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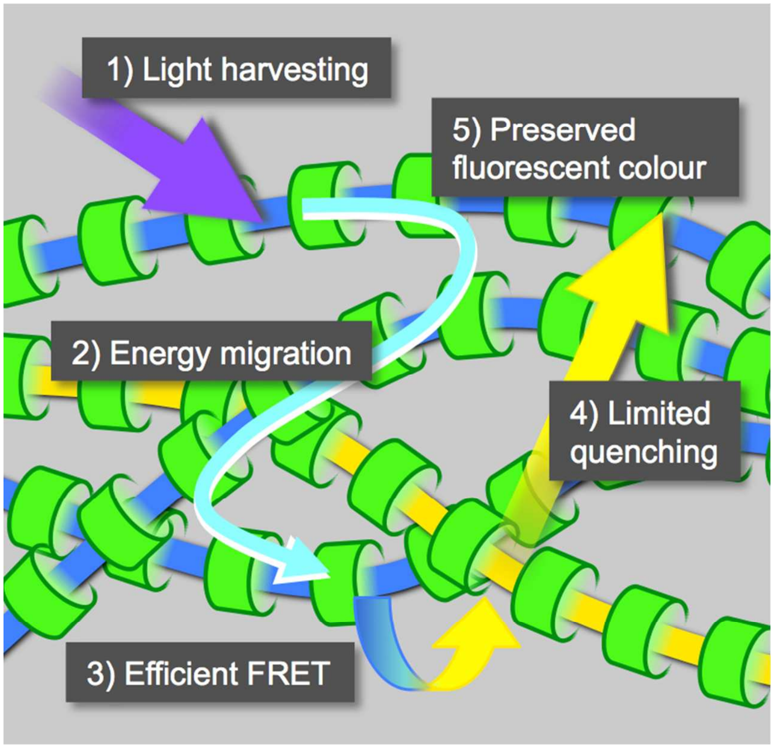

Conjugated polymers encapsulated by the identical cyclic sidechains afford an effective host-guest ensemble for designing fluorescent polymeric materials.

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Blending conjugated polymers without phase separation for fluorescent colour tuning of polymeric materials through FRET

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Fluorescence properties of conjugated polymer blends were investigated using a combination of excitation energy donor and acceptor conjugated polymers encapsulated by identical cyclic sidechains. Wearing this 'uniform', the polymers did not phase-separate in the blends. As such, these polymers provide an effective ensemble for designing fluorescent polymeric materials.

Conjugated polymer (CP) blends have attracted much attention in the fabrication of organic electronic devices, as they allow for tuning of the photophysical, electronic, and mechanical properties of polymeric materials.[1] Polymer blends can be briefly understood based on the free energy of mixing (ΔG_m) that determines whether a system undergoes phase-separation:

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where ΔH_m and ΔS_m are the enthalpy and entropy of mixing, respectively. For polymer blends, the contribution of ΔS_m is very small as compared with that of low-molecular weight materials. Consequently, polymer blends, in most cases, result in phase-separation ($\Delta G_m > 0$). The CP-based phase-separated structures are endowed with a variety of functions originating from the combination of the distinct polymeric domains, which offers many opportunities for the optimization of device performance.[1,2] However, control over the phase-separated structures—a process that involves a complex interplay between kinetics and thermodynamics—is yet to be established,[3] and this intricate process has, to a certain extent, hampered CPs from further applications.[1] As such, blending processes are optimized for the occurrence of phase-separation; alternatively, we wonder whether phase-separation is necessarily required (if avoidable). Polymer blends *without* phase-separation can be optically clear and thermodynamically stable. In addition, their photophysical properties are predictable as a function of the blending ratio and remain unchanged over time. Such CP-based materials will be useful for light-emitting applications such as sensors, lasers, and displays. To this end, the contribution of ΔH_m, which is particularly significant in CP-based blends due to strong π–π interaction, needs to be considered from a molecular design viewpoint.

Recently, a new type of CPs—so-called isolated CPs or insulated molecular wires—has attracted much attention.[4,5] Being interested in their unique structure-property relationships, we have designed and synthesized CPs of this kind based on a variety of conjugated backbones encapsulated by the same cyclic sidechains.[6] Owing to the absence of π–π staking, they are highly fluorescent even in the solid state. Remarkably, we found from AFM observations that these polymers were miscible. Such miscibility enabled facile mixing of fluorescence colours, which produced a white fluorescent polymeric film.[6] Although detailed photophysical studies on the polymer blends still remain to be conducted, we assert that their structural similarity and intrinsically weak inter-polymer interactions (i.e. the absence of π–π stacking) dictate the contribution of ΔH_m to be small compared to those in conventional CP blends. Intrigued by this unique structure-property relationship, we wanted to compare the photophysical properties of CP blends with and without phase-separation. In this communication, we report fluorescence properties of isolated CP blends. Though isolated CPs are expected to be good fluorescent materials, their blended systems have scarcely been investigated.[5b,c] We show that the absence of phase-separation in the isolated CP blends is indeed advantageous for the creation of CP-based fluorescent materials.

