

Energy and Electron Transfer from Fluorescent Mesostructured Organosilica Framework to Guest Dyes

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1. Supplementary Spectroscopic, X-Ray Diffraction, and Microscopic Data

Figure S1 shows the UV-vis absorption and fluorescence spectra of the solutions of the PBI dyes **1–4** in THF. The spectral shapes were very similar due to the same chemical structure of the PBI chromophore. The fluorescence quantum yields (Φ) of the PBI dyes were higher than 0.7 except for dye **4** exhibiting self-quenching with amino groups. However, protonation of the amino groups by the addition of a small amount of HCl aq. resulted in large enhancement of Φ from 0.03 to 0.83.

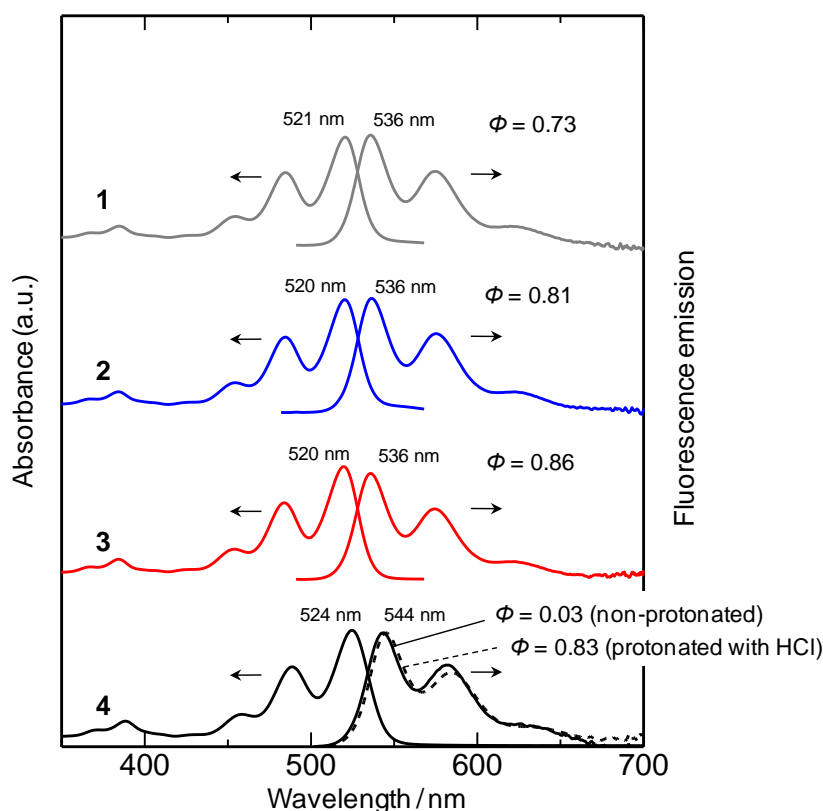


Figure S1. (a) UV-vis absorption and (b) fluorescence (excited at $\lambda = 490$ nm) spectra of solutions of **1–4** in THF.

Figure S2a show the UV-vis absorption spectrum of the **Brij76-TPPy/3** film containing 5 mol% of **3**. The absorption maximum wavelength of the doped dye is 519 nm, which is almost the same with that in a THF solution (520 nm). Upon direct excitation of the PBI moiety at $\lambda = 490$ nm, the dye **3** exhibited monomer-band emission as shown in Figure S2b. These results indicate that the dye **3** is well dispersed in the host **Brij76-TPPy** film without aggregation.

