

Supporting Information

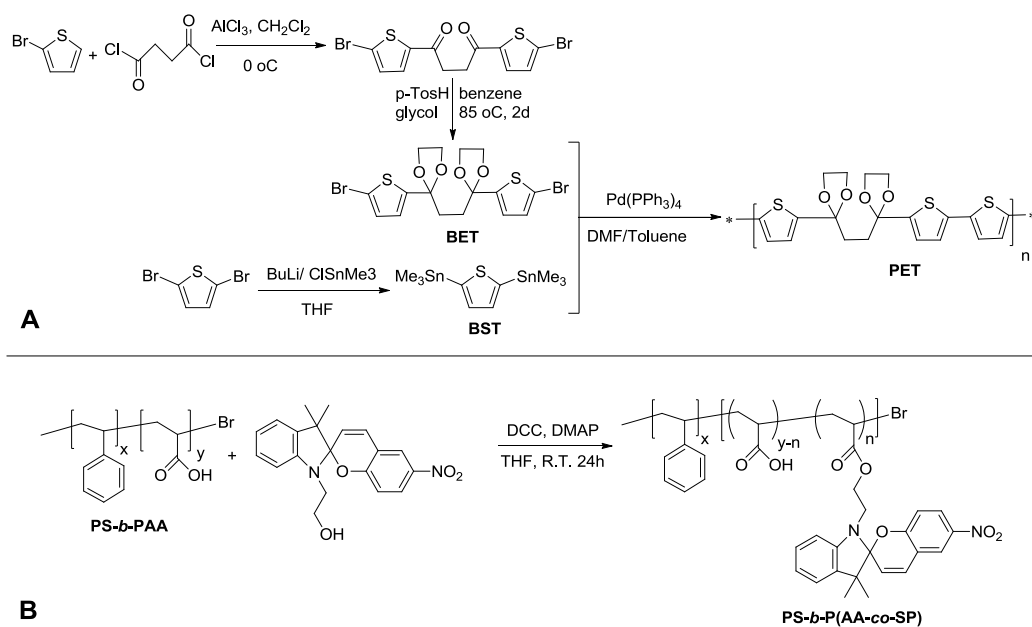
One-pot Fabrication of Amphiphilic Photoswitchable Thiophene-Based Fluorescent Polymer Dots†

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Scheme S1. Synthesis of polythiophene derivative PET (A) and amphiphilic photochromic copolymer PS-*b*-P(AA-co-SP) (B).

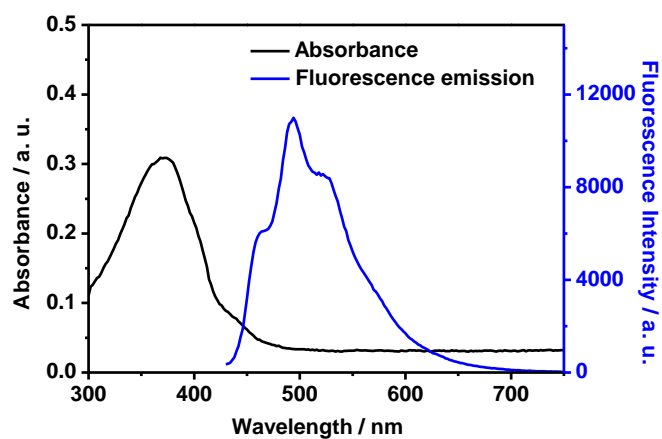


Figure S1. Absorption and fluorescence emission spectra of PET in diluted THF solution (0.5 mg mL^{-1}).

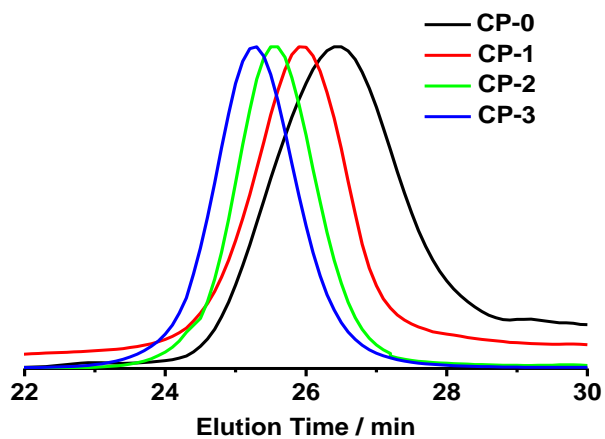


Figure S2. GPC traces of photochromic copolymers (CP-1, CP-2, CP-3, Table 1) and their initial copolymer (CP-0, Table 1).

