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Directed Self-Assembly of Metallosupramolecular Polymers at the Polymer–Polymer Interface

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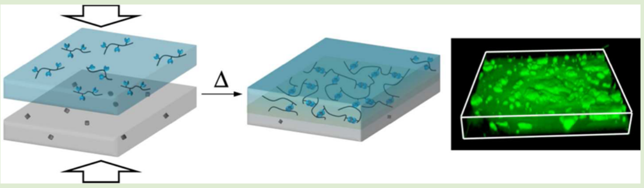
Supporting Information



ABSTRACT: Directed self-assembly of a metallosupramolecular polymer is achieved at the interface between two polymer films by simple melt pressing. Blends of a 2,6-bis(*N*-methylbenzimidazolyl)pyridine (MeBip) side-chain functionalized polystyrene in a polystyrene matrix and $Zn(NTf_2)_2$ in a poly(methyl methacrylate) matrix were pressed together above the T_g of the matrix polymers resulting in diffusion of the components and subsequent self-assembly of the metallosupramolecular polymer at the polymer–polymer interface. The formation of the metallosupramolecular polymer was monitored by spectroscopy and microscopy and it was found that the interfacial self-assembly occurs at the processing temperatures (ca. 210 °C) within 5 min. It was further shown that this materials system resulted in robust films that exhibited a new emergent property, namely, phosphorescence, which is not exhibited by any of the individual components nor the metallosupramolecular polymer itself.

The area of directed self-assembly, where external factors are designed to influence the self-assembly of a system in a specific desired manner, have been attracting attention in recent years.[1] Directed assembly can be achieved using many different techniques and processes such as addition of templates or the use of directing fields (such as magnetic, electric or flow). Interfaces, such as liquid–liquid,[2] air–liquid[3] solid–air,[4] and solid–liquid,[4,5] are another tool that can be utilized to control the assembly of molecules.[6] An area that has received a lot less attention is directed assembly at the polymer–polymer interface. Considering that melt processing is usually the method of choice for most industrial polymer processes, developing facile ways to be able to organize components within a polymer film offer many opportunities. Specifically, interactions at polymer interfaces are important for a variety of applications including layer adhesion,[7–9] compatibilization of immiscible polymer films and blends,[10,11] and electronic devices.[12] Furthermore, the continued development of melt-processed multilayer films[13] that have many polymer–polymer interfaces offers an attractive medium for directed self-assembly.

In recent years the study of metallosupramolecular polymers and networks,[14–16] which generally consist of two complementary self-assembling components, a multiligand containing organic component and a metal ion, has received a growing amount of attention, in part, as these materials are known to display stimuli-responsive properties[17,18] and have been used in many different applications ranging from organic light-emitting diodes (OLEDs)[19,20] to sensors.[21,22] The ability to target the location of the self-assembly of such systems has also become an area of interest. Examples of interfacial assembly of metallosupramolecular polymers at liquid–liquid,[23] air–liquid,[24] and solid–liquid[25] interfaces have been reported. However, to our knowledge, no examples have yet been reported of self-assembly at a polymer–polymer interface. Thus, to develop new interfacial materials, we have investigated the possibility of being able to direct the self-assembly of a metallosupramolecular polymer using solventless conditions at the solid–solid interface between two polymer films.

The proposed method of directed self-assembly at the polymer–polymer interface is shown in Figure 1. Two different polymer blends, one polymer matrix containing a polymer with ligand containing side chains and one matrix containing a metal salt, are brought into contact above the T_g of the matrix polymers. This should allow for diffusion of the two self-assembling components and, upon finding the complementary component, metal-coordination should occur within the two layer films. The use of a transition metal-ion, which binds the ligand in a 1:2 fashion, will result in the formation of a metallosupramolecular polymer that will either phase-separate from the polymer matrix and/or form a cross-linked polymer network greatly inhibiting any subsequent diffusion. The result then would be a metallosupramolecular polymer formed close to the interface of the two layers. Side-chain ligand containing polymers are well documented,[26–28] and in solution they have been found to yield insoluble,[29] swellable,[30] or gel[31,32] network structures upon the addition of the appropriate ligand binding metal ions.

