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Communications

Phenoxazine-Based Emissive Donor−Acceptor Materials for Efficient Organic Light-Emitting Diodes

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Recent advances in organic light-emitting diodes (OLEDs) have demonstrated their potential in displays.[1,2] To improve the performance and durability of OLEDs, a highly desired feature of the next generation of emissive materials is the capability of accepting both electrons and holes while exhibiting high luminescence quantum yield.[2] This means that the light-emitting molecule should have very stable radical cations *and* radical anions,[2] a requirement that is very similar to that for electrogenerated chemiluminescence.[3] A molecular design approach to such multifunctional materials for OLEDs is to combine distinct electron donor (D) and acceptor (A) units into a suitable emissive D−A molecule.[1f,2] Numerous triarylamine and carbazole (**1**) derivatives have been extensively studied as electron donors in hole transport or emissive materials in OLEDs.[1,4] Although scarcely explored as building blocks in current OLED materials compared to carbazole (**1**), phenothiazine (**2**) and phenoxazine (**3**) are stronger and potentially better electron donors because of their 0.7 eV lower ionization potentials and, thus, more stable radical cations.[5,6]

We report herein the synthesis, cyclic voltammetry, photophysics, and electroluminescence (EL) of new donor−acceptor (D−A) molecules incorporating phenoxazine as the donor and phenylquinoline[7] as the acceptor. Very bright (9510 cd/m^2 at 9.2 V) and efficient (3.4 cd/A at 6580 cd/m^2) green OLEDs, fabricated and tested in ambient air, were achieved from the intramolecular charge transfer (ICT)

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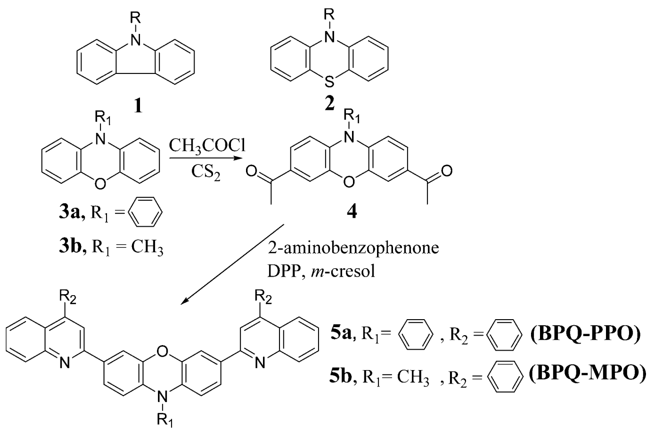
Scheme 1



fluorescence of the D−A molecules, implying highly efficient radiative electron transfer.

The D−A molecules, 10-phenyl-3,7-bis(4-phenyl-quinolin-2-yl)-10*H*-phenoxazine (BPQ-PPO, **5a**) and 10-methyl-3,7-bis(4-phenyl-quinolin-2-yl)-10*H*-phenoxazine (BPQ-MPO, **5b**), were synthesized by Friedlander condensation (Scheme 1)[3c,7a] and were purified by column chromatography and recrystallization from benzene. Their molecular structures were confirmed by ^{1}H NMR, Fourier transform infrared spectroscopy, mass spectroscopy, and X-ray single crystal determination (see Supporting Information). Differential scanning calorimetry showed that BPQ-PPO has a glass transition (T_g) at 149 °C and no melting transition up to 350 °C whereas BPQ-MPO had a T_g at 137 °C, a 197 °C recrystallization peak, and a melting transition at 311 °C. Thermogravimetric analysis showed a high onset decomposition temperature (T_d): BPQ-PPO (484 °C) and BPQ-MPO (442 °C). The high T_g and T_d observed for the two molecules suggest robust thermal stability of amorphous thin films for devices.

Cyclic voltammograms (CVs) of BPQ-PPO and BPQ-MPO in benzene/acetonitrile (2:1, v/v) showed that both have reversible oxidation and reversible reduction (Figure 1). Both D−A molecules can be repeatedly scanned in the range of −2.6 to 1.0 V (vs saturated calomel electrode, SCE) with many cycles without change in the redox characteristics. The half-wave oxidation ($E_{1/2}^{ox}$) and reduction ($E_{1/2}^{red}$) potentials of BPQ-PPO are 0.79 and −2.00 V (vs SCE), respectively. For BPQ-MPO, $E_{1/2}^{ox} = 0.71$ V and $E_{1/2}^{red} = -2.02$ V. The observed $E_{1/2}^{ox}$ of BPQ-MPO is close to the value reported for 10-methylphenoxazine (0.65 V vs SCE).[8] The reduction potentials of the two D−A molecules are identical to that of 2-phenylquinoline ($E_{1/2}^{red} = -1.99$ V vs SCE).[3c,9] From the observed half-wave potentials, we estimated the ionization potential (IP) and electron affinity (EA) values, respectively, of 5.2 and 2.4 eV for BPQ-PPO and 5.1 and 2.4 eV for BPQ-MPO. The highly reversible electrochemical oxidation and reduction of BPQ-PPO and BPQ-MPO suggest good prospects for efficient electron/hole injection/transport and recombination in OLEDs.