In this study, we used thiophene- (**A1** and **A2**) and fluorene-based CPs (**D1** and **D2**) (Chart 1) as a combination that promotes fluorescence resonance energy transfer (FRET). Isolated **A1**—a yellow fluorescent energy-accepting CP—was synthesized according to similar procedures reported previously by us (supplementary information).[6] **A2** is a reference polymer that has the same conjugated backbone as **A1** but is not sheathed. Poly(methyl methacrylate) (**PMMA**), polystyrene (**PS**), **D1**, and **D2**, were used as host polymer matrices for **A1** or **A2**. In the polymer blends, blue fluorescent isolated **D1** and unsheathed **D2** act as energy-donating CPs for **A1** and **A2** owing to the overlap between the donor fluorescence and acceptor absorption (Fig. S1, ESI‡).

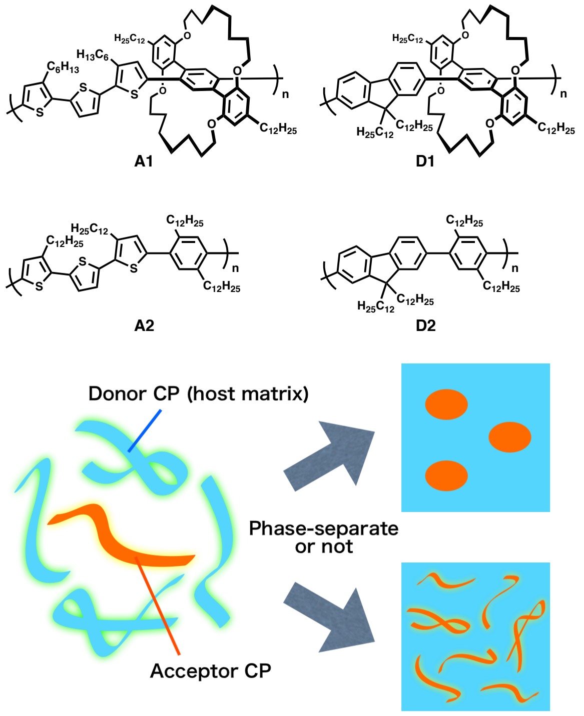

Chart 1 Structures of polymers used in this text and schematic illustration of the polymer blends with and without phase-separation.

Fig. 1 shows the absorption and fluorescence spectra of **A1** in diluted solution and pristine film. Because interpolymer electronic communication is prevented by the cyclic sidechains, **A1** shows virtually identical spectra in solution and film, displaying fluorescence quantum yields (Φ_f) of 0.36±0.01 and 0.15±0.01, respectively. As reported previously,[4-6] $\Phi_{f(film)}$s of isolated CPs are relatively high among fluorescent CPs but are not as high as $\Phi_{f(solution)}$s; this indicates that exciton migration through long-range dipole-dipole interactions among the isolated CP chains is not completely suppressed in the film. Notably, $\Phi_{f(solution)}$s of **A1** were independent of the solvent (Table S1 and Fig. S2, ESI‡), indicating that Φ_f of **A1** is not significantly affected by the polarity of the matrix. Therefore, changes in $\Phi_{f(matrix)}$ of **A1** in the different polymer matrices (**PMMA**, **PS**, **D1**, or **D2**, see below) can be attributed not to the difference in the refractive indices of these polymer matrices but to the difference in the local concentration (i.e. phase-separation) of **A1** in the blends.

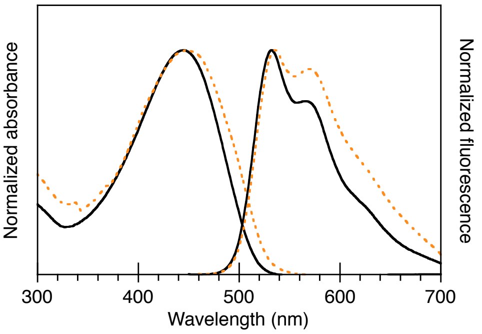

Fig. 1 Absorption and fluorescence spectra of **A1** in solution (black lines, dichloromethane) and film (dotted orange lines). λ_{ex} = 445 and 447 nm for solution and film, respectively.

Polymer blends of **A1/D1**, **A1/PMMA**, **A1/PS**, and **A2/D1** systems were investigated by AFM (Fig. S3, ESI‡). **A1** was not miscible with **PMMA** or **PS**. In contrast, **A1** and **D1** appeared to be miscible as we did not observe any phase-separated morphology in the blended films, probably because both polymers are sheathed by the identical cyclic sidechains. In fact, unsheathed **A2** underwent phase separation with sheathed **D1**. This assertion will be further supported by the photophysical studies discussed below.