To investigate the potential for directed self-assembly in a two layer film, a 2,6-bis(*N*-methylbenzimidazolyl)pyridine (MeBip) side-chain functionalized polystyrene was prepared using reversible addition–fragmentation chain transfer poly-

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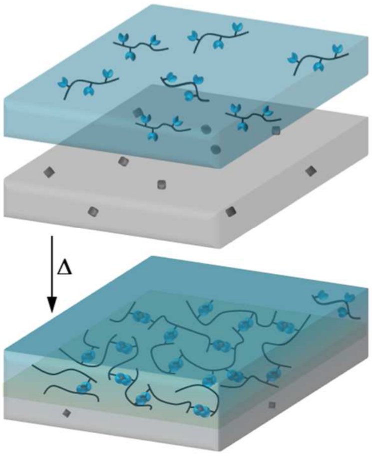

Figure 1. Schematic representation of the directed self-assembly of a metallosupramolecular polymer arising from diffusion of a ligand-functionalized polymer and metal-ions within polymer matrices when placed in contact above the T_g of the matrices.

merization (RAFT) as shown in Figure 2. Copolymers of styrene and 4-vinylbenzyl chloride were targeted and the molar ratio of the two monomers was kept constant for the two molecular weights studied to keep the fraction of side-chain functionalized units consistent. Two different molecular weight polymers were synthesized by stopping the polymerization after either 6 or 24 h to yield number average molecular weights (M_n) of ~10000 and ~50000 g/mol with PDIs less than 1.1 (as determined by GPC; see Supporting Information, Figure S1) to give polymers $\mathbf{1}_{10}$ and $\mathbf{1}_{50}$ (Figure 2a) where the subscript 10 or 50 is used to differentiate the two polymers' molecular weights. Synthesis of the MeBip side-chain functionalized polymers was then achieved by reacting an excess of ligand **2** with the two polymers ($\mathbf{1}_{10}$ and $\mathbf{1}_{50}$) to yield polymers $\mathbf{3}_{10}$ and $\mathbf{3}_{50}$, respectively (Figure 2b).

All polymers were fully characterized by $^1H/^{13}C$ NMR and GPC (see Supporting Information, Figures S2–12). ^1H NMR shows that all of the observed peaks are quite broad, consistent with typical NMR of polymers, and no clear peaks from the polymer end groups are apparent. It should be noted that it is likely that the trithiocarbonate end group has reacted during the reaction of **2** with $\mathbf{1}_n$ as strong bases and nucleophiles are known to react with this functional group.[33,34] Confirmation that the majority of the benzyl chloride units have been converted in the benzyl ether moieties comes from ^{13}C NMR with the disappearance of the $-CH_2Cl$ carbon peak at about 48 ppm and the emergence of a $-CH_2O-$ carbon peak at about 68 ppm (see Supporting Information, Figures S9–12). Furthermore, ^1H NMR allows for an estimation of the ratio of ligand functionalized to nonfunctionalized aryl units along the polymer backbone. The ratio of the integration of the aromatic peak to the benzylic peak suggests about 12 and 14% of the units are ligand functionalized in $\mathbf{3}_{10}$ and $\mathbf{3}_{50}$, respectively, which is in good agreement with the monomer feed ratio of 4-vinylbenzyl chloride to styrene (11%).

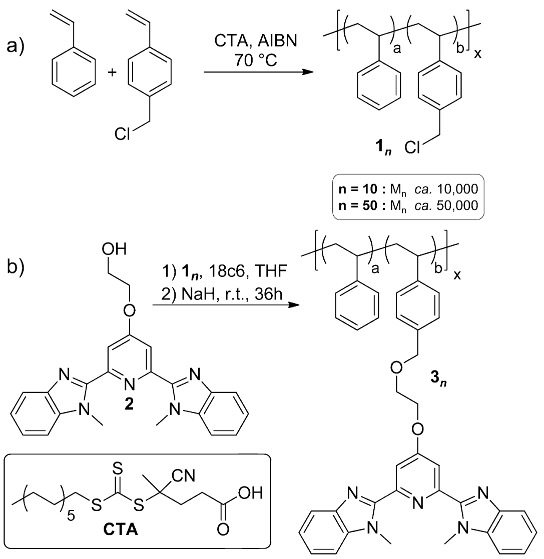

Figure 2. (a) Synthesis of random copolymer $\mathbf{1}_n$ by RAFT polymerization and (b) functionalization with ligand **2** to yield a side-chain functionalized polymer $\mathbf{3}_n$.