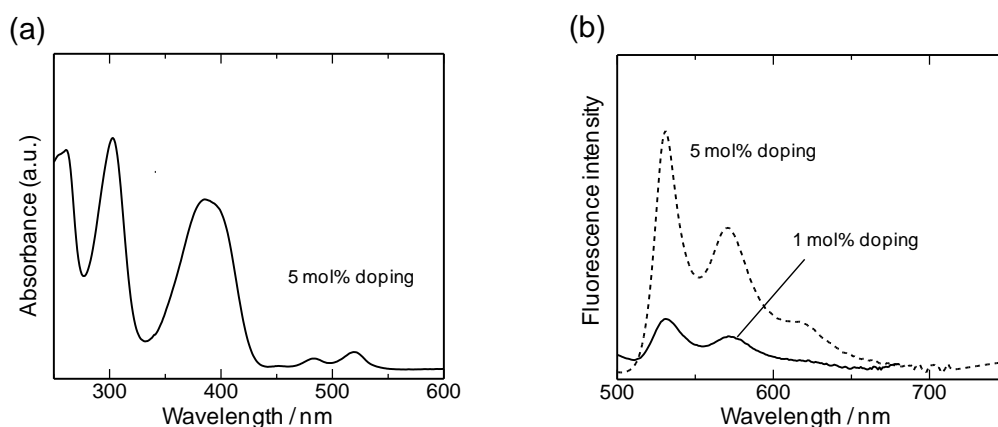


Figure S2. (a) UV-vis absorption and (b) fluorescence (excited at $\lambda = 490$ nm) spectra of **Brij76-TPPy/3** films.

Figure S3 shows a transmission electron microscope (TEM) image of **P123-TPPy** and XRD patterns of the host films, **P123-TPPy**, **Brij76-TPPy**, and **P123-silica**. For the TEM image of **P123-TPPy** (annealed at 200 °C for 6h and immersed in ethanol to extract P123), we can see channel-like structures with a periodicity of ca. 6–9 nm (Figure S3a). As shown in Figure S3b–d, all the films have periodic mesostructures with d -spacing values of 5.6–10.5 nm. The TPPy-based films, **P123-TPPy** and **Brij76-TPPy**, exhibited several higher order diffraction peaks, which indicates that these films form a 2D hexagonal mesostructure.

Figure S4 shows optical microscope images of the **P123-TPPy** films containing PBI dyes **1–4** (5 mol%). We can see that only dye **1** forms micrometer-scale large aggregates observable under optical microscopy. Different distribution of the other three dyes (**2**, **3**, and **4**) is not distinguishable by optical microscopy.

