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Ultrafast Dynamics of Triplet Excitons in Alq₃-Bridge-Pt(II)porphyrin Electroluminescent Materials

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Achieving control over the dynamics and migration of excited states is crucial for maximizing the performance of both small-molecule- and polymer-based organic light-emitting diodes (OLEDs).[1] Since triplets and singlets are generated by electron—hole recombination in a 3:1 ratio,[2] utilizing triplet excited states in radiative processes is of utmost importance and the ability to harvest the energy of triplet excited states is important for obtaining the maximum light output in OLEDs.[3] The triplet energy of organic hosts (donor, D) may be harvested by a phosphorescent dopant acceptor (A) dispersed in a host. While the dispersion of a dopant in a host is easy to do, potential phase separation during deposition may result in uneven distribution of the donor—acceptor (D-A) distances and diminished light output from the device.[4]

This may be circumvented in materials with a donor and acceptor connected in defined distances, shown recently in donor—bridge—acceptor (D−B−A) electroluminescent materials.[5] The efficacy of the triplet-energy transfer depends on the triplet-energy levels alignment of the components. In systems with $^3D > {}^3B > {}^3A$, an efficient exothermic intramolecular triplet-energy transfer takes place via a molecular wire mechanism[6] resulting in improved OLED efficiency.[5] On the other hand, an endothermic triplet-energy back transfer from phosphorescent acceptor centers to low-lying triplets of a bridge or host (A → B) can substantially reduce the electroluminescence (EL) efficiency.[7] Evaluating the extent of a triplet-energy transfer mechanism in detail and its effect on the EL is necessary for designing highly efficient D−B−A OLED materials. Alas, observing the dynamics of triplet-energy transfer is often precluded by low efficiency of the intersystem crossing (ISC) compared to competing fluorescence, nonradiative decay, singlet energy transfer, or electron transfer.[8]

To understand the dynamics of the triplets in D−B−A materials and its effect on the OLED performance, we designed multichromophoric systems 1a−d (Figure 1) comprising Alq₃ and PtTPP as the donor—acceptor pair connected by bridges of varying triplet energy ($^3Alq_3 = 2.15$ eV, $^3PtTPP = 1.89$ eV, $^3B = 1.86-2.18$ eV).[9] Triplet transfer from Alq₃ to the oligofluorene (F_n) bridge was observed directly on a dyad model (Alq₃-F_n) at 77 K upon selective excitation of Alq₃ $\pi-\pi^*$ absorption at 450 nm. The photoluminescence spectra revealed a fluorene-type ($^{0-0}T_1-S_0 = 2.18$ eV, $\tau = 214 \pm 16$ ms) and Alq₃-type phosphorescence ($^{0-0}T_1-S_0 = 2.15$ eV, $\tau = 33.2 \pm 0.5$ ms).[9] This suggested effective donor-to-bridge ($^3D \rightarrow {}^3B$) triplet transfer. We assumed that the $^3D \rightarrow {}^3B$ triplet transfer would be equally or more efficient in 1a−d with equal or lower bridge triplet-energy levels ($k_{TTET} \approx 10^{11}$ s^{-1}).

The triplet transfer between the bridge and phosphorescent acceptor ($^3B \rightarrow {}^3A$) was investigated by time-resolved photoluminescence (PL) and femtosecond transient spectroscopy. The excitation of the PtTPP (ISC ≈ 1 ps)[10] allowed for examining the ultrafast
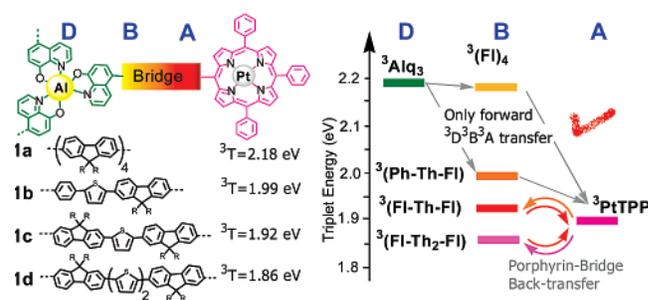

