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Molecular-Wire Behavior of OLED Materials: Exciton Dynamics in Multichromophoric Alq₃-Oligofluorene-Pt(II)porphyrin Triads

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A successful development of flat displays utilizing organic light-emitting diodes technology (OLED)[1] depends on the availability of organic semiconductors capable of emitting light with high electron-to-photon quantum efficiency. Because of the spin statistics of hole-electron recombination[2] that produces three triplets per one singlet, triplet emitters are preferred over singlet emitters to increase the device efficiency. While the energy of singlet states is easily harnessed by a plethora of fluorescent chromophores such as conjugated polymers (e.g., polyfluorene)[3] and complexes of metals with low spin−orbit coupling (e.g., Al^{III} trisquinolinolate, Alq₃),[4] triplet excitons are more difficult to utilize.[5,6] Generally, two types of materials may be used: electroluminescent complexes such as cyclometalated Ir(III) complexes or blends of singlet electrolumi-nophores (e.g., Alq₃) doped with a triplet emitter, for example Pt^{II} octaethylporphyrin.[7,8] The success in the preparation of materials of high charge-to-photon conversion efficacy by blending/doping depends on our ability to harvest the energy of triplet states. Alas, solution-processing of blends is often plagued by defects originating from phase separation of the components.[9] Single-molecular materials with a donor and acceptor (dopant) in a predefined distance to facilitate effective triplet energy transfer would be of practical advantage.[10]

The energy transfer (ET) between a donor (D) and acceptor (A) or between a host and dopant involves usually components of both Förster and Dexter processes.[11] However, in conjugated materials involving donor−bridge−acceptor (DBA) systems, the Dexter exchange mechanism, usually limited to a short distance (<10 Å), may show only a weak dependence on the D−A distance and is then regarded as superexchange. Both Dexter exchange and superexchange mechanisms allow for singlet−singlet and triplet−triplet processes.[11c] In the superexchange regime, the efficacy of the singlet and triplet ET from a donor to an acceptor decreases exponentially with the D−A distance, with the rate constant for these processes being limited by the rate of the Marcus theory of electron transfer.[12] Since the rate of triplet−triplet ET depends on both electron and hole transfers generated during the ET event within the D−A pair,[12b] the superexchange mechanism is of practical importance to OLEDs utilizing a host-dopant emissive layer.

In cases of donor > bridge > acceptor energy alignment, the ET is weakly dependent on the bridge length, which then behaves as an incoherent wire.[11c,13] Recent findings suggest that molecular-wire behavior is achieved in cases with properly aligned singlet[14] or triplet energy levels.[15] Because of the 3:1 triplet−singlet exciton ratio in OLEDs, the alignment of the triplet levels in particular could result in lossless energy transfer and improved emission of the acceptor. While such triads are of fundamental interest, their
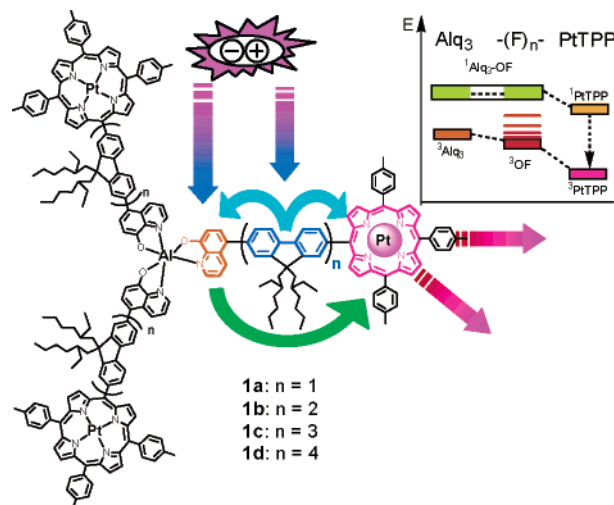
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Figure 1. Structure and energy alignments in triads **1a−d**.

solid-state photonic properties are of practical importance for fabrication of OLEDs as they could yield super-effective doping.

In this work, we present donor-bridge-acceptor triads **1a−d** (Figure 1) consisting of Alq₃, oligofluorene bridge, and Pt^{II} tetraphenylporphyrin (PtTPP), in which ET is facilitated by energy alignment of the components. Here, Alq₃- and the fluorene fragments appear to form a single fluorophore owing to strong electronic coupling facilitating the singlet exciton migration to the porphyrin (singlet energy: Alq₃-fluorene = 2.25 eV, PtTPP = 2.0 eV). The corresponding triplet levels are Alq₃, ^{3}E = 2.17 ± 0.10 eV;[16] fluorene bridge F₁−F₄, 2.86 to 2.18 ± 0.10 eV;[17] and PtTPP, 1.91 eV.[18] Synthesis of **1a−d** is outlined in the Supporting Information (SI).

