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Thermoplastic Fluorescent Conjugated Polymers: Benefits of Preventing π–π Stacking**

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Organic materials that emit colorful fluorescence in condensed phases such as solids (crystals, thin films, or glasses),[1–5] liquid crystals,[6] and liquids[7] are useful for various applications ranging from organic light-emitting diodes and wavelength-tunable lasers to ultrasensitive sensors. Under these extremely concentrated conditions, however, photophysical processes are rather complex involving energy migration/transfer, charge separation, self-absorption, and excimer formation, which often give rise to low fluorescence quantum yields (Φ_F).[8] Therefore, rational molecular designs are essential, and inevitably, the intermolecular interactions in the condensed phases that govern these nonradiative decay processes need to be taken into consideration.

Among fluorescent organic materials, π-conjugated polymers (CPs) are attractive for organic optoelectronic applications owing to their distinguishing mechanical properties, processability, and electronic conductivity. In fact, CPs have been key materials in the field of organic optoelectronics.[9] An effective strategy for attaining solid-state emissive CPs is to isolate the π-conjugated backbone and inhibit interpolymer interactions.[3–5] For example, Swager et al.[3] have created a variety of highly emissive CPs that have rigid protecting frameworks such as triptycenes, and Anderson and co-workers[4] have exploited polyrotaxane-type CPs, that is, CPs that are sheathed by many cyclodextrins. In addition to these pioneering researches, some so-called insulated molecular wires (IMWs) were found to be emissive even in the solid state due to the absence of π–π stacking interactions; $\Phi_{F(film)}$ values of the IMWs in the literature are in the range of 4–62% and are generally around 10–20%.[3–5] However, conjugated systems have been limited to mostly poly(phenylene ethynylene) and polyphenylene systems, and accordingly, the hues of the fluorescence are still insufficient for filling the entire visible spectrum. This shortcoming behind small molecular fluorophores[1] arises mainly from the difficulty in designing and synthesizing IMWs in which three-dimensional architectures are equipped along the one-dimensional polymer backbones. Here, we introduce a new monomer, which is readily available and versatile, for producing a variety of IMWs. Our IMWs are intriguing not only from a photophysical point of view but because of their physical properties as polymeric materials; the polymers are miscible and thermoformable which are less developed properties with respect to CPs. All of the unique properties are a result of the absence of π–π stacking, and we describe the structure–property relationships of these IMWs.

On the basis of our previous reports on thiophene-based IMWs,[10] new monomers **1** and **1H** were synthesized through five well-established reaction steps with a total yield of over 80% (Figure 1a). The double ring closing metathesis (RCM) reaction is a key step in producing the three-dimensional architecture;[11] notably, this double RCM is so efficient, even without highly diluted conditions, that all the steps are scalable to a multiple gram reaction scale. The X-ray crystal structure of **1H** gives clear evidence of the cyclic structure in which the 1,4-dibromobenzene monomer is isolated while leaving the terminal bromide groups for further modification and polymerization (Figure 1b). Starting from monomer **1** (having solubilizing dodecyl chains), four kinds of IMWs were synthesized through Suzuki–Miyaura, Yamamoto, or Stille coupling reactions (i.e. **P1** to **P4**, see Supporting Information). In this study, thiophene-based polymers were mainly developed (**P2**, **P3**, and **P4**) because the installation of thiophene effectively influences the HOMO–LUMO gaps, and thus, various fluorescence colors can be realized.[12] All of the polymers are highly soluble in common organic solvents, and the molecular weights were determined by gel permeation chromatography (GPC) using a polystyrene standard (Figure 1c). The repeating units are analogous to a tetra-aryl benzene scaffold that poses a propeller-like conformation,[13] thereby twisting the conjugated backbone. We expect that the exciton is confined not only intermolecularly (by the sheath) but also intramolecularly (by the twisting), which can limit energy migration and lead to high $\Phi_{F(film)}$.[14]

In general, CPs show significant absorption and fluorescence spectral changes upon film formation because of the