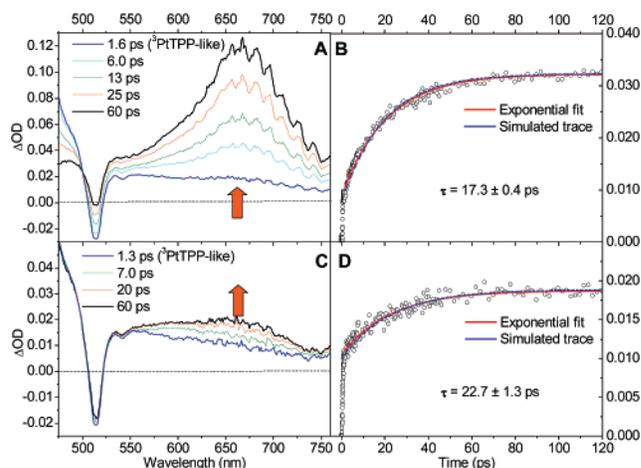**Figure 1.** Structure of triads 1a−d and their triplet energies.

Figure 2. (A) Transient spectral evolution of 1d upon excitation at 510 nm; (B) kinetic trace monitored at 750 nm indicating the ultrafast appearance of the new absorption band of bridge triplet; (C) transient evolution of 1c excited at 510 nm; (D) kinetic trace at 670 nm indicating the ultrafast appearance of the new absorption band of bridge triplet.

dynamics of triplet excited states. The PL studies of 1a−b revealed that the triplet state of the metalloporphyrins exhibit the usual quantum yield and lifetime ($\Phi_{ph} = 8.1\%$, $\tau = 41.9 \pm 0.2$ μs).[5] This is explained by the fact that triplet-energy levels of the bridges lie significantly higher ($^3E = 2.18$, 1.99 eV) than those of PtTPP, thus preventing endothermic energy back-transfer. In contradistinction, 1d shows lower triplet energy of the bridge ($E_T = 1.86$ eV) and diminished emission ($\Phi_{ph} = 0.3\%$), even though it displays typical PtTPP-based PL spectra ($\lambda_{max} = 670$ and 740 nm). Upon selective excitation of PtTPP at 510 nm,[11] the femtosecond transient spectra of 1d showed the features associated with ^{3}PtTPP to be rapidly replaced by a broad transient at 600−750 nm assigned to the triplet state of the bridge (Figure 2).[9] The spectral evolution was fitted to a single-exponential lifetime of $\tau = 17.3 \pm 0.4$ ps attributed to ultrafast triplet states equilibration between the porphyrin and the bridge.

Interestingly, 1c displayed borderline behavior between 1a−b and 1d. Thus, 1c showed similar steady-state emission properties

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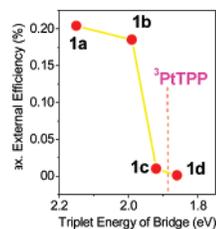
Table 1. Calculated Rate Constants for the Exothermic and Endothermic Triplet-Energy Transfers[9]

compd	k_{obs} (s^{-1})	$k_{exothermic}$ (s^{-1})	$k_{endothermic}$ (s^{-1})
1c	4.41×10^{10}	4.01×10^{10}	3.91×10^{9}
1d	5.78×10^{10}	5.61×10^{10}	1.73×10^{9}

Table 2. Quantum Efficiency Values for OLEDs Fabricated Using **1a**−**d**

OLED	$E_T{}^a$	η_{max} (%)^b
1a	2.18	0.208
1b	1.99	0.180
1c	1.92	0.007
1d	1.86	0.001

^{a} Triplet energy of the conjugated bridge. ^{b} Maximum external efficiency of the OLED.