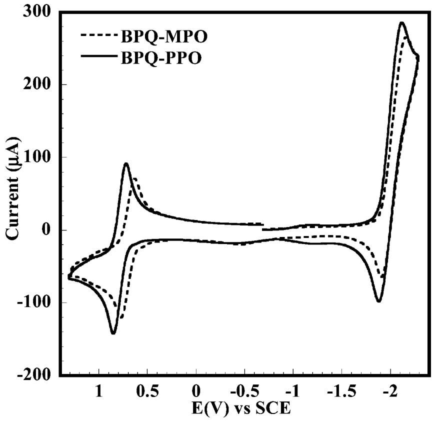


Figure 1. CVs of a 1 mM solution of BPQ-PPO or BPQ-MPO in benzene/MeCN at a Pt electrode (0.1 M TBAPF$_6$; scan rate = 200 mV/s).

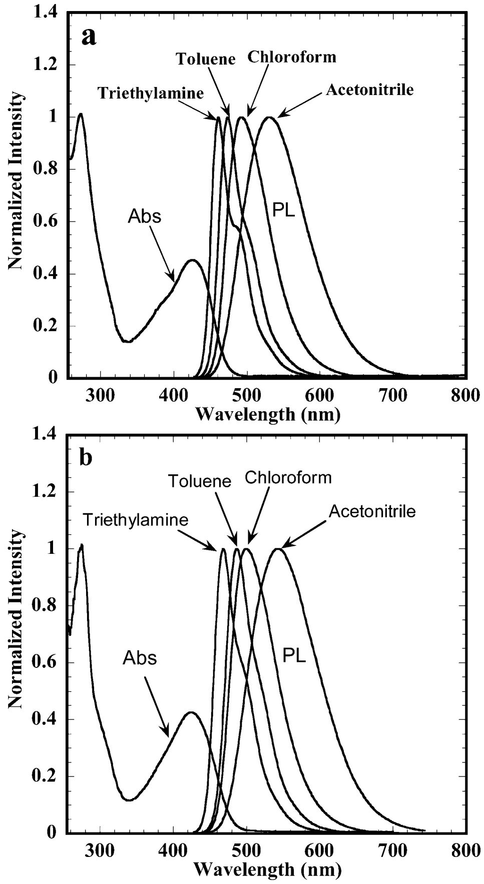


Figure 2. Absorption (in MeCN solution) and PL emission spectra (420-nm excitation) of (a) BPQ-PPO and (b) BPQ-MPO in solvents of varying polarity.

Figure 2a shows the optical absorption spectrum in acetonitrile (MeCN; 5 × 10^{-6} M) and photoluminescence (PL) emission spectra of BPQ-PPO in solvents of varying polarity. The 272-nm band in the absorption spectrum can be assigned to the $\pi-\pi^*$ transition whereas the 426-nm band is due to ICT.[6a] Weak solvatochromism was observed in the charge-transfer absorption band (not shown). A much larger positive solvatochromism was observed in the PL emission (Figure 2a), implying that the excited-state energy levels are influenced more than those in the electronic ground state. Both the emission maximum (λ_{max}^{em}) and the full width at

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half-maximum (fwhm) increased with solvent polarity, varying from $\lambda_{max}^{em} = 461$ nm (fwhm = 44 nm) in nonpolar triethylamine to 530 nm (fwhm = 102 nm) in highly polar MeCN. Similar large ICT effects were observed in the PL emission of BPQ-MPO (Figure 2b). The emission spectrum of BPQ-MPO was red-shifted by 7−13 nm compared to that of BPQ-PPO in any solvent. The PL quantum yields of both D−A molecules in toluene were similar, 80% for BPQ-PPO and 83% for BPQ-MPO.

