BODIPY star-shaped molecules as solid state colour converters for visible light communications


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Y2: 350, 477, and 625 nm for Y3; and 366, 480, and 625 nm for Y4. The absorption band below 400 nm is attributed to the fluorene arms and increases in intensity with the arm length. Y1 has a peak in absorption at 450 nm matching well the emission of the blue LEDs used for lighting, and this feature shifts slightly to longer wavelengths for longer arms as seen in Figure 1. The peak emission wavelengths were in the red region of the spectrum, 663, 679, 682, and 682 nm for Y1, Y2, Y3, and Y4, respectively. The red PL emission comes from an extended conjugation across the BODIPY core and adjacent fluorene units as has been described previously.24 The bathochromic shift from Y1 to Y2 is also evident in solution23,24 and indicates that there is a further delocalisation of the excited state across the BODIPY and neighbouring fluorene units.

Time-resolved fluorescence measurements were conducted using the time correlated single photon counting (TCSPC) technique, exciting the materials at 375 nm and detecting at the corresponding peak PL wavelengths. The 375 nm excitation is absorbed by the oligofluorene arms, and results in a fast energy transfer to the emitting state that is delocalised across the BODIPY core. The energy transfer is very fast and cannot be resolved by the TCSPC apparatus. The resulting PL dynamics are shown in Figure 2 and have bi-exponential decays. The lifetime values are given in Table I for the nanosecond range and show Y3 having the shortest average decay. The PLQY of the films also differ, showing lower values compared to solutions. In films, the PLQY values range from 22% to 56%, whereas in solution form they were previously measured to be 55%–62%.23

Films of Y3 were selected for bandwidth and data transmission measurements as they have the shortest lifetime and high PLQY. Samples were encapsulated under glass using the UV cured epoxy NORLAND 68 on top of the BODIPY Y3 film. UV curing was performed with an 8 W lamp at 365 nm for 1.5 min. The encapsulation process was conducted in a nitrogen-filled glove box which had a controlled and inert atmosphere to avoid exposure to water and oxygen molecules, thus reducing photo-oxidation effects during measurements. The photophysical properties of Y3 were not changed by the encapsulation process.

The capacity of the data link scales with its modulation bandwidth. To assess the bandwidth of Y3, the experimental setup presented in Figure 3(b) was used. The fast (broad bandwidth) excitation source and detector used were a diode laser emitting at 450 nm and an avalanche photodiode. To eliminate any residual excitation light at the detector, a reflectance geometry was adopted in combination with a suitable long-pass dichroic filter. The excitation source was driven by an amplified sinusoidal voltage generated by the network

![FIG. 1. (a) Molecular structure. (b) Absorption and emission spectra of Y-BODIPY films.](image1)

![FIG. 2. Time-resolved fluorescence measurements of Y-BODIPY films (black) and their fit (red) with the instrument response function (dashed line).](image2)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PLQY (%)</th>
<th>$A_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_{av}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1</td>
<td>22.4</td>
<td>0.44</td>
<td>2.35</td>
<td>0.56</td>
<td>5.3</td>
<td>4</td>
</tr>
<tr>
<td>Y2</td>
<td>55.9</td>
<td>0.53</td>
<td>5.87</td>
<td>0.47</td>
<td>10.72</td>
<td>8.2</td>
</tr>
<tr>
<td>Y3</td>
<td>40.6</td>
<td>0.48</td>
<td>1.9</td>
<td>0.52</td>
<td>4.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Y4</td>
<td>49.2</td>
<td>0.26</td>
<td>2.07</td>
<td>0.74</td>
<td>5.08</td>
<td>4.3</td>
</tr>
</tbody>
</table>
an analyser; this was combined with a DC voltage from a power source using a bias-T. The signal received from the avalanche photodiode (APD) was recorded by the network analyser. To measure the bandwidth of the system, the AC amplitude of the received signal was recorded as a function of the modulation frequency. To factor out the bandwidth contribution of the different components of the experimental setup, first the bandwidth of the measuring system was evaluated by directing the excitation light into the detector. This bandwidth was subsequently subtracted by the network analyser from the recorded bandwidth spectrum for the material. Figure 3(a) shows the results of the bandwidth measurement of the Y3 BODIPY as well as, for comparison, the bandwidth of a commercial phosphor plate CL-840 (Intematix ChromaLit). It is evident in Figure 3 that the BODIPY material has a much higher −3 dB bandwidth (75.5 MHz) than that of the phosphor (5 MHz). The Y3 film bandwidth is also twice that measured with the same material in solution.

The data transfer capabilities were also studied using the same setup as for the bandwidth measurements. The excitation laser was modulated in intensity using a binary On-Off Keying (OOK)26 modulation scheme, i.e., a binary “one” was represented by a light pulse of duration 1/Rb, where Rb is the data rate and a “zero” was represented by the absence of the pulse. At the receiver, a simple threshold decoding was used in which the received signal was compared against a fixed threshold level based on the expected signal level for “zero” and “one.” If the received signal was above the threshold level, it was assumed to be “one,” otherwise “zero.” Figure 4 shows the measured bit error rate (BER) as a function of transmitted data rate for OOK modulation. The measurements were taken using a pseudorandom binary sequence (PRBS) of 214−1, of which ~82,000 bits were analysed at the receiver for errors. Hence, the minimum BER level is limited to 10−4 to have statistically high confidence level. By considering the forward error correction (FEC) floor of 3.8 × 10−3 (as recommended by the International Telecommunication Union (ITU) standard), a data rate of 370 Mb/s was achieved which is 4 times higher than previously reported for BODIPY colour convertors in solution.

To summarise, BODIPY-cored oligofluorene star-shaped conjugated systems have been studied in the solid state to establish their feasibility as a red colour converter for VLC applications. The solid-state films exhibit PL lifetimes shorter than their solution based counterparts and therefore result in a higher bandwidth, for Y3, of 73 MHz and a data transmission rate of 370 Mb/s, which are, respectively, two and four times higher than measured for Y3 in solution. This bandwidth is 16 times higher than common commercially available phosphors and shows that these organic materials are promising as colour convertors for VLC.

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