

## Inhibition of Energy Transfer between Conjugated Polymer Chains in Host/Guest Nanocomposites Generates White Photo- and Electroluminescence

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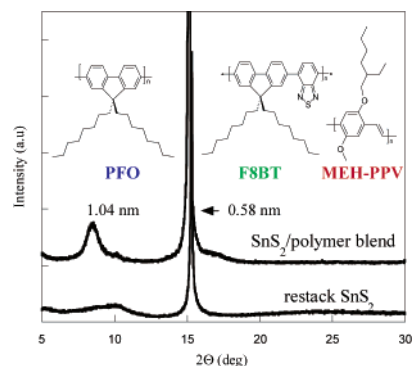
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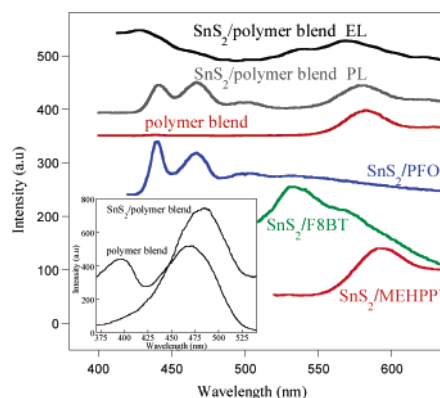
The production of white light from a single material has proved an elusive challenge. Typically, the three primary colors that must be combined, red, green, and blue, are generated separately from distinct emitting materials that are macroscopically blended or processed into a multilayer. This can be achieved by using inorganic materials, which often require laborious deposition protocols to prepare crystalline thin films, or organic or polymeric light-emitting compounds, which are less expensive, flexible, and more processable. Conjugated polymers have received a great deal of interest for a variety of applications, especially in displays; however, the production of white light has been problematic because the width of an emission peak from a single polymer species is generally not broad enough to cover the entire spectrum of visible light. White polymer light-emitting diodes (PLEDs) were prepared by introducing small amounts of red and green-emissive moieties grafted onto,<sup>1,2</sup> or doped into,<sup>3–7</sup> a blue-emitting polymer. Energy transfer from the wide-gap host polymer to the smaller-gap species, followed by concurrent emission from the three chromophores, yields white light. The “purity” and stability of such white emission, however, were extremely sensitive to synthesis and processing parameters and device operating conditions. Consequently, achieving pure and stable white electroluminescence in PLEDs has often required trial-and-error efforts with respect to most, if not all, stages of light-emitting materials design, film processing, and device fabrication.

Here, we report a new and general strategy for the synthesis of a single nanocomposite material that yields pure and stable white photoluminescence (PL) and electroluminescence (EL). In the nanocomposite, red, green, and blue (RGB) emissive conjugated polymers are confined into the interlayer galleries of a semiconducting inorganic host material. The layered semiconducting host, SnS<sub>2</sub>, not only supports the transport of charge carriers, but also serves as a *barrier* to energy transfer between polymer chains. By significantly reducing this energy transfer, emission from the three RGB chromophores is observed simultaneously. This mechanism for white-light emission is in contrast to that previously reported for PLEDs, where efficient energy transfer between polymer chains was *essential* for obtaining white light.

The RGB polymers used are blue-emitting PFO, green-emitting F8BT, and red-emitting MEH-PPV, (see Figure 1). A solution blend of these three polymers, with the ratio 10 MEH-PPV/60 F8BT/30 PFO wt %, was prepared and then *collectively* intercalated into layered SnS<sub>2</sub> (for nanocomposite synthesis and film formation see ref 8 and the Supporting Information).<sup>8</sup> Polymer-intercalation into the galleries of SnS<sub>2</sub> is established by the expansion of the *c*-axis normal to the layered structure, as evident from X-ray diffraction (XRD) measurements. Figure 1 shows XRD patterns for SnS<sub>2</sub> films without polymer and intercalated with the conjugated polymers blend. The XRD pattern of the polymer-intercalated SnS<sub>2</sub> shows, in addition to the *c*-axis interlayer reflection at 0.58 nm ( $2\theta = 15.0^\circ$ ),<sup>9</sup> a strong new reflection at  $\sim 1.04$  nm ( $2\theta = 8.5^\circ$ ) associated with the intercalation of conjugated polymers into the interlayer



**Figure 1.** Chemical structures of blue-emitting PFO, green-emitting F8BT, and red-emitting MEH-PPV, and XRD patterns of a restacked SnS<sub>2</sub> film (no polymer), and a blend–intercalated/SnS<sub>2</sub> nanocomposite film.



**Figure 2.** PL spectra of separate SnS<sub>2</sub>/conjugated-polymer-intercalated nanocomposites, a blend of only the three polymers (excitation 380 nm), and the PL (excitation 380 nm) and EL of a blend–intercalated/SnS<sub>2</sub> nanocomposite film. Inset: excitation spectra for emission at 580 nm of a blend of only the three polymers and the blend–intercalated/SnS<sub>2</sub> nanocomposite.

galleries. The  $\sim 0.46$  nm expansion is due to the tendency of conjugated polymers to adopt a planar conformation in layered compounds<sup>8</sup> and indicates that a SnS<sub>2</sub> interlayer gallery accommodates a planar polymer monolayer only.<sup>10</sup>

The emissive properties of the conjugated polymers are maintained upon their intercalation into the SnS<sub>2</sub> galleries, as shown in the PL spectra of the nanocomposite films in Figure 2. The PL peak positions of SnS<sub>2</sub>/MEH-PPV, SnS<sub>2</sub>/F8BT, and SnS<sub>2</sub>/PFO nanocomposites, are slightly red-shifted compared to spectra from pristine films of the individual polymers alone, consistent with the extended conjugation lengths of the intercalated polymer segments.

