Electrooptics

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Synthesis and Characterization of a Multicomponent Rhenium(I) Complex for Application as an OLED Dopant**

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Dedicated to Professor John J. McGarvey

Current studies in the field of organic light-emitting diodes (OLEDs) are aimed at improving display technology through production of devices with increased efficiency, flexibility, and long lifetimes.[1] An OLED converts electrical energy into light by allowing holes and electrons, which are transported from opposing electrodes, to combine to form an exciton, or localized excited state, in an emissive material. Subsequent relaxation of the exciton results in the emission of light.[1] A successful OLED requires facile and balanced charge transport as well as a high conversion efficiency of excitons to light.[2] As electrons and holes are transported through the lowest unoccupied molecular orbitals (LUMOs) and highest occupied molecular orbitals (HOMOs), respectively, in OLED components, the relative band gap and HOMO and LUMO energies of these materials is of crucial importance to the efficiency and brightness of an OLED.[3] Balanced charge injection is required so that charge recombination does not occur close to the electrode/polymer interface, because a metal electrode can deactivate excitons, lowering the efficiency of electroluminescence of the device.[2]

To fulfill these requirements, OLEDs often contain a number of layers that individually perform the roles of charge transport and light emission.[4] Each layer requires materials with the correct HOMO and LUMO energies to either promote or disrupt the flow of charge in the device. In many devices the emissive layer consists of a polymer such as poly(*N*-vinylcarbazole) (PVK) doped with a transition-metal complex, which acts as the charge-recombination and emission center.[5,6] Maximization of the brightness of a device is a key consideration in the production of OLEDs, which is why phosphorescent metal complexes are favored over fluorescent organic materials in many situations.[7] The dopant used also greatly affects the wavelength and broadness of the emission, as well as the efficiency of the device, so that an OLED may be tuned by appropriate selection of the metal center and ligand(s).

Herein, we describe our endeavors to design an electroactive material composed of simple modular units, each of which performs a specific function, namely electron transfer, hole transfer, and emission. Furthermore, we chose units that may be easily derivatized, thereby giving great flexibility to this design strategy. Wong et al.[8] and Gong et al.[9] have synthesized integrated molecules containing all three functionalities and shown that they are effective as a single charge-transport and emitting layer in OLEDs. Trifunctional polymers have also been prepared.[10] We designed and synthesized a trifunctional molecule that comprises the key units for an OLED material: an emissive chromophore based on a Re^I polypyridyl complex containing dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz), an electron-transporting 1,3,4-oxadiazole group, and a hole-transporting terthiophene unit. Re^I polypyridyl complexes are known to be highly emissive[11,12] and have been used as emitting dopants in a variety of OLED structures.[13–15] 1,3,4-Oxadiazole heterocycles are widely used as electron-transporting groups owing to their electron deficiency and good thermal stability.[2] The terthiophene subunit can act as a hole-transport group[16] and can also be easily functionalized and polymerized.[17] These units were linked to form a trifunctional molecule as outlined in Scheme 1.

Ligand 2-(11-dipyrido[3,2-*a*:2′,3′-*c*]phenazine)-5-phenyl-1,3,4-oxadiazole (**2**), which was prepared from dppz-CO_2H,[18] was treated with $[Re(CO)_5Cl]$ to give *fac*-**3**. Ag^+-induced solvolysis of **3** in MeCN[19] and reaction of the resulting complex **4** with (*E*)-1-((2,2′:5′,2″-terthiophen)-3′-yl)-2-(4′-pyridyl)ethane (**5**) gave the multifunctional complex **6** as the hexafluorophosphate salt (Scheme 1). Elemental analysis suggested the presence of a single molecule of solvent (ethyl acetate), and both ^1H and ^{13}C NMR spectra were consistent with the desired product. Despite numerous attempts using different solvents and counterions, we were unable to grow crystals of **6** of suitable quality for X-ray analysis.

Spectroscopic data for dppz, **2**, **3**, **5**, and **6** are presented in Table 1 and Figure 1. The ligand dppz is commonly thought to contain partitioned orbitals, as it displays limited communication between the phenazine and bipyridyl sections of the ligand.[20,21] If ligand **2** behaves in a similar manner, it is expected that introduction of an electron-withdrawing oxadiazole moiety, or coordination of a metal center, should have little effect on the properties of the ligand. However, both ligand substitution and metal coordination resulted in a shift in the absorption maxima. The emission maximum of **2** is at the same wavelength as that of dppz but exhibits a higher quantum yield of emission. Complexes **3** and **6** both display broader emission bands than **2**, showing the influence of the rhenium(I) center. The absorption spectra of **3** and **6** show tails