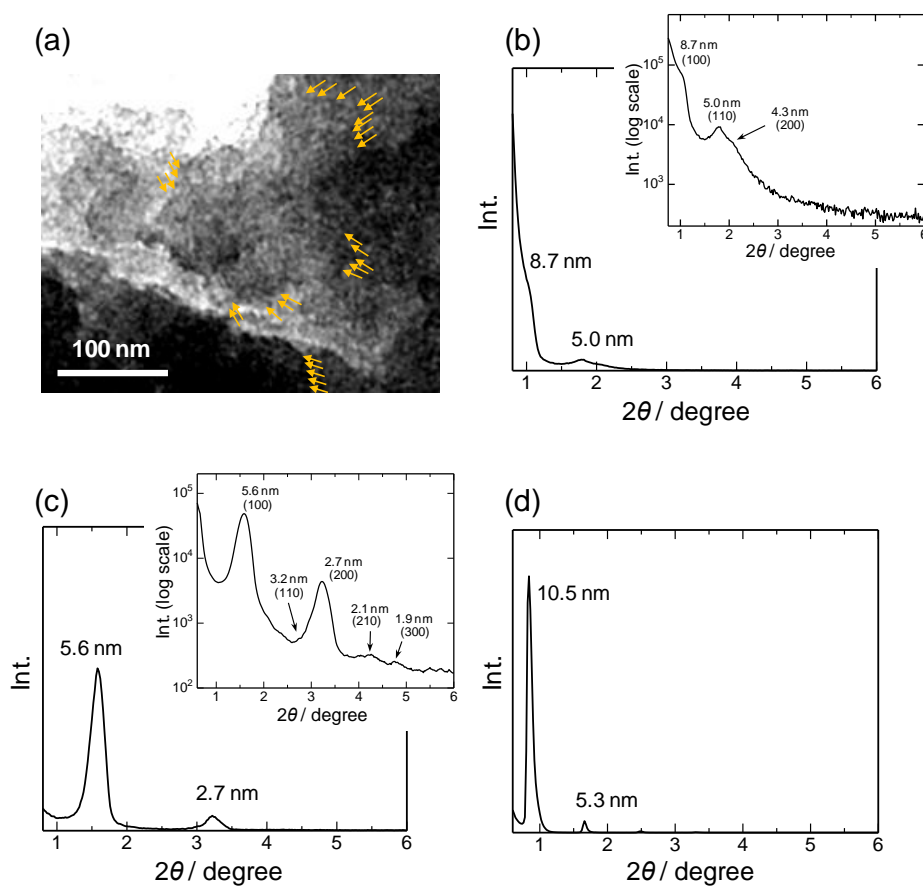


Figure S3. (a) TEM image of **P123-TPPy**. (b–d) X-ray diffraction patterns of mesostructured films: (b) **P123-TPPy**, (c) **Brij76-TPPy**, and (d) **P123-silica**.

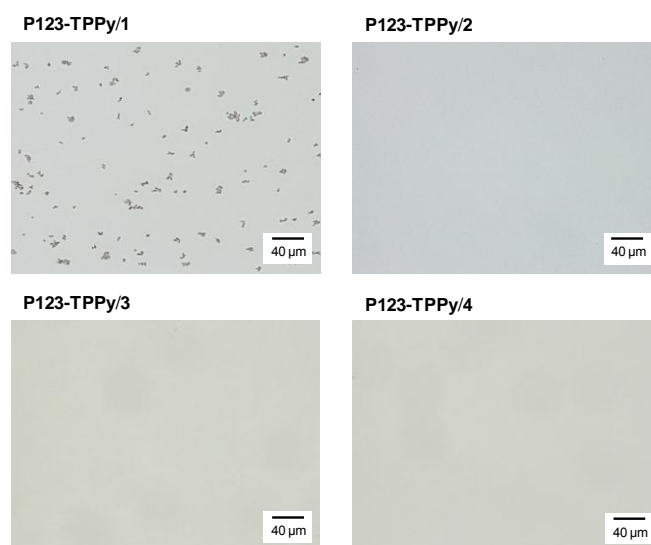


Figure S4. Optical microscope images of **P123-TPPy** films containing PBI dyes **1–4** (5 mol%).

2. Calculation of Critical Förster Radius

The critical Förster radius R_0 is expressed as equation (1):

$$R_0^6 = \frac{9000(\ln 10)\kappa^2\Phi_D I}{128\pi^5 N_A n^4} \quad (1)$$

Where Φ_D is the photoluminescence quantum yield of the energy donor (**P123-TPPy**), n is the refractive index of the film, N_A is Avogadro's number, κ^2 is an orientation factor ($\kappa^2 = 2/3$ for randomly oriented dipoles), and I is the overlap integral of the overlap function, $J(\lambda)$, over the full spectrum. From the spectral overlap between the emission of **P123-TPPy** and absorption of the PBI dye, $J(\lambda)$ and I are calculated using the equations (2) and (3):

$$J(\lambda) \cong \lambda^4 \times PL_{\text{corr}}(\lambda) \times \varepsilon(\lambda) \quad (2)$$

$$I = \int J(\lambda) d\lambda \quad (3)$$

Where $PL_{\text{corr}}(\lambda)$ is the fluorescence intensity of **P123-TPPy** as a function of λ , corrected to be

$$\int PL_{\text{corr}}(\lambda) d\lambda = 1 \quad (4)$$

and $\varepsilon(\lambda)$ is the molar decadic extinction coefficient of the PBI dye as a function of λ ($\varepsilon = 5.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at $\lambda = 520 \text{ nm}$). In the present study, an absorption spectrum of the PBI dye measured in a dilute THF solution was used.