The UV−vis absorption spectra of triads **1a−d** revealed typical features of these chromophores with Soret and Q-bands being centered at 405 and 510 nm, respectively. The $\pi-\pi^*$ absorption band at 340−370 nm originating from the oligofluorene fragment increased in intensity with an increasing number of fluorene units. Alq₃ absorption (λ_{max} = 380−420 nm)[19] is overlapped with the Soret band of the PtTPP (Figure 2). The PtTPP Q-bands (490−540 nm) overlap with Alq₃ emission (490−580 nm), which accounts for effective ET according to both the Förster and Dexter/superexchange model.

Excitation in the Q-band resulted only in phosphorescence from the PtTPP (λ_{max} = 670 and 740 nm, τ = 43.6 ± 0.8 μs, Φ_{ph} = 7.5 ± 0.5%). When excited at 420 nm (Soret and $\pi-\pi^*$ quinolinolate bands) the emission of **1a−d** is dominated by PtTPP phosphorescence while **1c−d** show <1% contribution from Alq₃ fluorescence ($\lambda_{max} \approx$ 540 nm). This behavior is consistent with nearly complete
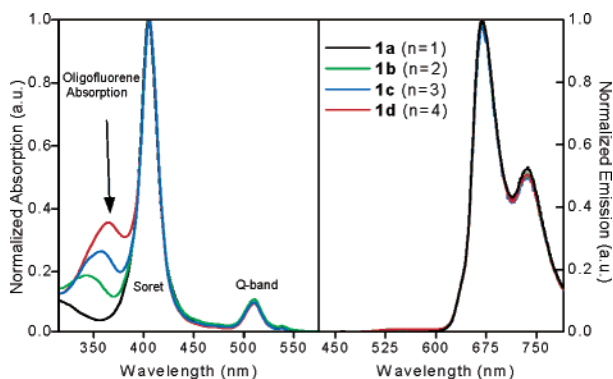
Figure 2. UV−vis absorption spectra of compounds **1a−d** and their corrected emission spectra when excited at 420 nm.
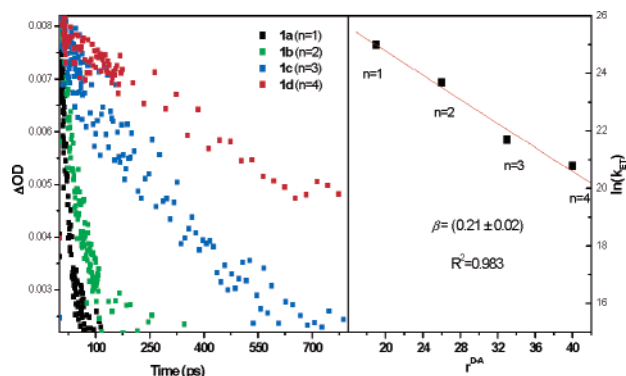

Figure 3. Transient absorption spectroscopy data (pumping at 475 nm): (left) decay traces of **1a−d** monitored at 520 nm showing ET from Alq₃− fluorene to PtTPP; (right) distance dependence of the energy transfer rate for **1a−d** used to calculate the distance-attenuation factor β.

energy transfer from Alq₃ to PtTPP even though the D−A distance considerably exceeds the Förster radius (24 Å).

To investigate the dynamics of the energy transfer we studied the triads **1a−d** using femtosecond transient absorption spectroscopy. Unfortunately, selective excitation of the Alq₃ moiety is not possible because of high absorption of PtTPP. However, excitation at 475 nm (mainly residual $\pi-\pi^*$ absorption of Alq₃) allowed us to monitor the disappearance of an absorption band from the Alq₃-fluorene singlet centered at 520 nm along with additional bleaching from the PtTPP ground-state Q-band.[20] The lifetime of the Alq₃-fluorene singlet ranged from 14 to 860 ps. The estimated rates of ET ¹(Alq₃-fluorene) to ¹PtTPP were (**1a**) 7.1×10^{10} s⁻¹; (**1b**) 1.9×10^{10} s⁻¹; (**1c**) 2.7×10^9 s⁻¹; (**1d**) 1.0×10^9 s⁻¹. The observed energy transfer rates are 2 orders of magnitude higher than the rates calculated from the Förster model for the D−A distances (19−40 Å), which indicates strong participation of the superexchange mechanism.