The thermal stability of the Mebip-functionalized polymers was investigated as the materials are exposed to temperatures >200 °C during the preparation of the polymer blends and the directed self-assembly step. Thermogravimetric analysis (TGA) was used to determine at what temperatures the polymers showed degradation and the temperature limit for use in preparing blends (see Supporting Information, Figures S13–14). While the TGA of the precursor polymers ($\mathbf{1}_n$) shows that they are only stable up to ca. 200 °C, the MeBip-functionalized polymers ($\mathbf{3}_n$) show no decomposition below 250 °C; exhibiting one degradation peak at about 400 °C with a degradation onset that occurs slightly below 300 °C. Thus, the functionalized polymers ($\mathbf{3}_n$) are stable at the processing temperatures of 210 °C.

$\mathbf{3}_n$ was blended into a polystyrene (PS) matrix ($\mathbf{PS{\cdot}3}_n$) and $Zn(NTf_2)_2$ was blended into a poly(methyl methacrylate) (PMMA) matrix (**PMMA·Zn**) using a twin-screw micro-compounder at 210 °C and mixed for 30 min before extruding. Both blends were prepared at two different concentrations (10 and 25 wt % of $\mathbf{3}_n$ or $Zn(NTf_2)_2$) to determine if the loading has any effect on the size or location of the self-assembly. $\mathbf{PS{\cdot}3}_n$ and **PMMA·Zn** were then melt pressed into films 150 ± 50 μm thick to be used in the two-layer directed assembly experiments. It is important to note that in the following directed assembly experiments we kept the relative wt % of the two components in the matrices the same. This corresponds to a molar ratio of about two Zn^{2+} ions for every ligand.

A series of two-layer systems with $\mathbf{PS{\cdot}3}_{10}$ or $\mathbf{PS{\cdot}3}_{50}$ (at both 10 and 25 wt %) films and PMMA (without any Zn^{2+} ions) or **PMMA·Zn** (at 10% and 25 wt %) films were heated at 210 °C in a melt press at 2 metric tons for varying lengths of time. The formation of a metallosupramolecular polymer was monitored by the change in the films absorption and emission spectra, which occur upon metal complexation to the ligand.[35] Figure 3a,b show the comparison of the change in the absorption spectra from the two-layer films prepared with $\mathbf{PS{\cdot}3}_n$ with either PMMA alone or with **PMMA·Zn**. The two-layer films containing Zn^{2+} display an increase in the absorbance from 335 to 375 nm (λ_{max} = 340 nm) and a decrease in the free ligand absorbance at 315 nm. This change in absorbance matches closely with the previously reported MeBip/Zn^{2+} complexes in solution[22] and is consistent with the formation of the metallosupramolecular polymer in the solid-state.

A change in emission was also observed in the fluorescence spectra when compared to the control film. Figure 3c,d show

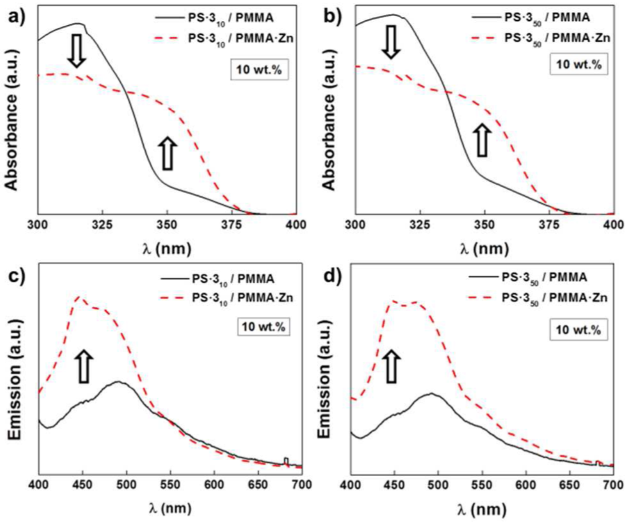

Figure 3. UV−vis spectra of two-layer films prepared with (a) **PS·3$_{10}$** with PMMA (black line) or with **PMMA·Zn** (red dash; 10 wt %) and (b) **PS·3$_{50}$** with PMMA (black line) or with **PMMA·Zn** (red line; 10 wt %). Photoluminescence spectra of two-layer films prepared with (c) **PS·3$_{10}$** with PMMA (black line) or with **PMMA·Zn** (red line; 10 wt %) and (d) **PS·3$_{50}$** with PMMA (black line) or with **PMMA·Zn** (red dash; 10 wt %).

