

# A novel fast color-converter for visible light communication using a blend of conjugated polymers

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**Abstract:** Visible Light Communications (VLC) is a promising new technology which could offer higher data transmission rates than existing broadband RF/microwave wireless technologies. In this paper, we show that a blend of semiconducting polymers can be used to make a broadband, balanced color converter with a very high modulation bandwidth to replace commercial phosphors in hybrid LEDs for visible light communications. The resulting color converter exploits partial Förster energy transfer in a blend of the highly fluorescent green emitter BBEHP-PPV and orange-red emitting MEH-PPV. We quantify the efficiency of the photoinduced energy transfer from BBEHP-PPV to MEH-PPV, and demonstrate modulation bandwidths (electrical-electrical) of  $\sim 200$  MHz, which are 40 times higher than commercially available phosphor LEDs. Furthermore, the VLC data rate achieved with this blend using On-Off Keying (OOK) is many times ( $\sim 35$ ) higher than that measured with a commercially available phosphor color converter.

**Keywords:** organic semiconductor, color converter, energy transfer, solid-state lighting, LED

Increasing user demand for fast wireless data communications is placing pressure on the existing broadband RF/microwave wireless technologies, which have limited bandwidth (BW) and a congested spectrum. The application of advanced materials for solid-state lighting may offer a solution to this problem through the emergent field of Visible Light

Communications (VLC), which uses LEDs for both illumination and wireless data transfer.<sup>1-4</sup> The main motivations for this technology include the increasing use and performance of solid-state lighting, its potential for a dual use as a high data rate transmitter, and the ability to access 100s THz of additional unregulated bandwidth for wireless communications.<sup>5</sup> While the spectral range of choice for optical fibre communications is in the near infrared at 1.5  $\mu\text{m}$  (to match the transmission window of silica fibres) for free space data communications, the use of visible light has inherent advantages for simple user alignment of the data link and secure knowledge of where the data has been transmitted. The most common efficient approach for LED illumination is to use phosphor converted white LEDs (pcLEDs).<sup>6-7</sup> In this approach a blue InGaN LED is coated with a yellow phosphor so that a fraction of the blue light is absorbed and re-emitted at longer wavelengths to give a two-color white. While acceptable for illumination, the phosphor materials in pcLEDs are a well-known bottle-neck for VLC.<sup>2-3</sup> This is due to their long photoluminescence (PL) lifetime which limits the intrinsic system bandwidth to a few MHz. Even the introduction of a blue filter at the receiver which suppresses the yellow emission,<sup>8</sup> or the use of pre-equalization techniques,<sup>9</sup> only leads to modest improvements in the modulation bandwidth ( $\sim 30$  MHz). To overcome this limitation, and permit ultra-high modulation bandwidths new materials for color converters are required which have shorter radiative lifetimes.

Organic semiconductors are an exciting alternative candidate for VLC color converters due to their visible band gaps, high radiative rates and photoluminescence quantum yield (PLQY), and their scope for simple integration with nitride semiconductors.<sup>10-14</sup> Organic down-converter materials have previously been used with blue-emitting inorganic LEDs to generate white light.<sup>10, 12-15</sup> We recently demonstrated the use of a yellow-emitting organic semiconductor as a high bandwidth material for a two-color white VLC datalink.<sup>10</sup> However this two-color cool white transmitter had a low color-rendering index (CRI) of only 53; to

combine high quality white color rendering with data transmission, better color converter materials with high brightness, short radiative lifetime and PL throughout the green and red regions are needed. Among the existing red-emitting organic materials, there are not suitable candidates that combine high PLQY with very short (sub nanosecond) PL lifetime and strong absorption in the blue region. Therefore, an efficient green-emitting material is desirable which absorbs the blue light of the LED and transfers part of its energy to the red-emitting material.

In this paper, we report a study of blends of highly fluorescent green emitting poly[2,5-bis(2',5'-bis(2''-ethylhexyloxy)phenyl)-p-phenylenevinylene] (BBEHP-PPV)<sup>16</sup> and orange-red emitting poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) as novel fast color-converters to replace commercial phosphors in hybrid LEDs for visible light communication. We found a partial Förster energy transfer from green-emitting BBEHP-PPV to orange-red emitting MEH-PPV and quantify this efficiency of the photoinduced energy transfer using PL lifetimes. Furthermore we demonstrate capabilities of this blend for VLC by measuring its modulation bandwidth and data rate. The achieved 3 dB modulation bandwidth (electrical-electrical) is 40 times higher than commercially available phosphor LEDs, and 5 times higher than previously reported red-emitting organic color converters.<sup>11</sup> Similarly the achieved VLC data transmission rate of 350 Mbits/s with this blend using On-Off Keying (OOK) is significantly (35 times) higher than that measured with a commercially available phosphor color converter.