Fluorescence spectra of sheathed **A1** and unsheathed **A2** were measured in different media as a function of concentration (Fig. S4, ESI‡). The fluorescence maxima of both polymers were unchanged upon concentration in toluene solution (Fig. 2, black marks). As can be expected from the result of Fig. 1, the fluorescence spectra of **A1** were insensitive to concentration owing to its isolation even at very high concentrations. In contrast, the fluorescence maximum of **A2** in a **D1** matrix significantly changed upon increasing concentration (Fig. 2, orange diamonds, Fig. S4b, ESI‡). The red-shifted fluorescence observed under higher concentrations indicates that **A2** self-assembles and phase-separates in **D1** host matrix.

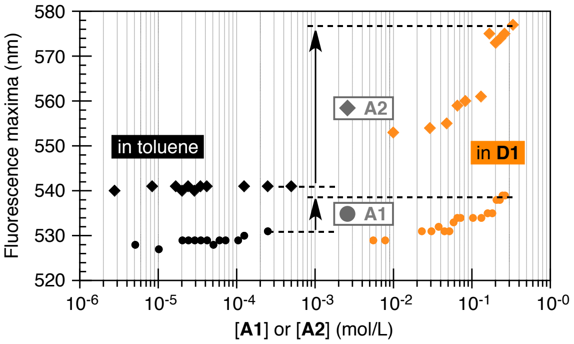

Fig. 2 Plots of fluorescence maxima of **A1** (filled circle) and **A2** (filled diamonds) as a function of their concentrations measured in a toluene solution (black) and **D1** matrix (orange). λ_{ex} = 480 and 450 nm for **A1** and **A2**, respectively. Fluorescence spectra are shown in (Fig. S4, ESI‡).

Next, we evaluated Φ_f of **A1** in different media (Fig. 3). In toluene, $\Phi_{f(solution)}$ was rapidly decreased upon increasing the **A1** concentration, which is thought to be due to a dynamic quenching process that accompanies collisional encounters between **A1** chains. When diluted in **PS** and **D2** matrices, **A1** showed relatively high $\Phi_{\mathrm{f(matrix)}}$s; however, the values abruptly decreased upon increasing the **A1** concentration. Lower $\Phi_{\mathrm{f(matrix)}}$s under concentrated conditions are consistent with $\Phi_{\mathrm{f(film)}}$ of the pristine **A1** film; therefore, we conclude that phase-separation was induced above the concentration at which Φ_{f} discontinuously deteriorated. In **PMMA**, $\Phi_{\mathrm{f(matrix)}}$ was low throughout the concentration range investigated. We infer that **A1** and **PMMA** are not miscible and phase-separate even at lower concentrations; in fact, **A1** was not soluble in ester solvents such as ethyl acetate. In contrast to the above observations, $\Phi_{\mathrm{f(matrix)}}$ of **A1** in the **D1** matrix was maintained at moderate values even at higher concentrations (Fig. 3, orange circles). The gradual decrease in Φ_{f} is probably due to physical contacts between **A1** chains in the blend, which give rise to a sort of static quenching process. This result indicates that transition behaviours like phase-separation were not induced in the **A1**/**D1** blend.

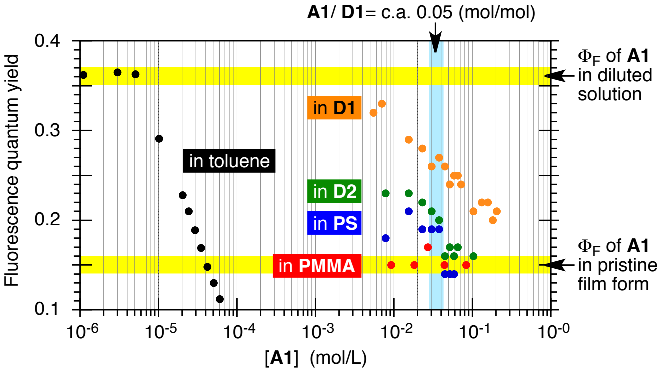

Fig. 3 Plots of fluorescence quantum yields of **A1** measured in different matrices as a function of concentration†: in toluene solution (black), and in **D1** (orange), **D2** (green), **PS** (blue), and **PMMA** matrices (red). $\lambda_{\mathrm{ex}} = 480$ nm.