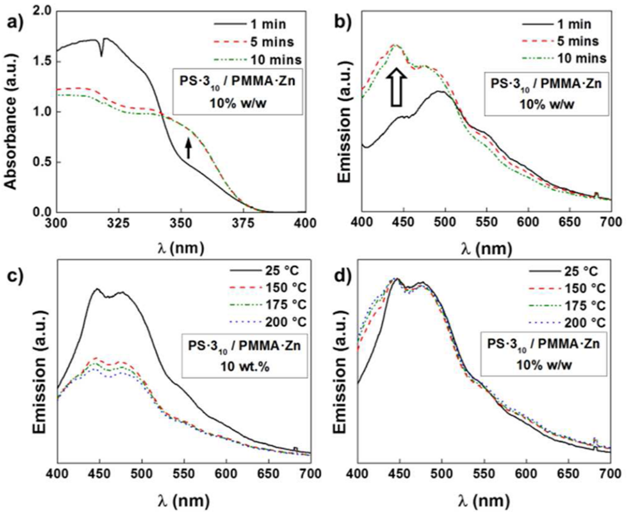

Figure 4. Influence of contact time on the self-assembly. (a) UV−vis spectra and (b) PL spectra of **PS·3$_{10}$/PMMA·Zn** (10 wt %). (c) Unnormalized and (d) normalized variable-temperature PL spectra of a two-layer film of **PS·3$_{10}$/PMMA·Zn** (10 wt %) showing evidence of metal-coordination at 200 °C.

that metal-coordination results in an increase in the emission intensity at about 450 nm. While the fluorescence of the uncomplexed polymer in the polystyrene matrix looks different from solution,[22] prior work[36] has shown that a λ_{max} for the MeBip/Zn^{2+} complex emission occurs between 400 and 450 nm and, thus, the emission data are also consistent with the formation of the metallosupramolecular polymer.

Information on the rate of the metallosupramolecular polymer formation during processing of films was obtained by monitoring the UV−vis and PL of films that were melt pressed at 210 °C for set periods of time. It was found that for all complementary two film blends (at both loadings) the absorption and emission showed that the metallosupramolecular polymers are formed after about 5 min (Figure 4a,b) of melt pressing. Films pressed for only 1 min displayed similar absorbance and emission to the control films. However, films pressed for a total of 5 min displayed increased absorption from 335 to 375 nm and emission below 500 nm. Pressing for additional time (10 or 15 min total) showed no significant changes in the spectra other than slight differences in intensity. While all spectra were corrected for the film thickness, it is likely that the small changes in intensity result from the change in the film's thickness after pressing. As such the data suggest that while a small amount of additional self-assembly/diffusion may take place after 5 min, the majority of the complexation occurs between 1 and 5 min for all of the systems studied.

There are two possible mechanisms for the formation of the metallosupramolecular polymer; namely, the two components diffuse through the matrices and either complex at the processing temperatures or the metallosupramolecular polymer is formed after the processing upon cooling. Therefore, the emission spectrum of a film that has been compression molded and contains the metallosupramolecular polymer was studied at elevated temperatures to see if the metallosupramolecular polymer is present at the processing temperatures. Figure 4c shows the unnormalized emission profiles for a **PS·3$_{10}$/PMMA·Zn** (10 wt %) two-layer film. Upon heating above the matrix polymers', T_gs, the emission intensity decreases as expected from increased molecular collisions, nonradiative transmission, and quenching which occur at elevated temperatures;[37] however, more importantly, the λ_{max} (ca. 447 nm), which is assigned to the emission of the metal−ligand complex, of the films at elevated temperatures match those of the compression molded films at room temperature (Figure 4c). Furthermore, no significant change in the peak intensity ratios at about 447 and 500 nm is observed at 200 °C (Figure 4d). Thus, while some decomplexation and exchange may be occurring at higher temperatures, the emission spectra are consistent with the metallosupramolecular polymers being formed during the processing conditions.