BBEHP-PPV<sup>16</sup> is a highly efficient fluorescent green polymer used previously for LEDs,<sup>17</sup> lasers<sup>16, 18</sup> and explosive sensors.<sup>16, 19</sup> It absorbs strongly around 450 nm and is therefore an attractive candidate to be integrated with efficient blue emitting GaN LEDs. MEH-PPV is a prototypical orange-red emitting polymer widely used for organic LEDs (OLEDs),<sup>20-23</sup> field effect transistors,<sup>24</sup> photovoltaics,<sup>25-30</sup> printed electronics<sup>31-32</sup> and organic

lasers.<sup>33-35</sup> MEH-PPV has a short PL lifetime ( $\sim 400$  ps), absorption overlapping with the emission spectrum of BBEHP-PPV, and PL in the orange-red region.

The photophysical properties of films of BBEHP-PPV, MEH-PPV and blends of the two were investigated by measuring UV-Vis absorption, photoluminescence (PL), PLQY and PL lifetime. Typical absorption and PL spectra of BBEHP-PPV, MEH-PPV and their blends are shown in **Figure 1(b) and 1(c)**. BBEHP-PPV has a single broad absorption peak at 435 nm and two distinguishable PL peaks at around 497 (0-0) and 532 nm (0-1) with a shoulder around 580 nm,<sup>18</sup> while MEH-PPV has a absorption peak at 500 nm and emission peaks at 587 nm (0-0) and 640 nm (0-1). The solid-state PLQY was measured using excitation wavelengths of 450 and 500 nm; the values obtained are given in **Table 1**. MEH-PPV has a PLQY of  $\sim 17\%$ ; the PLQY of BBEHP-PPV is  $\geq 75\%$ , making it one of the most highly efficient green-emitting semiconducting polymers. The PL lifetimes of films were measured by exciting MEH-PPV at 470 nm and BBEHP-PPV at 379 nm, and the PL decay was measured using detection wavelengths of 496 and 595 nm for BBEHP-PPV and MEH-PPV respectively. The resulting PL decays are shown in Figure 1(d) and 1(e). Lifetimes (to  $1/e$  of the initial value) of 380 ps and 825 ps were obtained for neat films of MEH-PPV and BBEHP-PPV respectively. These lifetimes are much shorter than commercially available phosphors, recently reported red-emitting BODIPY color convertors,<sup>11</sup> and other previously reported organic luminescent color converter materials.<sup>15</sup>

We next blended the two materials in ratios of BBEHP-PPV: MEH-PPV (90:10, 75:25) and investigated the energy transfer from BBEHP-PPV to MEH-PPV. The absorption spectra of the blends (Figure 1(b)) in both cases have a strong peak around 435 nm (BBEHP-PPV) and a relatively weak peak around 535 nm (MEH-PPV). The PL spectra of the blends are a combination of those of the two materials, and are very broad ranging from 470 to 800 nm (Figure 1(c)). In order to obtain more information about the energy transfer, we calculated the

relative contribution of the two materials in absorption and emission spectra. We found that in the 90:10 blend, 18% of the 450 nm excitation light is absorbed by MEH-PPV, whereas 52% of the photons are emitted from MEH-PPV (detail given in supplementary information). Similarly for the 75:25 blend, 37% light is absorbed and 66% is emitted by MEH-PPV (details given in supplementary information). These indicate that an energy transfer process occurs between the materials.