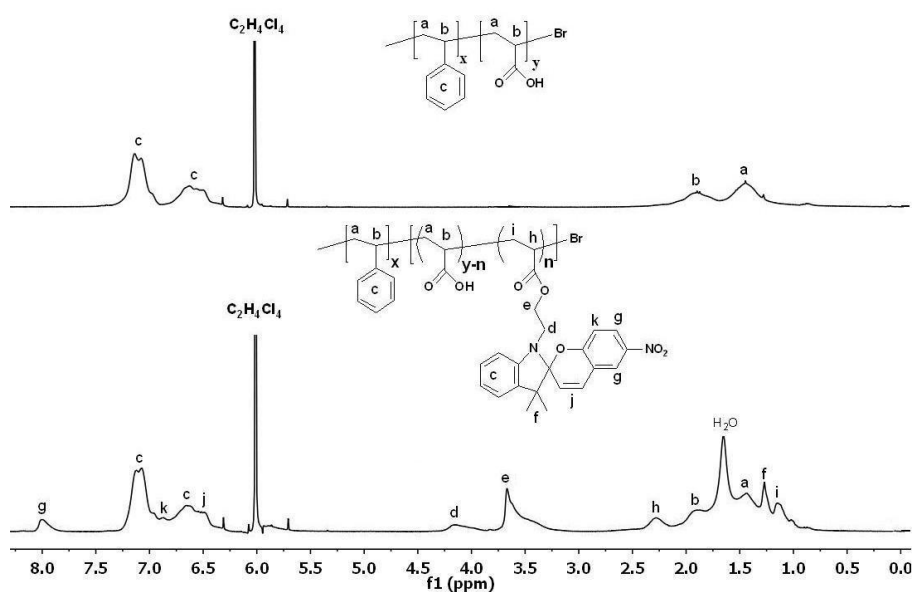


Figure S3. ^1H NMR spectra of the initial copolymer $\text{PS}_{50}\text{-}b\text{-PAA}_{47}$ (top) and target photochromic copolymer $\text{PS}_{50}\text{-}b\text{-P}(\text{AA}_{36}\text{-}co\text{-SP}_{11})$ (bottom).

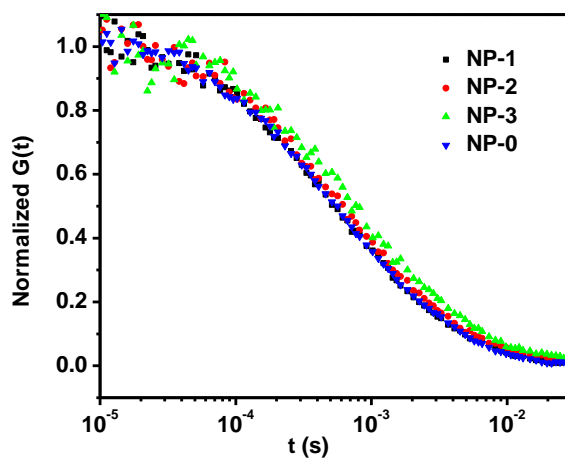


Figure S4. Normalized autocorrelation curves for the diffusion of Pdots (NP-0 to NP-3) in bulk water.

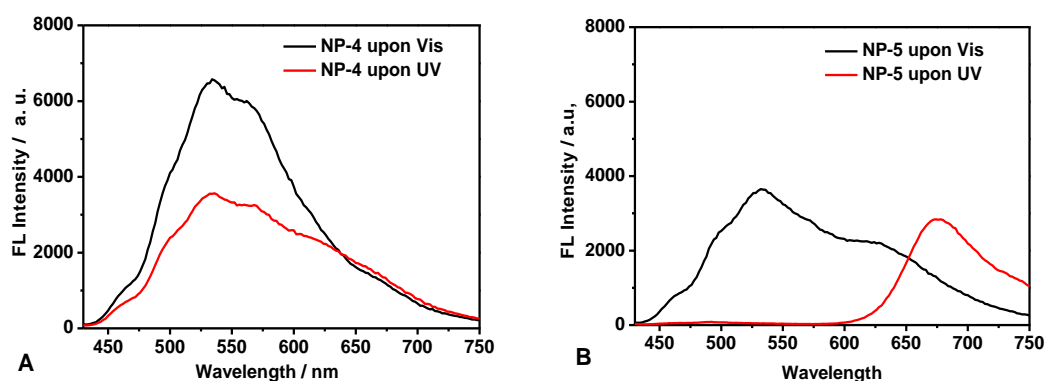


Figure S5. Fluorescence emission spectra ($\lambda_{\text{ex}} = 420 \text{ nm}$) of two Pdots dispersion samples (Table 2), NP-4 (A) and NP-5 (B) upon UV/visible light irradiation.