to those of **1a**−**b** ($\tau = 40.3 \pm 0.3$ μs, $\Phi_{ph} = 7.1\%$), but rapid appearance of an additional absorption band centered at 650 nm was also observed in the femtosecond experiment (Figure 2). On the basis of model experiments, this band was assigned to the triplet state of the bridge populated by endothermic energy transfer from the porphyrin. The transient evolution was fitted to a single-exponential lifetime of $\tau = 22.7 \pm 1.3$ ps, which also corresponds to equilibration of the triplet excited states. From the rate constants of **1c**−**d** equilibration the rates of energy transfer for exothermic and endothermic processes were calculated (Table 1).[9] In both cases, ultrafast energy transfer rates were determined for the exothermic triplet-energy transfer processes ($k_{TTET} = (4-6) \times 10^{10}$ s^{-1}) providing a clear proof of excellent electronic communication that takes place in the triplet-energy transfer in **1a**−**d** triads.

From the perspective of triplet-energy transfer alone, the EL performance of **1a**−**d** was expected to follow the **1a** $\approx$ **1b** > **1c** > **1d** order. Although in **1c** the endothermic energy transfer from PtTPP to the bridge is relatively inefficient (<10%),[9] it does open a potential deactivation pathway during the OLEDs operation. Similarly, the EL of **1d** was expected to be even lower compared to **1c**. To explore the effect of the triplet dynamics on the electroluminescent performance, **1a**−**d** were incorporated as an emitter and electron-transport layer into simple double-layer spincast OLEDs (ITO/PEDOT:PSS/**1a**−**d**/CsF:Al). The **1a**−**d** OLEDs afforded similar EL spectra, but strikingly different outputs quantified as electron-to-photon efficiency (η_{max}) (Table 2). OLEDs based on **1a**−**b** with high triplet energy of the bridge displayed the highest EL efficacy (η_{max}) in accordance with facile exothermic triplet-energy transfer to PtTPP. For **1c**, however, a significant drop in η_{max} was observed and even more so in the case of **1d** OLED. We attribute the unexpected drop in the device efficiency in **1c** to ^{3}PtTPP → ^{3}bridge back-energy transfer becoming more dominant in the solid state. The higher degree of quenching in the solid state is presumed to be due to the more planar conformations enforced for the D−B−A triads, which would result in slightly lower triplet levels of the conjugated bridges.[12] Conversely, in a fluid solution a high degree of molecular motion in the bridge induces conformational gating effects precluding back-energy transfer observed in the solid films.[13]

In conclusion, a series of multichromophoric emitters were prepared to study the dynamics of triplet excited states and their influence on the electroluminescent behavior. The exothermicity of the forward donor-to-bridge triplet transfer appears to be a less stringent requirement, as even the almost isoenergetic Alq$_3$ and

quaterfluorene bridge in **1a** show facile triplet transfer and electroluminescence. Similarly to electron-transfer processes, approximate matching between the energy levels of the donor and the bridge is crucial for promoting the molecular wire behavior.[14] Also, ultrafast rates for exothermic intramolecular triplet-energy transfer between the bridge and phosphorescent acceptor were observed ($k_{TTET} = (4-6) \times 10^{10}$ s^{-1}). Finally, endothermic energy transfer was also observed to occur, albeit at a slower rate. Although the extent of endothermic energy transfer was limited to a few percent in solution for **1c**, a substantial decrease was observed in the electroluminescence efficacy. We conclude that the triplet exciton dynamics dominates the electroluminescence properties of conjugated D−B−A materials. The triplet-energy transfer operates on an ultrafast time scale and requires careful energy alignment of the components ($^3\Delta E_{D-B} \approx {}^3\Delta E_{B-A} \geq 0.1$ eV) to prevent endothermic energy transfer and severe quenching of the electroluminescence. To the best of our knowledge, this is the first time triplet dynamics were directly observed in donor−acceptor electroluminescent materials and direct connection to device efficiency was established. We believe that the outlined design concepts are general and could be utilized in the development of highly efficient OLEDs.

Supporting Information Available: Synthesis and characterization of compounds **1a**−**d**, their spectroscopic properties, energy-transfer rates measurements, and construction of the OLEDs. This material is available free of charge via the Internet at http://pubs.acs.org.

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