Confirmation of the energy transfer process was obtained by time-resolved measurements. The PL decays of BBEHP-PPV (measured at 496 nm) for a neat film and for the blends are shown in Figure 1 (d). The blends show a faster PL decay at 496 nm (1/e lifetime of 269 and 278 ps obtained for 75:25 and 90:10 blends) compared to neat BBEHP-PPV (~ 825 ps), confirming that there is a non-radiative energy transfer from BBEHP-PPV to MEH-PPV. The emission of the blend at 595 nm (due to MEH-PPV) is similar to neat MEH-PPV for the first few ns, and slightly longer-lived thereafter (see Figure 1(e)). In order to quantify the energy transfer, we calculated the energy transfer rate  $k_{et}$  and efficiency  $\eta_{et}$  by comparing the decays of neat BBEHP-PPV and BBEHP-PPV in the blend (Figure 1 (d)) using equations 1 and 2<sup>36-38</sup>

$$k_{et} = \frac{1}{\tau_{\text{BBEHP-PPV}}(\text{blend})} - \frac{1}{\tau_{\text{BBEHP-PPV}}(\text{neat})} \quad (1)$$

$$\eta_{et} = 1 - \frac{\tau_{\text{BBEHP-PPV}}(\text{blend})}{\tau_{\text{BBEHP-PPV}}(\text{neat})} \quad (2)$$

where  $\tau_{\text{BBEHP-PPV}}(\text{neat})$  and  $\tau_{\text{BBEHP-PPV}}(\text{blend})$  are measured lifetimes of neat BBEHP-PPV and BBEHP-PPV in blend respectively. The values of the energy transfer rate  $k_{et}$  and

efficiency  $\eta_{et}$  for both blends are given in Table 1. The energy transfer efficiency from BBEHP-PPV to MEH-PPV for both blends was similar (Table 1). This indicates that the increased red emission from the 25% MEH-PPV blend arises from a higher direct absorption in MEH-PPV.

The significant absorption at 450 nm and broader PL emission than commercial LED phosphors (e.g. phosphor CL-840 (Intermatix ChromaLit<sup>TM</sup>), see Figure S2 in supplementary information) make the polymer blends an attractive candidate for generating high quality white light for VLC. To assess their potential for white light generation, we calculated the CIE coordinates of the color converter blends (given in Table 1), which are plotted in Figure 2. For comparison, we also plot CIE coordinates of neat BBEHP-PPV, neat MEH-PPV, previously reported Super Yellow (SY) color converter,<sup>10</sup> a blue LED and the commercial phosphor (CL-840). The tricolor combination of LED, BBEHP-PPV and MEH-PPV provides a wide gamut suitable for good color rendering, and the 90:10 and 75:25 blends are very suitable for color conversion to generate white light. For example, when mixed with the 450 nm peak emission from a nitride LED to generate white light (at a correlated color temperature of 6337 K) the color rendering index (CRI) would be 76, a value much higher than the CRI of 53 for the fast two-color white VLC transmitter in reference 10, and comparable with a CRI of 80 for the CL840 phosphor. The CRI value of the polymer blend is also similar to reported values for organic down-converters, but with significantly shorter PL lifetime.<sup>15, 39</sup>

Indeed, the sub-nanosecond lifetime of the blend indicates the great potential of the material for a high modulation bandwidth. This is important for VLC because the capacity of a communication channel is proportional to its bandwidth<sup>40</sup> and modulation bandwidth depends on excited state lifetime of the material. For experimental demonstration of the VLC

capabilities of the blends, color converter films were spin-coated on a glass substrate for BBEHP-PPV:MEH-PPV (100:0, 90:10 and 75:25) blend ratios. The intrinsic modulation bandwidths of the films were determined following a similar experimental procedure to that reported previously,<sup>11</sup> by measuring their response to a small signal modulation of the excitation. Figure 3 shows that the achieved bandwidth is more than 200 MHz for all three films, which is significantly higher than the commercial phosphor,<sup>8-9</sup> previously reported organic semiconductors<sup>10-11</sup> and blue LEDs<sup>41</sup> used in VLC.

A collimated-beam free space VLC data link was next tested using a laser diode excitation source with on-off keying (OOK) modulation.<sup>4, 11</sup> For the receiver an avalanche photodiode (APD) was used. The inset of Figure 4 shows an eye diagram for the color converted data link operating at 250 Mb/s. The open eyes show that the difference between zero and one bits is clearly resolved at this data rate for each color converter blend. The recorded bit error rates (BER) using a stream of  $10^5$  data bits, (randomly chosen 1 or 0), for different data rates are presented in Figure 4. The achieved data rates using a simple threshold detection (without any equaliser), are more than 350 Mb/s over a proof-of-principle distance of 5 cm which is 3 times higher than previously reported for OOK with an oligofluorene-BODIPY organic semiconductor.<sup>11</sup> We also note that the data rates for the polymer blends is higher than for BBEHP-PPV alone (see Figure 4).