Figure 5a shows a picture of the distinctive change in emission upon formation of the metallosupramolecular polymer. A film of the 10 wt % **PS·3$_{10}$** (left side of the picture) was partially overlapped with a film of 10 wt % **PMMA·Zn** (right side of the picture) and, upon pressing the two films together at 210 °C, self-assembly of the metallosupramolecular polymer occurred only in the overlapped region. The change in emission after self-assembly when viewed under UV light (λ_{ex} = 365 nm) is easily discernible. Unexpectedly, green colored phosphorescence is observed upon removal of the UV light source which gradually fades after ∼2−3 s. It was found that exciting the melt pressed two-layer film with a hand-held UV lamp (λ_{ex} = 365 nm) for about 5 min produced this effect upon removal the light source. The phosphorescence (broad emission, λ_{max} 505 nm with a shoulder at 540 nm, see Supporting Information, video and Figure S15) is thought to originate from the metallosupramolecular polymer and, as shown in Figure 5b, the green emission is only located at the overlap in the two films. Interestingly, this behavior is not seen in the two-layered films prepared without Zn(NTf$_2$)$_2$ nor the nonblended metallosupramolecular polymer itself. Phosphorescence of Zn^{2+} complexes with nitrogen-containing ligands[38] in glassy solutions at low temperatures (ca. 77 K) have been observed before and have been attributed to a $^3(\pi-\pi^*)$ transition in the metal−ligand complex.[39,40] The mechanism behind the phosphorescence in these two-layered

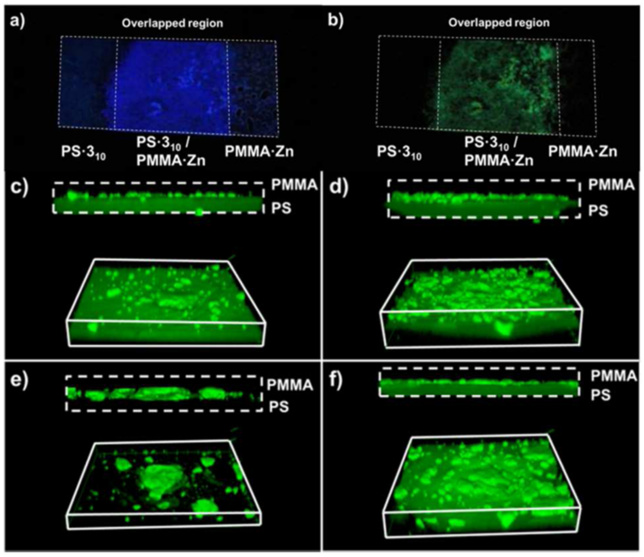

Figure 5. (a) Image of the change in emission color and intensity upon formation of a metallosupramolecular polymer from **PS·3$_{10}$**/**PMMA·Zn** (10 wt %; λ_{ex} = 365 nm; the edge of the films are outlined for clarification). Sample was prepared by only partially overlapping the films in the center to highlight the emission change (left, **PS·3$_{10}$**; middle, **PS·3$_{10}$**/**PMMA·Zn**; right, **PMMA·Zn**). (b) Image of the phosphorescence observed in the same film, which is only present at the overlapped area. The phosphorescence disappears after ~3 s (λ_{ex} = 365 nm). 3D images of the area on either side of the interface using confocal microscopy to look at the green fluorescence (ca. 450−600 nm; λ_{ex} = 405 nm), which shows intense fluorescence from metallosupramolecular polymers (c) **PS·3$_{10}$**/**PMMA·Zn** (10 wt %), (d) **PS·3$_{10}$**/**PMMA·Zn** (25 wt %), (e) **PS·3$_{50}$**/**PMMA·Zn** (10 wt %), and (f) **PS·3$_{50}$**/**PMMA·Zn** (25 wt %) located at/near the interface between the layers from an edge-on view (top) and surface (bottom). Scanning range is marked for clarity with dimensions 365 × 365 × 100 μm.

system is currently unclear and requires more studies. However, the matrix polymers seem to play a role in this behavior. In an effort to determine which components are necessary to observe phosphorescence, two different samples were prepared in which **3$_{10}$** and Zn(OTf)$_2$ were blended into either PS or PMMA at 10 wt %. Interestingly, after exciting both blends with UV light as before, phosphorescence was observed in the PMMA blend but not for the PS blend. Thus, it is apparent that phosphorescence in these film requires both the metallosupramolecular polymer and PMMA; however, further studies are needed to fully elucidate the mechanism(s) behind this response. It is also important to note these control 10 wt % **3$_{10}$·Zn**/**PMMA** blends do not form stable clear films as a result of significant phase-segregation as opposed to the two layer **PS·3$_{10}$**/**PMMA·Zn** films, highlighting an additional advantage of the directed self-assembled system (see Supporting Information, Figure S18).