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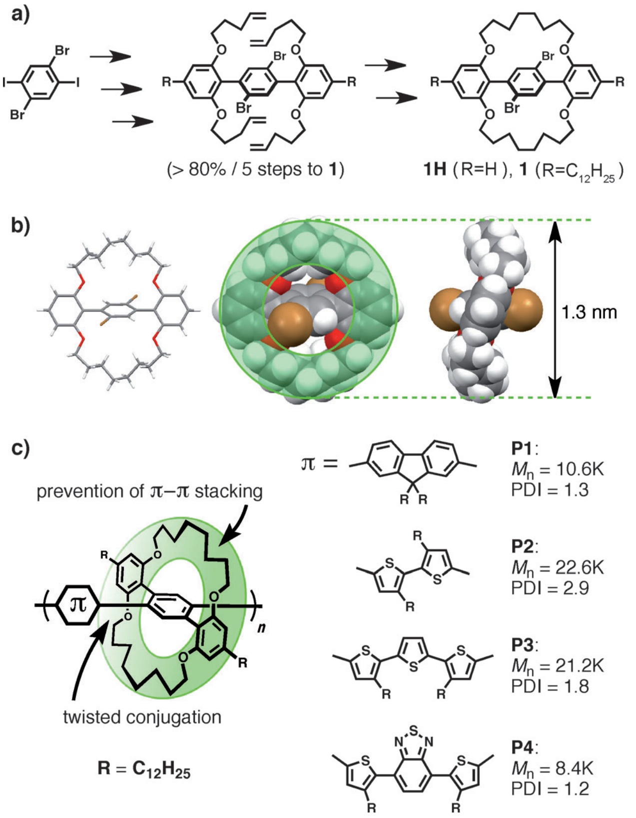

Figure 1. a) Synthetic route toward the monomers **1H** and **1**; see the Supporting Information for reagents and conditions. b) Axial (left and middle) and lateral (right) views of **1H** in crystallized form. c) Structures of **P1**–**P4** (R = $C_{12}H_{25}$).

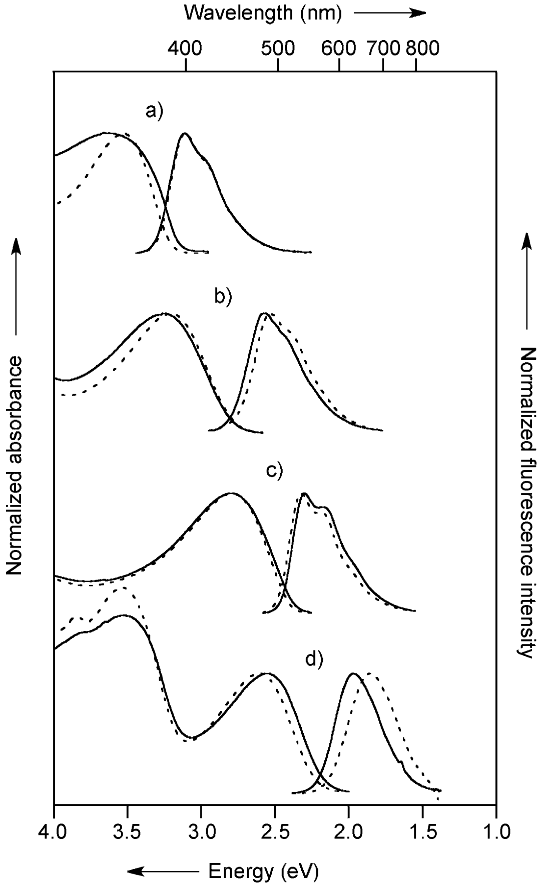

Figure 2. UV/Vis absorption (left) and fluorescence spectra (right: excited at the absorption maxima) of a) **P1**, b) **P2**, c) **P3**, and d) **P4** in DCM (dashed line) and drop-cast film form (solid line).