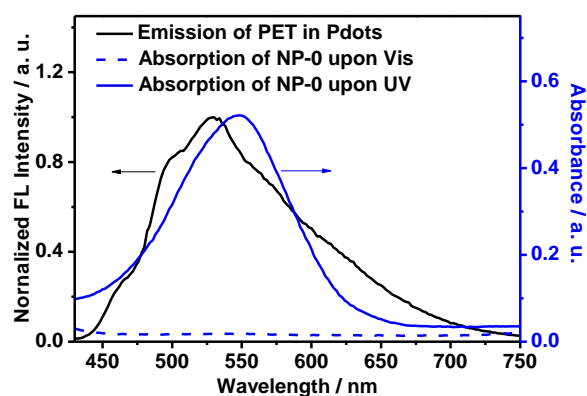


Figure S6. Fluorescence emission spectra of PET (black solid) and absorption spectra of the SP state (blue dashed) and MC state (blue solid) of spiropyran moieties in Pdots.

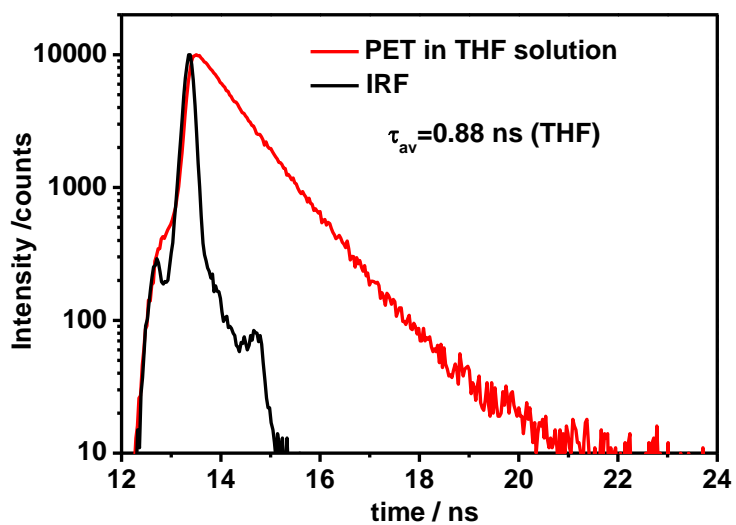


Figure S7. Fluorescence decay traces of PET in THF solution ($\lambda_{ex} = 415$ nm, wavelengths of the detection: 540 nm).

1. Determination of fluorescence quantum yield of the donor PET

The quantum yield can be described as follows:

$$\Phi_D = \Phi_S \times \frac{F_D}{F_S} \times \frac{A_S}{A_D} \times \frac{(n_D)^2}{(n_S)^2}$$

where Φ_S is the fluorescence quantum yield of the standard (rhodamine B in ethanol, 0.65, 25 °C)^[2], F_D and F_S are the integral areas of the fluorescence intensity of the donor and the standard at the same excitation wavelength, respectively; A_D and A_S are the absorbances of the donor and the standard at the defined excitation wavelength, respectively; n_S and n_D are the refractive indices at 25 °C of the solvent of standard (ethanol) and the matrix of donor (mainly PS), respectively.

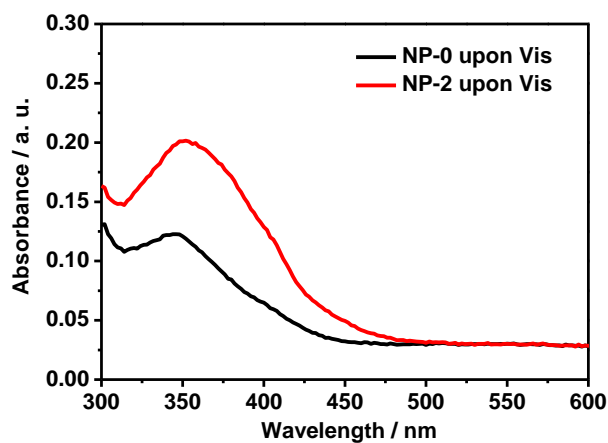


Figure S8. Absorption spectrum for Pdots dispersion samples NP-0 and NP-2 (Table 2).

To determine the quantum yield of PET in the Pdots, we first need to measure the actual absorbance of PET (at 450 nm) in the Pdots. In order to eliminate the effect caused by the photochromic copolymer in the Pdots, we also measured the absorption spectrum for the photochromic copolymer dispersion NP-0 (without PET), and the actual absorbance for PET at 450 nm can be obtained by subtracting the absorbance of the neat NP-0 dispersion at 450 nm from the apparent absorbance value of the photoswitchable Pdot dispersion NP-2 (Figure S8).