The absorption and PL emission spectra of evaporated thin films of BPQ-PPO and BPQ-MPO were generally similar to those in solution (see Supporting Information). BPQ-PPO thin films had absorption peaks at 277 and 447 nm and BPQ-MPO thin films had absorption peaks at 265 and 450 nm. As in solution, the lowest energy absorption band in the solid state is of charge-transfer character. BPQ-PPO thin films show green PL emission with $\lambda_{max}^{em} = 515$ nm (CIE = 0.26, 0.63; fwhm = 60 nm); BPQ-MPO thin films exhibit a red-shifted yellowish-green PL emission ($\lambda_{max}^{em} = 539$ nm, CIE = 0.36, 0.60; fwhm = 71 nm). Thus, substitution of the bulkier phenyl ring at the N position of phenoxazine in BPQ-PPO compared to the methyl group in BPQ-MPO allows variation in the wavelength of the ICT fluorescence.

Uniform green EL with satisfactory brightnesses (up to 900 cd/m^2) was observed from evaporated thin films of each D−A molecule in single-layer diodes, indium tin oxide (ITO)/D−A (45 nm)/LiF/Al. The achievement of bright light emission from such single-layer devices is direct proof of the ease of both hole and electron injection and transport in the phenoxazine−phenylquinoline molecules by virtue of their low IP, moderate EA, and D−A character. However, the efficiencies of such devices were low at 0.04−0.4 cd/A at ∼100 cd/m^2, largely as a result of poor charge recombination efficiency in the emissive layer. Substantially superior performance was obtained by using an additional layer of electron-blocking material such as 1,1-bis(di-4-tolylaminophenyl)cyclohexane (TAPC; IP = 5.3 eV, EA = 1.8 eV).[7b] Figure 3a shows the EL spectra of a BPQ-PPO diode, ITO/PEDOT/TAPC (35 nm)/BPQ-PPO (45 nm)/LiF/Al, at different applied voltages. The EL spectra slightly blue-shifted with increasing voltage, having peaks at 510 nm at 3−5 V and 504 nm at 9 V. Thus, the CIE coordinates varied only slightly from (0.23, 0.62) at 3−5 V to (0.20, 0.58) at 9 V, within the desired pure green. These EL emission maxima are slightly blue-shifted from the 515-nm PL emission maximum of BPQ-PPO thin films. The EL emission can be unambiguously assigned to the ICT[6a] excited state of BPQ-PPO formed by the recombination of the phenoxazine radical cation with the phenylquinoline radical anion. The current density−voltage−luminance characteristics of the device are shown in Figure 3b. The diode had a low turn-on voltage of 3.0 V. The maximum brightness was 9510 cd/m^2 and the maximum external quantum efficiency was 1.10% at 6580 cd/m^2 and a luminous efficiency of 3.42 cd/A. The brightness and efficiency of similar bilayer diodes based on BPQ-MPO (see Supporting Information) were slightly lower.

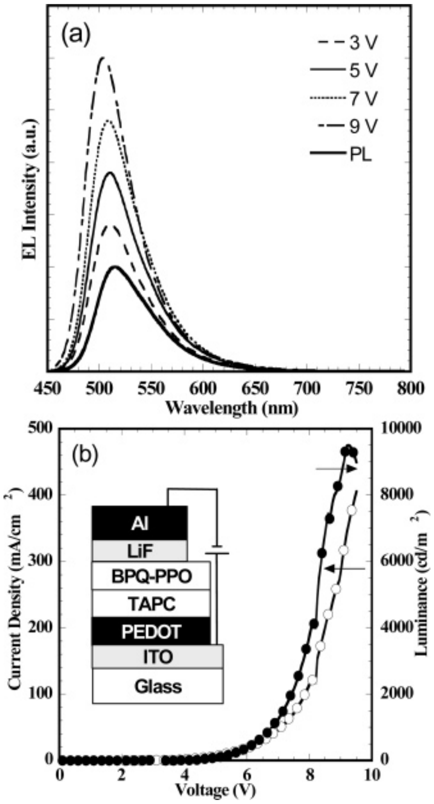

Figure 3. (a) EL spectra and PL spectrum of a BPQ-PPO OLED. (b) Current density−voltage−luminance characteristics of the device shown in the inset.

In conclusion, new highly fluorescent donor−acceptor molecules based on phenoxazine donors have been prepared and characterized. These molecules exhibited ICT fluorescence with 80−83% quantum yield in solution, had high glass transition temperatures (∼140−150 °C), and possessed reversible electrochemical oxidation and reduction that facilitate efficient hole/electron injection, transport, and recombination. Simple OLEDs made from these D−A materials exhibit high brightness and efficiency at low voltages in ambient air. These results demonstrate that phenoxazine is a very promising building block for the design of new emissive and charge transport materials for OLEDs and other organic electronics.

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Supporting Information Available: Synthetic and characterization details for compounds **3**−**5**. The detailed device fabrication and characterization procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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