interpolymer interactions.[15] In contrast, the spectra of our polymers in both solution (in dichloromethane, DCM) and film form are quite similar (Figure 2). Small peak shifts, for which we could not ascribe to any particular feature of the family, are probably due to solvent effects and/or a restriction of the conformational motion in the solid films. These results indicate that the cyclic side chains can effectively prevent the conjugated backbone from π–π stacking. The fluorescence colors of **P1**, **P2**, **P3**, and **P4** were violet, green, yellow, and red, respectively. All of the polymers showed relatively large Stokes shifts thought to be due to the twisted backbone, which is advantageous for attaining high $\Phi_{F(film)}$ values by limiting self-absorption and energy migrations. The absolute quantum yields (Φ_F) and fluorescence lifetimes (τ) of these polymers in solution and film form are summarized in Table 1 and Table S1 in the Supporting Information, respectively. **P1** to **P4** have moderate Φ_F values even in the film state, retaining roughly half the value of that determined in solution: see, ρ in Table 1.[16] These values are comparable with those of IMWs highlighted as solid-state emissive materials in the literature,[3–5] and the moderate $\Phi_{F(film)}$ values of the yellow (**P3**) and red fluorescence (**P4**), which are rare for IMWs, are particularly noteworthy.

Table 1: Photophysical data of the copolymers.[a]

Compound		λ_{abs}[b] [nm] (log ε)	λ_{em}[b] [nm]	Stokes shift [cm^{-1}]	Φ[c]	ρ: $\Phi_{F(film)}$/$\Phi_{F(solution)}$
P1	solution	351 (4.59)	399	3430	0.92	0.48
	film	338	398	4460	0.44	
P2	solution	386 (4.48)	490	5500	0.16	0.75
	film	381	482	5500	0.12	
P3	solution	443 (4.62)	534	3850	0.33	0.55
	film	443	539	4020	0.18	
P4	solution	476 (4.20)	669	6060	0.39	0.33
	film	481	631	4940	0.13	

[a] Solutions were prepared from DCM, which was drop-cast to prepare the films. [b] Only the longest absorption and fluorescence maxima are shown. [c] Absolute quantum yields determined with a calibrated integrating sphere system.

The investigation of polymer blends is important in polymer science.[17] However, blending polymers to combine their fluorescence colors has been practically difficult because of phase separation; one needs to carefully consider the complex phase diagrams of the polymer blends and optimize both the blending processes and conditions (e.g. the solvents and temperature). Furthermore, blended films with phase separation may not be optically clear and often deteriorate over time as the photophysical properties change. To address this issue, conjugated polymers with pendant or end-capping fluorophores have been synthesized.[18] In addition, a supramolecular copolymer approach that enables fluorescent components to be randomly mixed has recently been reported.[19] We envisage that our IMWs will be an alternative to these protocols in that phase separation does not occur when the IMWs are blended since all the polymers are sheathed with the same cyclic side chains regardless of the conjugated backbones. To test this idea, a solution of **P1**/**P3** (1:1 wt/wt) was spin-coated onto glass plates, and we found that a homogeneous transparent film without any light scattering was formed (transmittance at 800 nm (T_{800}) > 99 %, thickness = 100 nm). In contrast, the T_{800} values of **P1**/polystyrene (**PS**: amorphous polymer) and **P1**/**P3HT** (crystalline polymer) blended films decreased slightly to 95 % (60 nm thick) and 92 % (60 nm thick), respectively, suggesting the formation of heterogeneous structures. In fact, atomic force microscopy (AFM) images of the films clearly showed phase separation in the **P1**/**PS** and **P1**/**P3HT** films, whilst that of the **P1**/**P3** film was uniformly flat (Figure 3). Furthermore, even after annealing (100 °C for 3 h: Figure 3 b or RT for 3 months: Figure S3), we did not observe any phase separation in the **P1**/**P3** film. These observations indicate that no discrimination occurs with our IMWs and there is no phase separation in the blended films. We deduced that the Flory–Huggins parameters of our IMWs blends are small owing to not only their structural similarity but also the intrinsically weak interpolymer interaction, although this expectation is still preliminary in the absence of consideration of the molecular weights.