Confinement of the conjugated polymer chains within the spatially restrictive planar galleries of the layered material, however, provides additional molecular property benefits that can be exploited to promote white emission. Specifically, strong interactions between the conjugated molecular guests and the SnS<sub>2</sub> sheets prevent the

$\pi$ -stacking of polymer chains. Theoretical studies have shown that the  $\pi$ - $\pi$  interactions are responsible for the efficient energy transfer in polymer films, owing to high interchain exciton hopping rates.<sup>11</sup> Consequently, the reduced interchain interactions from diminished  $\pi$ -stacking is expected to hinder the energy transfer between polymer chains accommodated within a *single* SnS<sub>2</sub> grain or even a *single* gallery.

As shown in the PL spectrum of Figure 2, light emission from the blend-intercalated/SnS<sub>2</sub> nanocomposite is clearly white (CIE coordinates 0.34, 0.29) composed of emissions from the blue, green, and red intercalated polymer chains.<sup>12</sup> No polymer phase separation was observed using a lifetime spectrometer with a 200 nm resolution, indicating that the color light-emitting species are collectively intercalated and uniformly dispersed in the micrometer-sized SnS<sub>2</sub> grains.

The PL of the nanocomposite was compared to that of a polymer-only film (no SnS<sub>2</sub>) deposited from the same solution used for the intercalation (10 MEH-PPV/60 F8BT/30 PFO wt %), as shown in Figure 2. Although the blend consisted mainly of the blue- and green-emitting polymers, the polymer blend emitted in the red, far from white emission and consistent with expected efficient energy transfer from the blue and green polymers to the red polymer.<sup>13</sup> The white emission from the blend-intercalated/SnS<sub>2</sub> nanocomposite film is a result of simultaneous emissions from the blue, green, and red intercalated polymer chains. Crucially, this occurs because energy apparently cannot flow from the high-gap blue- and green-emitting polymer chains to the low-gap red-emitting polymer chains, despite their close proximities (<200 nm) in single SnS<sub>2</sub> grains, owing to diminished polymer-polymer  $\pi$ -stacking. Each multicolor intercalated composite grain is, therefore, a white-light source which could find use in micrometer-sized devices and high-resolution displays.

The proposed mechanism of isolation-inhibited energy transfer in the white-emitting nanocomposites is supported by excitation spectra of the red-emission (Figure 2 inset). The peaks in the excitation spectra indicate which absorption wavelengths are responsible for the 580 nm red-emission. The excitation spectrum of the solely polymer blend shows two peaks centered at 395 and 470 nm and a shoulder at 490 nm, which are in excellent agreement with absorption peaks of pristine MEH-PPV, F8BT, and PFO, respectively. The red-emission from the polymer blend is, therefore, due to absorption of photons by the three polymers, followed by fast energy funneling to the low-gap red-emitter. The same experiment was performed on the blend-intercalated/SnS<sub>2</sub> nanocomposite film, revealing a significantly different mechanism. In this case, the spectrum is dominated by a single peak centered at 480 nm. This lone signal indicates that the red component in the white emission from the nanocomposites is due to absorption of the red-emitting polymers only and that there are no contributions from the blue- and green-emitting polymers.

The efficacy of the white-emitting nanocomposites in simple single-layer polymer LEDs was examined in a conventional device configuration: ITO/poly(ethylenedioxythiophene): poly(styrene

sulfonic acid) (80 nm)/nanocomposite film  $\sim$ 1500 nm/Ca 50 nm/Ag 150 nm. For comparison, a device based on a polymer blend (without SnS<sub>2</sub>) in the same configuration was also fabricated and tested. The EL spectrum of the polymer-blend device is similar to its PL spectrum emitting in the red. In contrast, blend-intercalated/SnS<sub>2</sub> nanocomposites exhibits white EL (Figure 2) with noticeable blue, green, and red peaks yielding nearly pure-white CIE coordinates (0.30, 0.30). The brightness,  $\sim$ 1 cd/m<sup>2</sup> at 10 V, is relatively low, because of partial absorption of the emission by the inorganic semiconductor in the 1–2  $\mu$ m thick films ( $E_g = 2.18$  eV, 570 nm).<sup>8</sup> Nevertheless, there are substantial opportunities for significant improvements in brightness, which can be expected to accrue from higher polymer loadings, reduced film thicknesses, and device structures. Moreover, judicious selection of the host matrix could also be used to enhance device performance. In the white LED reported here, the barrier to hole-injection and barrierless electron-injection into SnS<sub>2</sub> (ionization potential and electron affinity  $-7.56$  and  $-5.30$  eV, respectively)<sup>14</sup> is likely to result in the build-up of electron density at the SnS<sub>2</sub>-anode and inorganic-organic interfaces. The high electron concentrations could generate local fields, enhancing hole-injection from the anode, and carrier recombination on the polymers. Device improvements will further benefit from increased molecular understanding of the physicochemical processes that underlie these complicated and important systems.

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**Supporting Information Available:** Illustration of the intercalation process. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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