities of these oligofluorenylthiophenes, electron-only devices with structures of ITO/BCP (20 nm)/**OF(2)-TTP-NPh** or **OF(2)-QTP-NPh** (50 nm)/LiF (1 nm)/Al (150 nm) were also fabricated and probed. With LiF/Al as an electron injecting electrode and BCP as a hole-blocking/electron-transporting material, the energy barrier for electrons traveling from the oligomer side to the BCP layer is negligible while the hole injection barrier between the ITO and BCP is ca. 1.6 eV, which effectively blocks the holes from entering the devices. As shown in the I−V plots of the electron-only devices (Figure 4), both oligofluorenylthiophenes can carry a significant amount of electron current. When compared with the double-layer OLED devices, the density of the electron current in the electron-only devices is about 1/3 of the total current through the double layer OLED at the same bias voltage, indicating the excellent electron-transport capability of these materials (see the Supporting Information).

In summary, a novel approach to design ambipolar light-emitting molecules based on diphenylamino-end-capped oligofluorenylthiophenes, in which the oligothiophene central core acts as an efficient electron-transporting unit, has been demonstrated. A facile synthesis of diphenylamino-end-capped fluorenylquarterthiophene was achieved by palladium-catalyzed Suzuki cross-coupling as a key step. We have also shown for the first time that oligothiophene moiety can act as an excellent electron-affinitive unit to facilitate electron transport when coupled with diphenylamino end-caps which can be used to enhance the performance of OLEDs. In addition to the excellent hole-transporting emitter-based devices, highly efficient undoped multilayer OLEDs using **OF(2)TTP-NPh** and **OF(2)QTP-NPh** as an electron-transporting emitter with a maximum luminance of 19 800 and 11 800 cd m^{-2} and luminance efficiency up to 5.3 and 1.0 cd A^{-1}, respectively, have been obtained. Our findings provide an alternative approach to design and tune electron-transporting materials for electronic applications.

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Supporting Information Available: Experimental procedures and spectral data for **OF(2)QTP-NPh** and device characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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