The exponential dependence of the energy transfer rate constant on the D−A distance yielded an attenuation factor β of 0.21 ± 0.02 Å⁻¹ (Figure 3), which is higher than β values ($\beta = 0.07−0.09$ Å⁻¹) observed for incoherent-wire behavior,[13b,15] yet significantly lower than values ($\beta = 0.32−0.66$ Å⁻¹) derived for superexchange in triads with *p*-phenylene or fluorene bridges. This observation is further confirmed by an experiment where excitation was performed at 340 nm ($\pi-\pi^*$ absorption of fluorene). We did not observe any transient absorption features attributable to fluorene models, which is consistent with the single Alq₃−F$_n$ fluorophore. Also, the dynamics were very similar to the ones observed upon excitation at 475 nm. We conclude that the triads **1a−d** display very fast energy transfer in the mixed incohererent wire/superexchange mechanism.
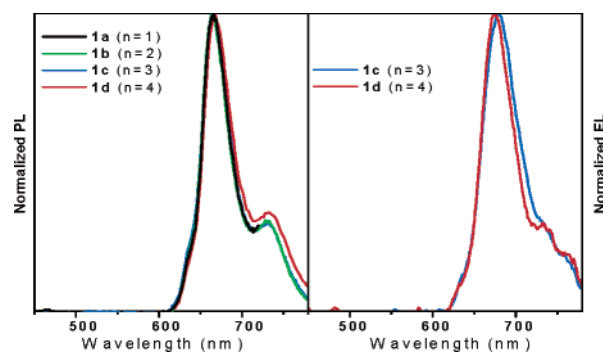

Figure 4. Uncorrected PL spectra of **1a−d** in thin films (1% w/w in polystyrene) and EL spectra of **1c−d** OLEDs.
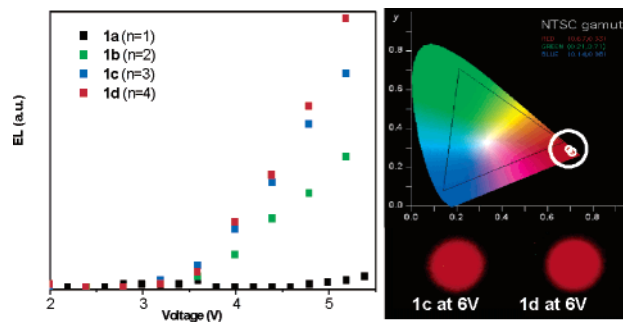

Figure 5. (left) Luminance curves of **1a−d** OLEDs; (right) chromacity diagram and CIE coordinates for the EL demonstrating their high color purity; (right bottom) **1d**-based OLED showing saturated red color.

In the transient spectroscopy experiments, the assignment of the lowest electronic state was supported by nanosecond UV−vis transient absorption spectroscopy, which showed no evidence of endothermic energy transfer[5] from the platinum porhyrin centers upon selective excitation of the Q-bands at 532 nm.[20] Although we were unable to either induce effective intersystem crossing (ISC) in the D−B section of the triad or selectively sensitize its triplet state to observe the triplet transfer processes by transient absorption spectroscopy, we believe that the energy transfer process described above indicates that the triplet transfer would exhibit similar wirelike behavior resulting in equally fast, or perhaps even faster, rates. This assertion is based on the following: first, in these rigidly linked D−B−A systems the superexchange mechanism is available for both singlet−singlet and triplet−triplet processes.[21] Thus, the incohererent wire/superexchange mechanism is also available for triplet excitons generated during the hole-electron recombination. Second, the delocalization of triplet excitons in conjugated materials is considered to be shorter than that of singlets,[10a] which puts more importance on the triplet energy alignment of the individual components. Triads **1c** and **1d** bearing terfluorene and quaterfluorene bridges show good alignment of the DBA triplet levels, which allows for the bridge-mediated hopping mechanism of energy transfer.[15] This hypothesis was further supported by the data obtained from OLEDs fabricated using triads **1a−d**.

The materials **1a−d** were incorporated as emitter and electron-transport layer (ETL) into simple unoptimized double-layer OLEDs (ITO/PEDOT:PSS/**1a−d**/CsF:Al)[20] fabricated by solution processing. All four OLEDs afforded saturated red color almost identical to the emission from thin films (Figure 4).