Figure S5 shows the overlap function $J(\lambda)$ for the combination of **P123-TPPy** (energy donor) and **2** (energy acceptor). The overlap integral was calculated to be $I = 9.93 \times 10^{-14} \text{ cm}^3 \text{ M}^{-1}$. Assuming $\Phi_D = 0.70\text{--}0.75$ and $n = 1.5$, the Förster radius R_0 is approximately 4.5 nm. Calculation of R_0 using absorption spectra of dyes **1**, **3**, and **4** gave almost the same value.

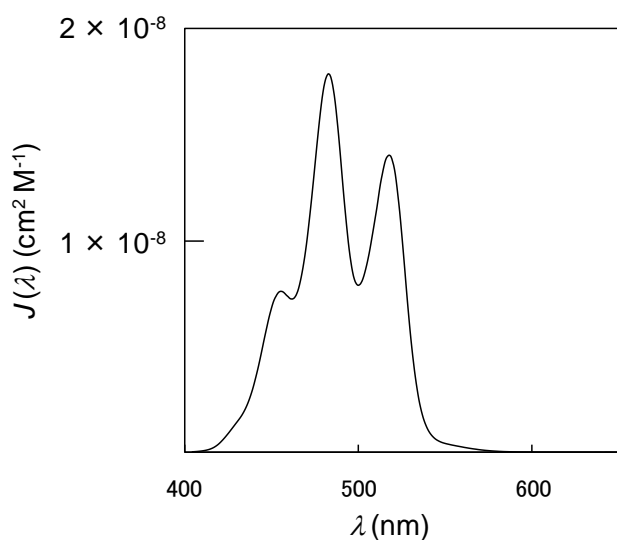


Figure S5. Overlap function $J(\lambda)$ of **P123-TPPy** (energy donor) and **2** (energy acceptor) calculated using the spectra shown in Figure 3.

3. Supporting Data for Transient Absorption Spectroscopy

Figure S6 shows the absorption spectra of TPPy cationic radical (TPPy^{•+}) and PBI anionic radical (PBI^{•-}), which were prepared by chemical oxidation or reduction of a corresponding reference compound, respectively.

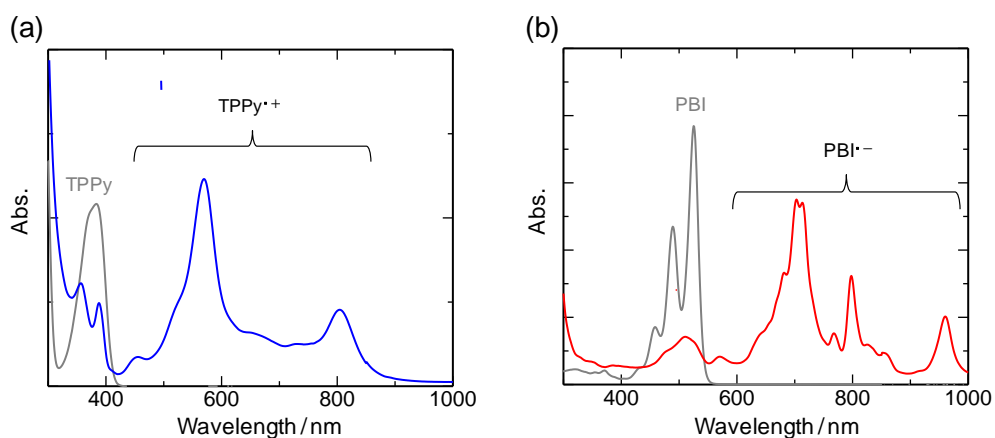


Figure S6. UV-vis spectra of (a) a TPPy cationic radical prepared by oxidation of 1,3,6,8-tetraphenylpyrene with SbCl_5 in CH_2Cl_2 and (b) a PBI anionic radical prepared by reduction of N,N' -bis(3-pentyl)perylene tetracarboxylic acid bisimide with hydrazine monohydrate in DMF.