To clearly demonstrate the advantage of the organic semiconductor color converters over conventional LED phosphors, the bandwidth and data rate of the commercial phosphor CL-840 was also measured in the link, giving values of 5 MHz and  $\sim 10$  Mbits/s respectively (Figure 3 and Figure 4). The polymer blend color converters therefore have a bandwidth of 40 times that of the phosphor, and a data rate 35 times higher in this case. We note that the length of data pattern used in our measurement is too short to prove definitively error-free

communication, but nonetheless the results strongly demonstrate the considerable improvement of the blend over conventional phosphor color converter.

In conclusion, we have demonstrated the use of organic semiconductors as a fast color-converter in hybrid LEDs for visible light communications. We show that a blend of green and orange-red semiconducting polymers is an attractive new material to replace commercial phosphors for VLC, due to its strong absorption at 450 nm and broad PL emission covering the green to red region. Energy transfer between the polymers allows the both chromophores to be efficiently excited by the blue light source, while phase separation of the two allows control over the color balance. Alternative schemes that suppress energy transfer<sup>42-43</sup> can decouple excitation of the chromophores, but this places an additional constraint on the fast red emitter to have high absorption of the blue light. The great potential of this polymer blend can be seen through its short excited state PL lifetime (less than 1 ns) and associated much higher modulation bandwidth (> 200 MHz) and high data transmission rate (> 350 Mb/s using OOK). The measured modulation bandwidths and data transmission with the polymer blends are more than 35 times higher than those achieved with conventional LED phosphors.

## **EXPERIMENTAL METHOD**

**Material synthesis:** Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) was purchased from Sigma-Aldrich (541443-1G). Poly[2,5-bis(2',5'-bis(2''-ethylhexyloxy)phenyl)-p-phenylenevinylene] (BBEHP-PPV) was synthesized following similar synthesis procedure reported previously.<sup>18</sup>

**Material characterization:** Solutions were prepared by mixing 10 mg of MEH-PPV and BBEHP-PPV in 1 ml of chlorobenzene. Films were made by spin coating the solution onto quartz substrates at 1200 rpm for 60 s inside a N<sub>2</sub> glove box. The absorption and photoluminescence spectra were obtained using a Cary 300 UV-Vis spectrophotometer and



an Edinburgh Photonics Instrument FLS980 respectively. The PL spectra were obtained at excitation wavelengths of 430 and 500 nm for BBEHP-PPV and MEH-PPV respectively. In the case of the blends, an excitation wavelength of 430 nm was selected to obtain PL spectra. PLQY was measured with a Hamamatsu integrating sphere C9920-02 luminescence measurement system using a range of excitation wavelengths (450, 500 nm). The fluorescence lifetimes of samples were measured by exciting films with PicoQuant picosecond pulsed lasers (470 nm for neat MEH-PPV and 379 nm for neat BBEHP-PPV and blend) and PL decay was measured at detection wavelengths of 496 and 595 nm using time correlated single photon counting (TCSPC).

***Bandwidth and data rate measurements:*** The experimental setup is shown in the inset of Figure 3. The excitation of the films used a modulated laser diode LD450 from Roithner LaserTechnik GmbH. The laser bias was a combination of a DC bias and AC modulation through a bias-T. For the DC bias an LDC205C - benchtop LD current controller from Thorlabs was used. The AC bias modulation was controlled by an Agilent network analyser 4395A and ZHL-6A amplifier from Mini-Circuits. Finally, an APD S8890 from Hamamatsu Photonics was used as a receiver. A similar standard technique reported previously was used to measure the small signal modulation bandwidth and data rate.<sup>11</sup>

## **ASSOCIATED CONTENT**

### **Supporting Information**

We investigated the energy transfer between BBEHP-PPV and MEH-PPV by calculating relative contribution of each material in absorption and emission spectra of blends. We also compared organic semiconductors blends with commercial phosphor plate CL-840. This material is free of charge via the Internet at <http://pubs.acs.org>.

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## Note

The authors declare no competing financial interest.