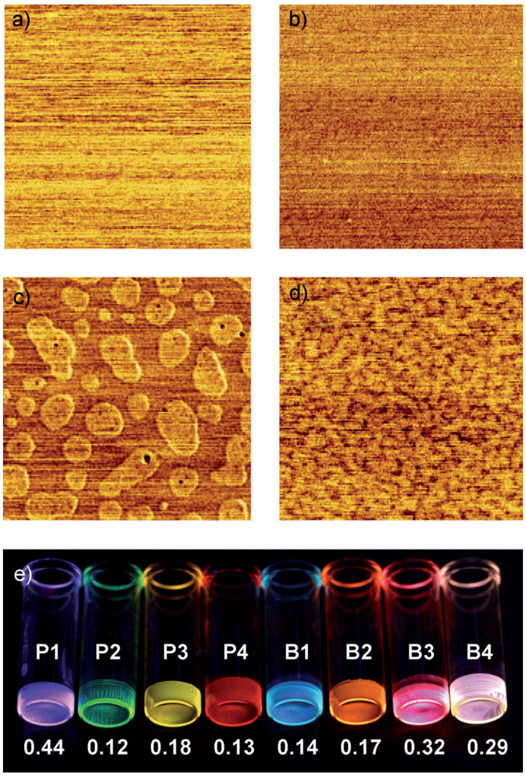

Figure 3. AFM phase images of the **P1**/**P3** blend a) before and b) after annealing at 100 °C for 3 h and the c) **P1**/**PS** and (d) **P1**/**P3HT** polymer blends; 2 μm × 2 μm. e) Photographs of the films of **P1**–**P4** and blend films **B1**–**B4** taken under UV (365 nm) illumination. The blending ratios **P1**/**P2**/**P3**/**P4** of **B1**, **B2**, **B3**, and **B4** are 100/10/0/0, 0/0/100/5, 100/0/0/5, 200/0/3/1, respectively. The polymer solutions were dried in glass vials and the films were formed at the bottom of the vials.

By taking advantage of the mutual compatibility of our IMWs, we mixed the IMWs to mix their fluorescence in the film state. Since fluorescence of **P1** to **P4** covers the entire visible spectrum, combinations of them can in principle generate any fluorescence color, and in fact, sky-blue (**B1**), orange (**B2**), pink (**B3**), and even white (**B4**) fluorescence were prepared (Figure 3 e and S4). For example, the white emission (CIE coordinate: [0.33, 0.34]; CIE = commission internationale de l'éclairage) was obtained by mixing **P1**, **P3**, and **P4** at a ratio of 200:3:1 (molar ratio of the repeating units). Considering that **P1** has the highest $\Phi_{F(film)}$ and is mainly excited in the mixture (λ_{ex} = 338 nm), excited energy is transferred from **P1** to **P3** and **P4**. This notion was indeed supported by additional experiments as described in the Supporting Information; for example, the fluorescence intensity and lifetime of **P1** decreased with blending **P3** (Figure S5). All the blended films retained reasonable $\Phi_{F(film)}$ values as indicated in Figure 3 e, from which we infer that the acceptor polymers can act as an energy sink (a dead end of the energy migration) in the polymer blends and thus do not decrease the total $\Phi_{F(film)}$ significantly.[20] In fact, **P4** in the **P1** matrix showed a better $\Phi_{F(film)}$ than the pure **P4** film (Figure S6). Importantly, the preparation of these homogeneous fluorescent films was reproducible and independent of the film preparation conditions (solvents and temperature), and the fluorescence color was stable for more than three months at room temperature.

Another intriguing physical property of our IMWs was revealed during differential scanning calorimetry (DSC) measurements (Figure 4 a; −50 to 300 °C, three cycles). In the first scan, the as-synthesized polymers showed relatively low melting points, and in the subsequent scans, the glass transition at around 20–60 °C was observed. Interestingly, after the measurements, plastic-like transparent lumps of the IMWs were recovered, which did not show any X-ray diffraction peaks (data not shown), indicating the amorphous nature of our IMWs. In addition, ^{1}H NMR spectra of the recovered materials confirmed no decomposition of the polymer structures.[21] Thus, our IMWs are thermoplastic quite unlike common CPs; accordingly, we explored the possibility of thermal processing. A drop-cast film of **P3** prepared on a Teflon plate was thermally annealed at 80 °C for 30 minutes, peeled off the substrate, and then dried overnight, thereby we obtained a fluorescent flexible self-standing film (Figure 4 b). A small piece of the film (80 μm thick and 5 mm wide) could sustain a weight of more than 200 g (> 5 MPa of tensile stress), was stretchable (> 300 % of tensile strain), and even foldable without the formation of any cracks (Figure 4 c and S7–9). Given the relatively low molecular weight and weak interpolymer interactions of our IMWs, the mechanical strength is remarkable. We assume that the internal free volume between the repeating units along the shish-kebab-like structure can physically interlock the polymer backbones, as has been reported by Swager, Thomas, and co-workers[22] for their triptycence-containing