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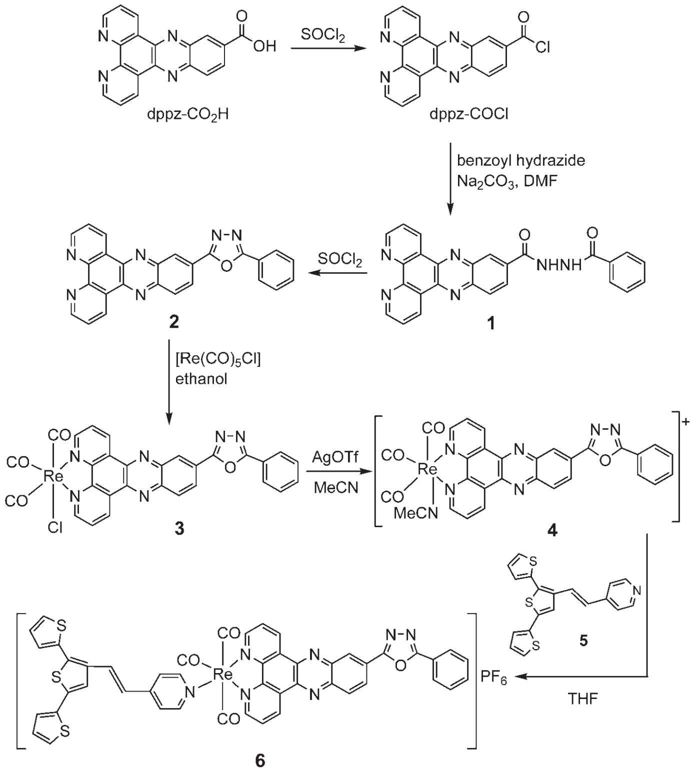

Scheme 1. Synthesis of the multicomponent molecule **6**. dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine; DMF = *N*,*N*-dimethylformamide; Tf = trifluoromethanesulfonyl.

Table 1: Spectroscopic data for dppz, **2**, **3**, **5**, and **6**.

Compound	λ_{max} [nm][a]	ε [$M^{-1}cm^{-1}$]	λ_{PL} [nm][b]	Quantum yield[c]	Stokes shift [cm^{-1}][d]
dppz	380	18000	427	0.009	2900
2	400	1300	427	0.040	1600
3	388	29000	497	0.001	2600
5	342	21000	487	0.130	8700
6	409	3400	474	0.003	3400

[a] Data were collected at room temperature from solutions in CH$_2$Cl$_2$ (concentrations in the 10^{-5} M range) degassed with N$_2$. [b] Maximum wavelength of photoluminescence upon excitation at $\lambda = 380$ nm. [c] Absolute values, calculated by the method of Wang et al.[22] [d] Calculated from the difference between the lowest energy absorption maximum and the emission wavelength maximum.

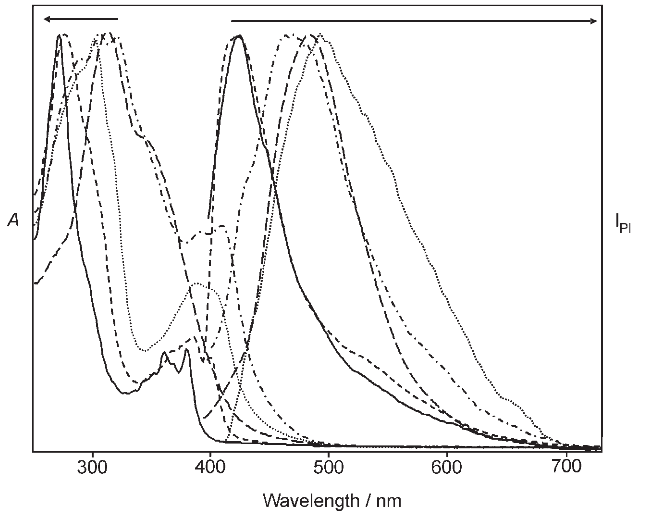

Figure 1. Normalized absorption (*A*) and photoluminescence (PL) data of dppz (——), **2** (----), **3** (•••••), **5** (– – –), and **6** (–•–•). Data were collected at room temperature from solutions (≈10^{-5} M) in CH$_2$Cl$_2$ degassed with N$_2$.

at lower energy, indicative of a metal–ligand state that is not present in the free ligand.

The Stokes shifts of dppz, **2**, **3**, **5**, and **6** were calculated in wavenumbers from the difference between the lowest energy absorption maximum and the emission maximum of each compound.[23] The oxadiazole moiety decreases the size of the Stokes shift of **2** relative to that of dppz. However, coordination of the rhenium(I) center increases the Stokes shift, as seen by a comparison of the data for **3** and **6** with those of **2** (see Table 1). The large Stokes shift as observed for **5** may be caused by significant structural differences between the ground state and excited state, as has been predicted for **5** and related molecules.[16] The Stokes shift of **6** is closer to that of **3** than of **5**, which suggests that the HOMO and LUMO of **6** are more similar to those of **3** than of **5**.[24]