The OLEDs showed pure red (CIE X, Y: 0.706, 0.277) emission demonstrating effective energy transfer taking place in the emissive layer comprised of **1a−d** (Figure 5, right).

Remarkably, the turn-on voltages as well as the maximum external quantum efficiencies were found to be highly dependent

Table 1. Triplet Energy of the Bridge (E_T),[17] Turn-on Voltages ($V_{turn-on}$), and Quantum Efficiency (η_{Max}) Values for OLEDs Fabricated Using **1a**–**d**[2] [a]

compound	$E_T \pm 0.10$ (eV)	$V_{turn-on}$ (V)[b]	η_{max} (%)[c]
1a	2.86	10.0	0.012
1b	2.43	4.3	0.039
1c	2.25	3.9	0.131
1d	2.18	3.9	0.204

[a] The performance of the OLEDs using **1c**–**d** improves with better triplet energy alignment of the components. [b] Defined as the bias needed to obtain a luminance of >0.2 cd/m^2. [c] External maximum efficiency of the diodes.[22]
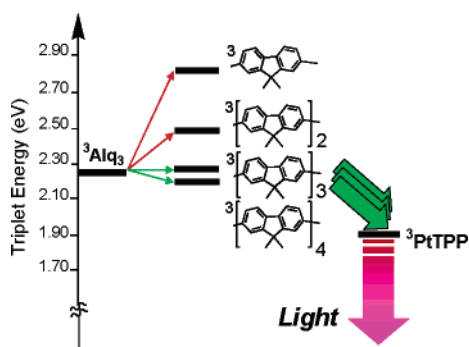

Figure 6. Schematic triplet energy alignment in materials **1a**–**d**.

on the structure and alignment of the triplet energies of the components of the emissive materials (Table 1). Thus **1a**, with the poorest alignment of the ^{3}donor–^{3}bridge–^{3}acceptor levels, requires the highest driving voltage and shows the lowest efficacy (η_{max}) of the electron-to-photon conversion. In the materials **1c**–**d** with longer oligofluorenes, turn-on voltages as low as 3.9 V were observed. Also, the quantum efficiency (η_{max}) was found to be an order of a magnitude better in materials **1c**–**d** with good triplet level alignment than that from compounds bearing shorter fluorene bridges (**1a**–**b**) (Table 1). Significantly higher luminance is obtained from optimized devices with advanced architectures, particularly when a hole-blocking layer is employed. Here, we prefer simple double-layer devices because the observed effects are easier to attribute to the effective energy transfer.

The trend in the electroluminescence performance is attributed to the stepwise decrease in the triplet energy of the oligofluorene moiety as the bridge length increases.[17] As depicted in Figure 6, the triplet energies for fluorene and bifluorene are higher than that of Alq$_3$, thereby acting as a barrier for the triplet–triplet energy transfer. In contrast, the triplet levels from terfluorene and quaterfluorene are situated closer to the triplet level of Alq$_3$ facilitating the exchange to the incoherent hopping mechanism for triplet–triplet energy transfer,[15] as the data from femtosecond transient spectroscopy suggest. Hence, the better device performance for **1c**–**d** agrees with effective intramolecular triplet energy transfer at long distances mediated by the wirelike mechanism.[23]

In conclusion, a series of multichromophoric emitters designed to study energy level/distance-dependence in energy transfer were prepared and their photophysical properties studied both in solution and in the solid state. The materials show effective singlet and triplet energy transfer. An improved OLED output was obtained for systems having longer oligofluorene bridges, which showed better alignment of triplet energy levels despite the longer donor–acceptor distance. In the OLEDs, the order of a magnitude increase in efficacy for materials with better triplet level alignment appears to be due to facile triplet energy transfer. The materials exhibit red

emission with high color purity. To the best of our knowledge this is the first example of molecular wire behavior demonstrated to take place in solid state and in functional OLEDs.

Note Added after ASAP Publication: In the version published on the Internet August 31, 2006, there were formatting errors in the Supporting Information on pages 26 and 29. The final version published September 1, 2006, and the print version are correct.

Supporting Information Available: Procedures and characterization of compounds **1a**–**d** and synthetic precursors. Additional transient spectra, lifetime fits, and construction of the OLEDs. This information is available free of charge at http://pubs.acs.org

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(23) We believe that the external quantum efficacy and the higher luminance in **1c**–**d** were not due to intermolecular energy transfer. In fact, the dilute-solution, thin film PL and EL were very similar, suggesting that no strong intermolecular interaction takes place.

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