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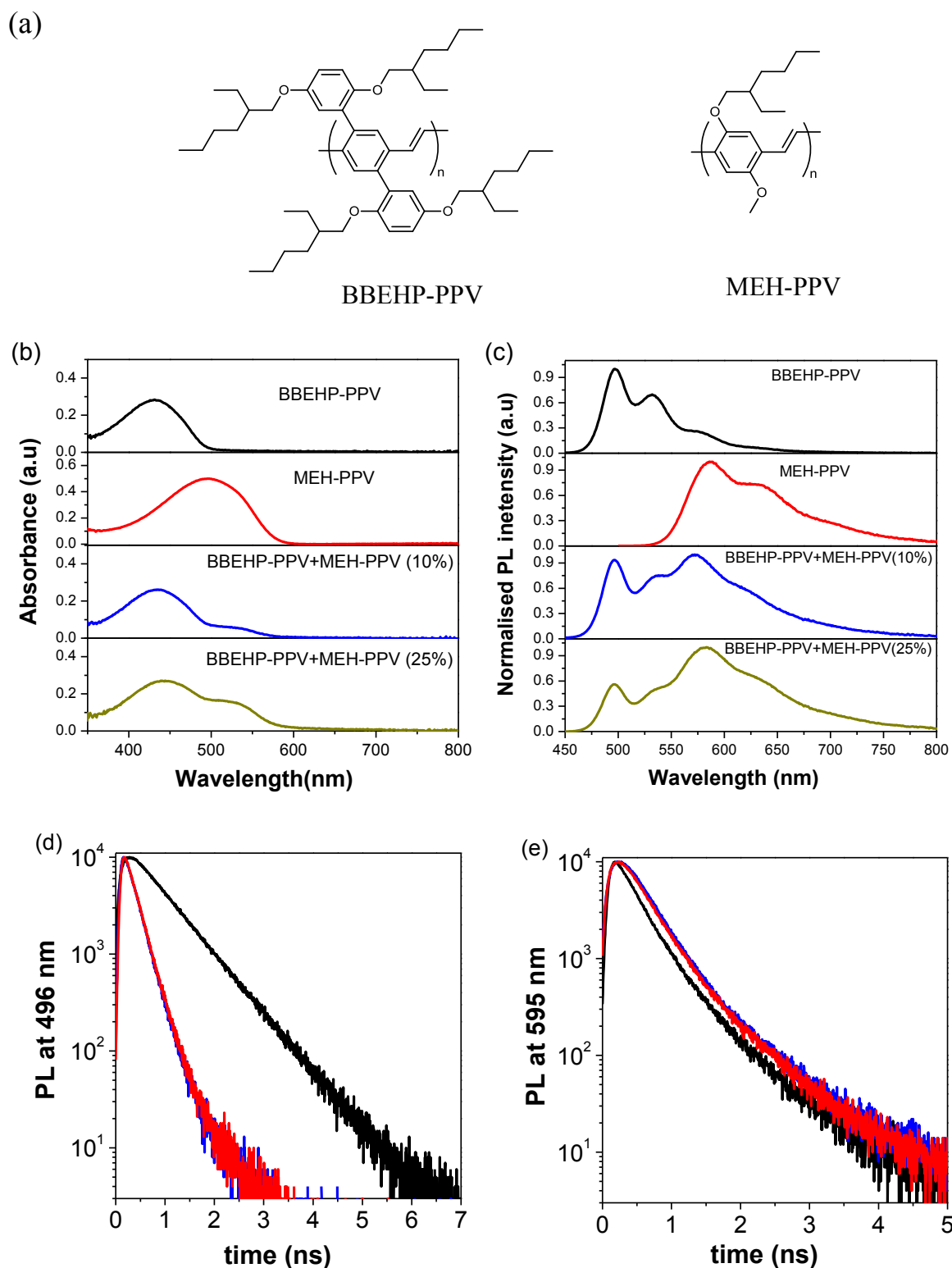
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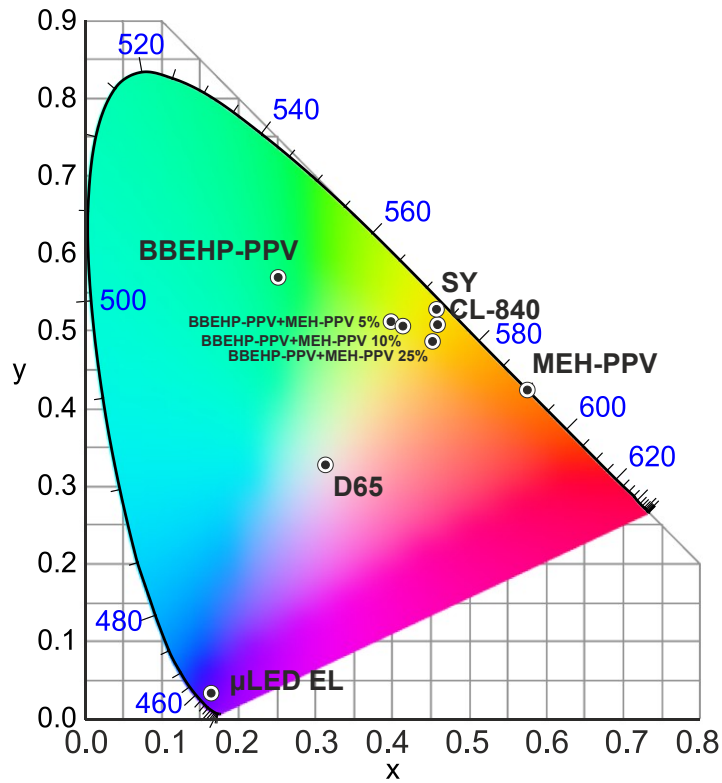
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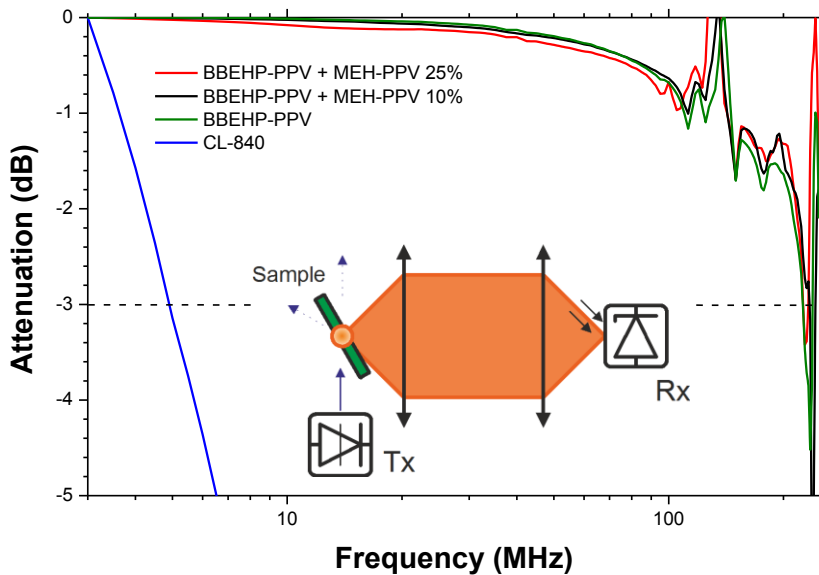
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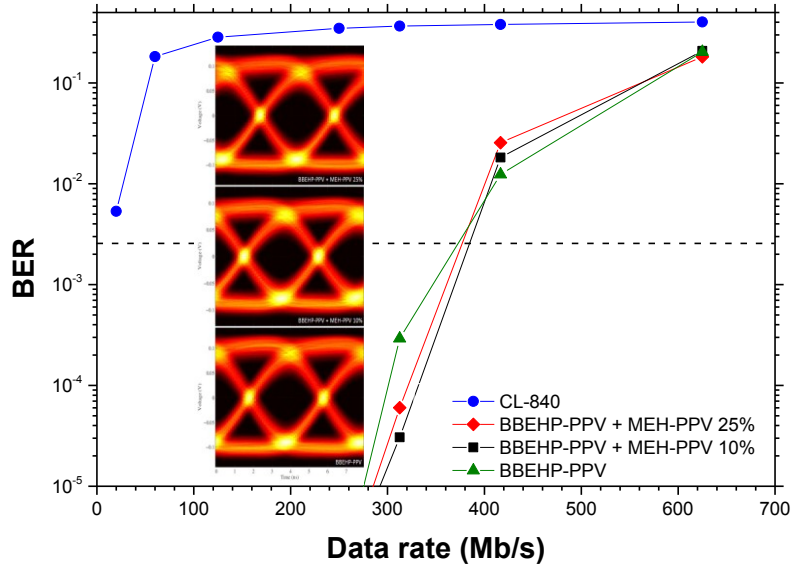
**Figure 1:** (a) Molecular structure of BBEHP-PPV and MEH-PPV (b) UV-Vis absorption and (c) PL spectra of BBEHP-PPV (black line), MEH-PPV (red line), and different ratios of BBEHP-PPV and MEH-PPV (blue and dark yellow) For blend, the PL spectra were obtained at an excitation wavelength of 430 nm. (d) Photoluminescence decays at 496 nm and (e) 595 nm obtained at excitation wavelengths of 470 nm (for MEH-PPV) and 379 nm (for BBEHP-PPV and blends of BBEHP-PPV+MEH-PPV). Black, blue and red lines in (d) and (e) correspond to 100:0, 90:10 and 75:25 ratios of BBEHP-PPV and MEH-PPV respectively.