The spectroscopic data suggests that the metallosupramolecular polymer is formed during melt pressing. If this is occurring then it would be expected that once incorporated into the metallosupramolecular polymer diffusion of the metal-ion and the polymeric **3$_n$** components would be greatly reduced by either phase separation or network formation. As such, one would expect that the majority of the metallosupramolecular polymer would be formed close to the PS/PMMA interface. To study this, confocal microscopy was used to obtain three-dimensional fluorescence images of the melt pressed films. The samples were excited at 405 nm and the emission from about 450−600 nm was monitored during the experiment, which will show both the free and the complexed **3$_n$**, although the complexed species will exhibit a higher emission intensity (Figure 3c,d). Scans through the depth of the two layer films gave direct evidence of the location of the self-assembled metallosupramolecular polymers. Both an edge-on view and a surface view of all of the two layer films (**PS·3$_n$** **PMMA·Zn**; 10% and 25 wt %) can be seen in Figure 5c−f, with the PMMA layer on top and the PS layer on the bottom. No fluorescence was observed in the PMMA layer, which confirms that there is no extensive diffusion of **3$_n$** into this layer. The PS layer does show a faint green emission, likely resulting from a small amount of uncomplexed **3$_n$** still present in the PS matrix. However, the greatest intensity is located primarily at the PS/PMMA interface. Thus, this data is consistent with the **3$_n$** and Zn^{2+} diffusing to the interface and, upon coordination, yielding a metallosupramolecular polymer that inhibits further diffusion.

The three-dimensional scans also allow for observation of the extent of assembly, that is, continuous layer versus agglomeration. As shown in Figure 5c−f, a large area of the interfacial surface is covered with the metallosupramolecular polymer network, and as would be expected, at higher loadings of **3$_n$** and Zn^{2+}, there is evidence of more metallosupramolecular polymer formed at the interface. Furthermore, as mentioned previously, it is important to note that, as the wt % of the two components is the same in their respective matrices, the approximate ligand to metal molar ratio is 1:2 in these experiments. So, an additional experiment was also carried out using a molar ratio of 2:1, which is more conducive to network formation. The confocal microscopy image (see Supporting Information, Figure S17) shows the formation of similar aggregates to those observed at the higher metal ion ratios. Thus, all samples appear to display a random dispersion of agglomerated self-assembled polymer along the interface, likely as a result of intramolecular coordination[41] and/or phase separation of the metallosupramolecular polymer from the matrices.

In summary, we have shown that melt pressing two polymer films, one a blend of a MeBip side-chain functionalized polystyrene in a PS matrix and the other a blend of Zn(NTf$_2$)$_2$ in PMMA, above the T_gs of the matrix polymers resulted in two-layer films that have a self-assembled metallosupramolecular polymer at the polymer−polymer interface. The degree and rates of self-assembly were monitored spectroscopically. It was shown that complexation was found to occur within 5 min and that higher loading of the assembling components into the polymer matrices yielded higher concentrations of the metallosupramolecular polymer at the interface. The ability to direct the self-assembly of components to the polymer interface provides a facile method to access films with complex solid-state architectures and the inherent optoelectronic properties of metallosupramolecular films could make them interesting for targeted assembly in device fabrication. Furthermore, from a systems (materials) perspective, akin to systems biology[42] and systems chemistry,[43] a new emergent property (phosphorescence) is observed. In this particular materials system, three of the four components appear to be required for phosphorescence, the PMMA, the PS ligand (**3$_n$**), and the Zn^{2+} salt. While more studies need to be carried out to further elucidate the exact mechanism of this process (e.g., the role of phase separation vs network formation, how viscosity of the matrix impacts this process and the effect of using different ratios of the two components in the matrices), the use of the interfacial assembly material described above has allowed the formation of robust phosphorescent films where each of the individual components in the system are required to achieve this.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Description of materials and instruments used, synthetic procedures, NMR, GPC, TGA, phosphorescence data, emission intensity versus depth, preparation of blends, and 2-layer films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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