Ultrafast Dynamics Of Triplet Excitons In Alq(3)-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). Since triplets and singlets are generated by electron–hole recombination in a 3:1 ratio, 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. 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.

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. The efficacy of the triplet-energy transfer depends on the triplet-energy levels alignment of the components. In systems with D > B > A, an efficient exothermic intramolecular triplet-energy transfer takes place via a molecular wire mechanism resulting in improved OLED efficiency. 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. 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.

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 (1Alq3 = 2.15 eV, 1PtTPP = 1.89 eV, 1B = 1.86–2.18 eV). Triplet transfer from Alq3 to the oligofluorene (F2) bridge was observed directly on a dyad model (Alq3-F2) at 77 K upon selective excitation of Alq3, π–π* absorption at 450 nm. The photoluminescence spectra revealed a fluorene-type (0 → 1 F2) at 2.18 eV, ρ = 214 ± 16 ms) and Alq3-type phosphorescence (0 → 3 Alq3 = 1.86 eV, τ = 33.2 ± 0.5 ms). This suggested effective donor-to-bridge (D → B) triplet transfer. We assumed that the 3D → 3B triplet transfer would be equally or more efficient in 1a-d with equal or lower bridge triplet-energy levels (kTTR = 1011 s⁻¹).

The triplet transfer between the bridge and phosphorescent acceptor (B → A) was investigated by time-resolved photoluminescence (PL) and femtosecond transient spectroscopy. The excitation of the PtTPP (ISC ≈ 1 ps) allowed for examining the ultrafast 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 (Φβ = 81.1%, τ = 41.9 ± 0.2 μs). This is explained by the fact that triplet-energy levels of the bridges lie significantly higher (E = 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 = 1.86 eV) and diminished emission (Φβ = 0.3%), even though it displays typical PtTPP-based PL spectra (λmax = 670 and 740 nm). Upon selective excitation of PtTPP at 510 nm, the femtosecond transient spectra of 1d showed the features associated with PtTPP to be rapidly replaced by a broad transient at 600–750 nm assigned to the triplet state of the bridge (Figure 2). The spectral evolution was fitted to a single-exponential lifetime of τ = 17.3 ± 0.4 ps attributed to ultrafast triplet state 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.
The higher degree of quenching in the solid state is presumed to be due to the more planar conformations enforced for the D bridge is crucial for promoting the molecular wire behavior. However, a significant drop in the device efficiency in the solid state is observed, 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 efficiency. We conclude that the triplet excitation 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 ($\Delta E_{B-D} \approx \Delta E_{A-B} \geq 0.1$ eV) to prevent endothermic energy transfer and severe quenching of the electroluminescence.

References


[9] For more details see Supporting Information.


JA073491X

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

<table>
<thead>
<tr>
<th>compd</th>
<th>$k_{ex}$ (s$^{-1}$)</th>
<th>$k_{therm}$ (s$^{-1}$)</th>
<th>$k_{therm}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>$4.41 \times 10^{10}$</td>
<td>$4.01 \times 10^{10}$</td>
<td>$3.91 \times 10^{9}$</td>
</tr>
<tr>
<td>1d</td>
<td>$5.78 \times 10^{10}$</td>
<td>$5.61 \times 10^{9}$</td>
<td>$1.73 \times 10^{9}$</td>
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</tbody>
</table>

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

<table>
<thead>
<tr>
<th>OLED</th>
<th>$\eta_{max}$ (%)</th>
<th>$\eta_{max}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2.18 0.208</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>1.99 0.180</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>1.92 0.007</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>1.86 0.001</td>
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</tr>
</tbody>
</table>

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