Electrochemical data for dppz, **2**, **3**, **5**, and **6** are presented in Table 2 and Figure 2. HOMO and LUMO energies were calculated from the electrochemical data by known methods.[25] The introduction of an electron-withdrawing oxadiazole group had the predicted effect, with compounds **2**, **3**, and **6** being reduced at less-negative potential than dppz. Complex **6** was reduced at less-negative potential than its components, and its LUMO is correspondingly lower in energy. This observation correlates with the complex being easier to reduce than dppz, **2**, **3**, or **5** and thus a suitable candidate for electron transport. The presence of a terthiophene moiety in **5** and **6** was reflected in the oxidation potentials of the compounds: Compounds **5** and **6** were oxidized at less-positive potentials than dppz, **2**, or **3**, indicating a greater propensity for **5** and **6** to lose an electron. Resultantly, the HOMO energies of **5** and **6** are greater than

Table 2: Electrochemical data for dppz, **2**, **3**, **5**, and **6**.

Compound	Reduction potential [mV][a]	Oxidation potential [mV][a]	*E*(HOMO) [eV][b]	*E*(LUMO) [eV][b]
dppz	−1600[26]	n.d.	−6.22[27]	−2.96[27]
2	−851 (irr)	1690 (irr)	−5.87	−3.31
3	−746	1620 (irr)	−5.79	−3.36
5	−1030 (irr)	1110	−5.35	−3.13
6	−648	1170 (irr)	−5.38	−3.45

[a] Potentials were measured with reference to decamethylferrocenium/decamethylferrocene. Determined from solutions in dichloromethane (1.0 mM), containing tetrabutylammonium perchlorate (0.10 M) as the supporting electrolyte. Samples were purged with N$_2$ for 5 min before use. Scan rate: 100 Mv s^{-1}. n.d. = not determined; irr indicates an irreversible process. [b] Calculated using the method of Li et al.[25]

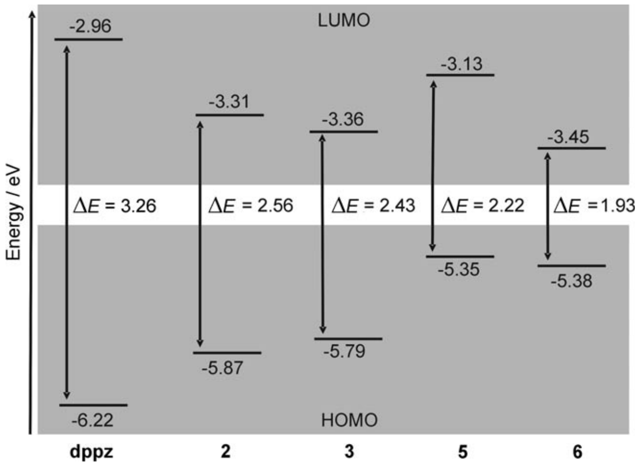

Figure 2. HOMO, LUMO, and band gap energies of dppz, **2**, **3**, **5**, and **6**.

those of dppz, **2**, or **3**, and thus **5** and **6** are expected to be better hole-transporting materials. The electrochemical data show that **6** has the smallest band gap energy of the compounds studied, and the relative energies of its HOMO and LUMO suggest that it favors transport of both holes and electrons.

Note that the HOMO and LUMO energies of **6** lie within the band gap of the host polymer PVK (Figure 3), so that the charges should accumulate and recombine on **6** rather than on PVK and emission should then occur from the relaxation of excitons localized on **6**. Theoretically, **6** looks to be a promising candidate as an OLED dopant as the small band gap should allow efficient charge transport. However, the small band gap of **6** may also cause inefficient conversion of excitons into radiation, as is reflected in the low quantum yield (Table 1). Nonetheless, the modular nature of complex **6** means that the individual components can be readily derivatized prior to assembly of the trifunctional molecule, thus allowing the electronic properties of the multifunctional compound to be tuned. We are currently engaged in studies aimed at derivatizing the modular components and making devices containing **6** and its derivatives.

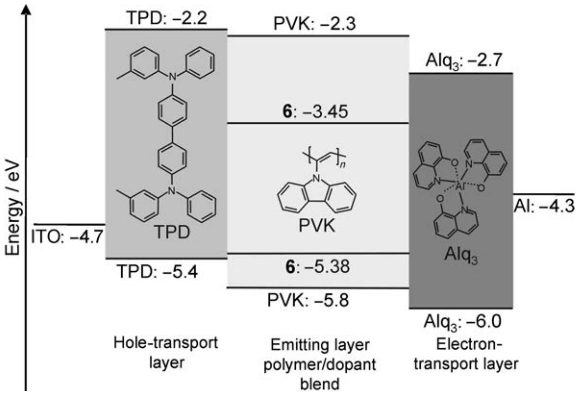

Figure 3. HOMO and LUMO energy levels of **6** superimposed onto a theoretical device containing *N,N*′-diphenyl-*N,N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), poly(*N*-vinylcarbazole) (PVK), and tris(8-hydroxyquinoline)aluminum (Alq_3). ITO = indium tin oxide.

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