The Φ_D of the photoswitchable Pdot dispersion was calculated to be 0.15.

2. Calculation of the Förster radii (R_0)

The Förster's distance or critical distance R_0 is the characteristic distance between the donor and the acceptor, at which the efficiency of energy transfer is 50%. The magnitude of R_0 is dependent on the spectral properties of the donor and acceptor molecules. If the wavelength λ is expressed in nanometers, then $J(\lambda)$ is in units of $M^{-1}cm^{-1}nm^4$ and the Förster distance, R_0 in angstroms (Å), is expressed as follows^[1-3] [Eq. (1)]:

$$R_0 = 0.2108 \times [K^2 \times \Phi_D \times n^{-4} \times J(\lambda)]^{1/6} \quad (1)$$

where K^2 is the orientation factor for the emission and absorption dipoles and its value depends on their relative orientation, n is the refractive index of the medium, and Φ_D is the quantum yield of the donor. $J(\lambda)$ is the overlap integral of the fluorescence emission spectrum of the donor and the absorption spectrum of the acceptor (Figure 6) [Eq. (2)]:

$$J(\lambda) = \int_0^{\infty} F_D(\lambda) \times \varepsilon_A(\lambda) \times \lambda^4 \times d\lambda \quad (2)$$

where $F_D(\lambda)$ is the fluorescence intensity of the donor in the absence of acceptor, $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor MC, λ is the wavelength. Under the current experimental conditions, the Förster distances (R_0) have been calculated assuming random orientation of the donor and acceptor molecules taking $K^2 = 2/3$, $n = 1.59$ (PS), and $\Phi_D = 0.15$ as listed in Table S1. For PET (donor) and MC (acceptor) we calculated $R_0 = 58.0 \text{ \AA}$. Energy transfer will be effective for $d \leq 87.0 \text{ \AA}$ (upper limit: $R_0 + 50\% R_0$).^[5]

Table S1. Calculated R_0 of the Donor-Acceptor pair

Donor	Acceptor	Φ_D^a	$J(\lambda)$ ($M^{-1}cm^{-1}nm^4$)	R_0	$D_{\text{effective}}^b$ (nm)
PET	MC	0.15	2.77×10^{16}	5.80	8.70

a: Rhodamine B in ethanol used as standard; b: Effective energy transfer distance ($R_0 + 50\% R_0$).

2. Calculation of the experimental energy transfer efficiency and estimation of the donor-acceptor distance

According to the Förster non-radiative energy transfer theory, the energy transfer efficiency E does not depend only on the distance (r) between the donor (PET) and the acceptor (MC), but also on the critical energy transfer distance (R_0) expressed by the following equation [eq (3)]:

$$E = \frac{R_0^6}{R_0^6 + r^6} \quad (3)$$

The FRET efficiency can be measured experimentally and is commonly defined as:

$$E = 1 - \frac{F_{DA}}{F_D} \quad (4)$$

Where F_{DA} and F_D is the maximum fluorescence intensity of the donor (PET in the Pdot dispersion) in the presence of the acceptor (MC form of the spiropyran moieties) or absence of acceptor (SP form of the spiropyran moieties), respectively.^[3]

By combining equation 3 and 4, we can obtain an expression [Eq. (5)] for the donor-acceptor separation distance for each sample, which can be experimentally determined from fluorescence data:

$$r = R_0 \left[\frac{(1-E)}{E} \right]^{1/6} \quad (5)$$

The calculated data are listed in Table 3 in the main text.

3. Estimation of N_A (number of spiropyran units residing around one donor within the effective energy transfer distance)

We need to assume that the distribution of spiropyran moieties or PET portions in the whole Pdot is homogeneous, and the existence or the distribution of the donor (PET) does not affect the distribution of the acceptor (spiropyran) and vice versa. The number of the acceptors (N_A) residing around one donor within the effective energy transfer distance (87.0 Å) can be regarded as the number of acceptors residing in a sphere with this donor as the center and with a radius of the effective energy transfer

distance (87.0 Å). Within this sphere, there is maybe more than one donor; however, all the acceptors are potentially available to receive the energy from the donor at the sphere center because the distance between all the acceptors and this donor are all within the effective energy transfer distance. In this study, N_A was estimated via the following equation:

$$N_A = \frac{N_{SP/PD} V_d}{V_N}$$

where V_N is the particle's volume, V_d is the volume of the sphere with its radius equivalent to the effective energy transfer distance (87.0 Å) and $N_{SP/PD}$ is the number of spiropyran moieties per particle.

References

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