Lidzey and co-workers investigated a polymer blend that comprises CP and **PS** by using scanning near-field optical microscopy (SNOM)[3a] and found that in the **PS**-rich phase, interchain exciton diffusion between CPs is significantly suppressed by dilution. Similarly, we expect that interchain exciton diffusion among **A1**s can be prevented in **D1** because **A1** is not locally concentrated (no phase-separation). Therefore, **A1** can have a better Φ_{f} in the **D1** matrix than in the pristine film and other host matrices.

Because the absorption of **A1** overlaps well with the fluorescence of **D1** (Fig. S1, ESI‡), FRET can occur from **D1** to **A1** in their polymer blends. Fluorescence spectra of **A1**/**D1** blends with different molar ratios are shown in Fig. S5, ESI‡. Note that **D1** was selectively excited under the measurement conditions ($\lambda_{\mathrm{ex}} = 338$ nm). With the addition of the **A1** acceptor, the fluorescence of the **D1** donor was significantly quenched while the fluorescence of **A1** appeared. The excitation spectrum ($\lambda_{\mathrm{moni}} = 580$ nm) of the blend suggested a contribution of the excited **D1** to **A1** fluorescence. In addition, the fluorescence lifetime of **D1** decreased with the addition of **A1**, evidencing the energy transfer (Fig. S7, ESI‡). Since the fluorescence spectra of **A1** and **D1** are well resolved and able to be integrated individually, the number of photons emitted from each polymer can be determined (Fig. S8, ESI‡). This number was then divided by the number of photons absorbed by **D1** and is plotted in Fig. 4. The values for **D1** correspond to Φ_{fD}, and changes in Φ_{fD} yield FRET efficiency ($\phi_{\mathrm{FRET}} = 1 - \Phi_{\mathrm{fD}}/\Phi_{\mathrm{fD0}}$, Fig. 4, green line). On the other hand, we defined the values for **A1** as the fluorescence efficiencies of **A1** (ϕ_{fA}). Here, ϕ_{fA} can be described as $\phi_{\mathrm{FRET}}\Phi_{\mathrm{fA(in\ D1)}}$, and as discussed above, $\Phi_{\mathrm{fA(in\ D1)}}$ is larger than $\Phi_{\mathrm{fA(film)}}$ (Fig. 3). Consequently, as indicated by the yellow bar and orange line in Fig. 4, the blended systems showed better fluorescence efficiency than isolated CP film when ϕ_{FRET} was high (**A1**/**D1** > 0.02).

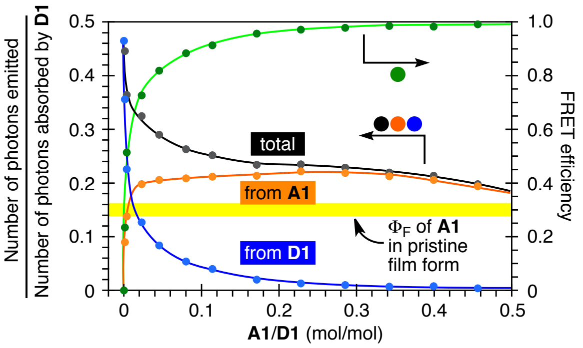

Fig. 4 Plots of the fluorescence (left *y*-axis) and FRET (right *y*-axis) efficiencies of the **A1**/**D1**. The *x*-axis, mol/mol ratio, is in terms of monomer units. Colour lines act as eye-guilds, while the yellow bar indicates the Φ_{f} of **A1** in the pristine film. $\lambda_{\mathrm{ex}} = 338$ nm.

We note that such a photophysical scheme—sensitization via FRET and suppression of quenching by 'dilution' effects in a donor host—can be readily realized with low-molecular weight materials because their large entropy of mixing allows for facile blending of a donor/acceptor ensemble.[7] Some of these systems have found application in efficient organic light-emitting devices.[8] In this context, we have succeeded in realizing the same scheme using CPs through preventing dissimilar conjugated backbones from phase-separation by encapsulation.

In summary, on the basis of the microscopic and spectroscopic studies, we have shown that isolated CPs sheathed by the identical cyclic sidechains make an effective host-guest ensemble for designing fluorescent polymeric materials. The fluorescence scheme established in the blend is as follows: (1) light-harvesting by **D1** with large absorption; (2) energy migration among **D1** units; (3) FRET from **D1** to **A1**; (4) suppression of the quenching process of **A1** by the dilution effect; and (5) preservation of the fluorescence colour of **A1** owing to the encapsulation. We believe this material design concept demonstrates a new potential of isolated CPs and will find various applications in sensors, lasers, and displays.

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Notes and references

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† This paper is dedicated to Professor Seiji Shinkai on the occasion of his 70th birthday.

‡ Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

§ Densities of **PS** and **PMMA** are 1.0 and 1.18 g/cm^3, and those of **A1**, **A2**, **D1**, and **D2** are assumed to be 1.0 g/cm^3. Absolute fluorescence quantum yields were determined by using integral sphere system.

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