**Figure 2:** Plot of CIE coordinates of the color generated on CIE 1931 chromaticity diagram as ratio of MEH-PPV and BBEHP-PPV in blends is varied. For a comparison, measured colors of MEH-PPV, BBEHP-PPV, CL-840 and SY<sup>[8]</sup> are also plotted.



**Figure 3:** Plot of attenuation vs frequency of small signal modulation. The dotted line corresponds to -3 dB level which defines the bandwidth of the system. The schematic in the inset represent the experimental setup used in the measurement. For comparison reasons the measurements were repeated for commercial phosphor plates.



**Figure 4:** Bit error rate versus data rate using On-Off keying modulation. The general accepted error floor for VLC is  $1.2 \times 10^{-3}$ , which dashed line represents. In the inset the eye diagram at 250 Mb/s is presented (top eye diagram corresponds to BBEHP-PPV+MEH-PPV (25%), centre to BBEHP-PPV+MEH-PPV (10%) and bottom eye diagram to BBEHP-PPV alone).

**Table 1:** Summary of PLQY, energy transfer rate  $k_{et}$  and efficiency  $\eta_{et}$ , CIE coordinates of MEH-PPV, BBEHP-PPV and different ratios of MEH-PPV and BBEHP-PPV.

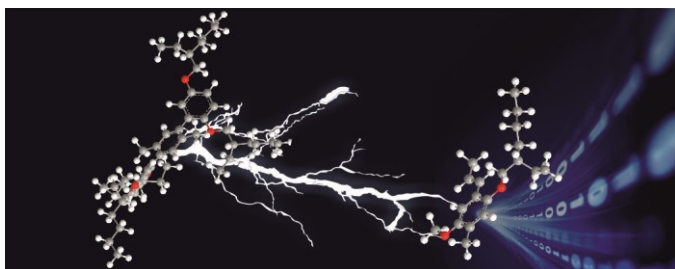
Material	PLQY(%) at $\lambda_{ex} = 450$ nm		PLQY(%) at $\lambda_{ex} = 500$ nm		$K_{et}$ ( $10^{10} s^{-1}$ )	$\eta_{et}$ (%)	CIE coordinates
	Overall	> 600nm	Overall	> 600nm			
MEH-PPV	17.0	15.1	17.0	14.9	-	-	0.57, 0.43
BBEHP-PPV	85.2	7.5	75.0	9.4	-	-	0.25, 0.57
BBEHP-PPV + MEH-PPV (90:10)	28.0	15.3	20.8	14.9	2.5	67	0.4, 0.51
BBEHP-PPV + MEH-PPV (75:25)	25.0	15.8	20.8	15.4	2.4	66	0.45, 0.49

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## **A novel fast color-converter for visible light communication using a blend of conjugated polymers**

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In this paper, a blend of semiconducting polymers is used to make a broadband color converter with a very high modulation bandwidth and potential for good colour rendering to replace commercial phosphors in hybrid LEDs for visible light data communications. The color converter exploits partial Förster energy transfer in a blend of the highly fluorescent green emitter BBEHP-PPV and orange-red emitting MEH-PPV. The modulation bandwidth of the blend is greater than 200 MHz, and is applied in a free space datalink with a transmission rate > 350 Mb/s using on-off-keying.