Figure S7 shows the optical properties of a **P123-silica/4** film (P123/4 = 100/8.7, w/w) containing no TPPy bridging group. The λ_{max} of the film is 492 nm, which is 32 nm shorter than that of the solution of **4** in THF (524 nm), and the fluorescence spectrum shows a broad excimer-band-like emission at $\lambda = 608$ nm. These results indicate that the dye molecules partially aggregate in the film due to the excessive doping.

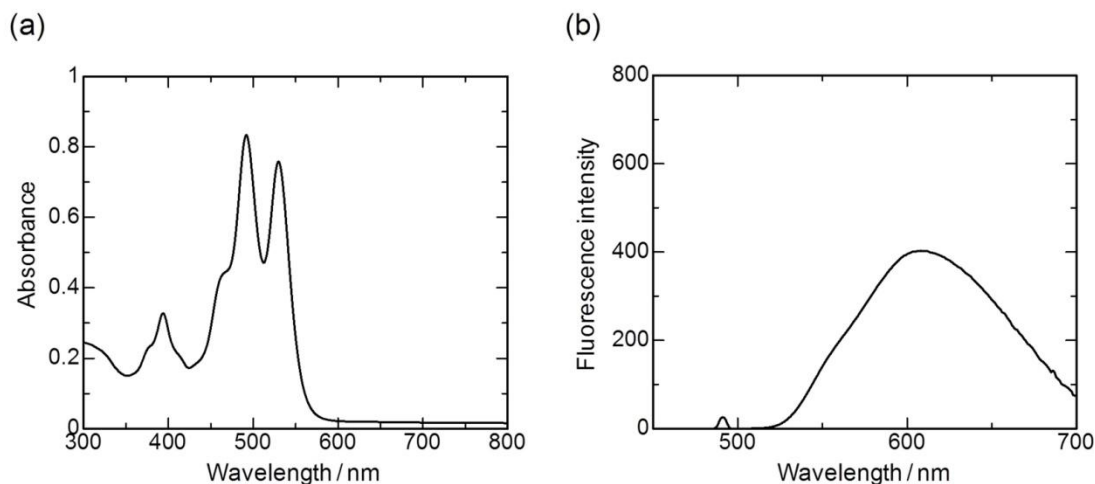


Figure S7. (a) UV-vis absorption and (b) fluorescence (excited at $\lambda = 490$ nm) spectra of the **P123-silica/4** film (P123/4 = 100/8.7, w/w).

The transient absorption spectra of the excessively-doped **P123-silica/4** film are shown in Figure S8. A broad absorption band at $\lambda = 765$ nm appeared, accompanied with an intense bleaching observed at $\lambda = 490$ and 532 nm. The absorption band at $\lambda = 765$ nm is attributable to the excited species of the partially formed dye aggregates.

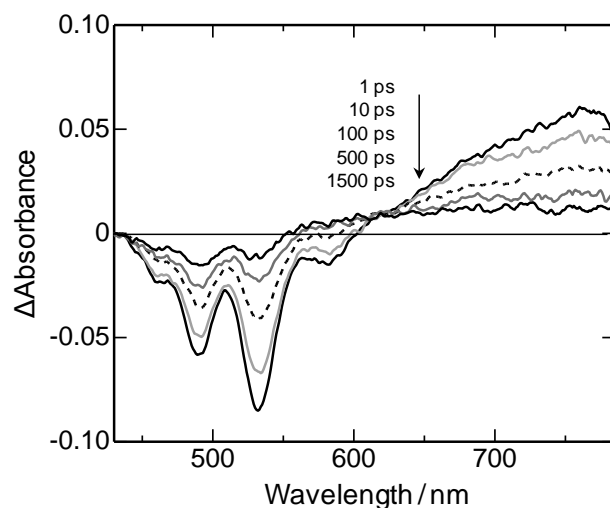


Figure S8. Transient absorption spectra of the **P123-silica/4** film after excitation at $\lambda = 530$ nm.