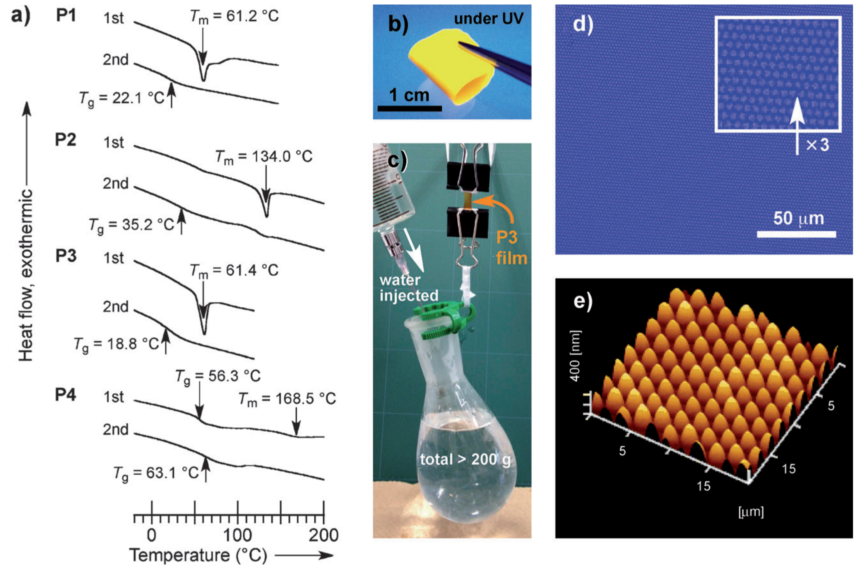

Figure 4. a) The first and second heating traces of the DSC thermograms of **P1**, **P2**, **P3**, and **P4**. Photographs of b) the fluorescent flexible self-standing film of **P3** and c) the same film sustaining a weight of more than 200 g (snapshots are shown in Figure S9). d) Fluorescence microscopic and e) AFM height images of the patterned **P1** film.

polyesters (Figure S10). In addition, we also attempted thermal patterning of the IMWs using a silicon mold with hexagonally arrayed holes ($\phi = 1.5$ µm). A spin-coated film of **P1** was pressed with the mold at 100 °C and 80 MPa for 20 minutes and then cooled to room temperature (Figure 4 d,e and Figures S11 and S12). The patterned structure showed structural coloration due to Bragg reflection, which indicates that the periodic structure covered a large area (5 mm × 5 mm). In addition, strong fluorescence was observed after the patterning process, and such highly fluorescent periodic structures could find potential use as a gain medium for lasing.[23,24] Importantly, these mechanical and thermal properties can be modified by the molecular design, for example, by simply changing the length and number of the solubilizing alkyl chains. Thus, **1** is a versatile building unit that can provide a variety of IMWs with tunable photophysical and mechanical properties.

In conclusion, we have synthesized a family of IMWs based on a new monomer that is readily available and versatile to produce IMWs with a variety of conjugated systems. Our IMWs are 1) emissive in the entire visible region, even in the film state, 2) miscible, allowing the combination of various fluorescence colors, and 3) thermoformable, like conventional plastics. These features have been rarely developed for CPs and can be attributed to the unique three-dimensional architectures, which distinguish our polymers from other organic fluorescent materials reported previously.[1–7] Simple structural customization on the basis of **1** is expected to provide IMWs with a myriad of properties, which we believe will be useful in various plastic optoelectronic applications such as electroluminescence, sensors, and lasers.

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