

Supporting Information

One-pot synthesis of amphiphilic reversible photoswitchable fluorescent nanoparticles and their fluorescence modulation properties

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Synthesis of the PEO-R-MA-40 Macromonomer (in reference 1)

Bromoundecyl-THP Ether (**BU-THP**). DHP (0.35 mol) was added dropwise to a magnetically stirred solution of 11-bromoundecanol (0.1 mol), and toluenesulfonic acid monohydrate (1 mmol) dissolved in dried THF (50 ml) at 0°C. With further stirring for half an hour, the solution was kept at the ambient temperature and continuously stirred for 5 hours. THF and the excess DHP were then removed by a rotary evaporator. The residue was dissolved in ether and washed twice with saturated brine to remove p-toluenesulfonic acid monohydrate. The organic layer was dried overnight with magnesium sulfate and filtered. After evaporation of the ether, the yellowish liquid (98% yield) could be used directly for the following step.

α -Methoxy Poly(Ethylene oxide) undecyl THP Ether (**PEO-R-THP**). Finely-ground potassium hydroxide (0.03 mol) and bromoundecyl-THP ether (0.03 mol) were added to a magnetically stirred solution of poly(ethylene glycol) methyl ether (0.01 mol) in 100 ml of a

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mixed solvents of THF and benzene (1:1, v/v). The reaction mixture was stirred under nitrogen atmosphere for 24 hours and then filtered. After evaporation of THF and benzene, the residue was washed with ether to remove any excess bromoundecyl-THP ether. The white precipitate was washed with ether and then dissolved in distilled chloroform. The chloroform solution was further washed with brine to remove KOH as well as the unreacted PEG, and it was dried overnight with magnesium sulfate. After filtration, chloroform was evaporated off and the white solid product (80% yield) was further dried in a vacuum.

ω -Methoxy Poly (Ethylene Oxide) Undecanol (**PEO-R-OH**). A solution of PEO-R-THP (0.03 mol) in acidified (HCl) ethanol (pH 3.0) was stirred and refluxed in an oil bath for 4 hours. After evaporation of the ethanol, the residue was dissolved in distilled chloroform. It was washed three times with saturated brine and dried overnight by magnesium sulfate. The white solid product (90% yield) was obtained after evaporating the chloroform and dried to a constant weight in a vacuum oven.

ω -methoxy poly(Ethylene oxide) undecyl α -methacrylate (**PEO-R-MA-40**). To a magnetically stirred solution of PEO-R-OH (0.0065 mol) and 4 ml triethylamine in 40 ml of dried CH_2Cl_2 at 0°C, methacryloyl chloride (0.0325 mol) was added dropwise under nitrogen over a period of half an hour. A solid salt was immediately formed, and it was kept in the ice bath for another hour. The mixture was further stirred overnight at room temperature. After the excess methacryloyl chloride, CH_2Cl_2 and triethylamine were removed, the residue was dissolved in distilled chloroform and washed twice with saturated sodium bicarbonate solution followed by saturated brine. A solid product was recovered from the chloroform solution after rotary evaporation. The pure product of PEO-R-MA-40 (75% yield) was

obtained by reprecipitating the crude product three times from chloroform and ether.

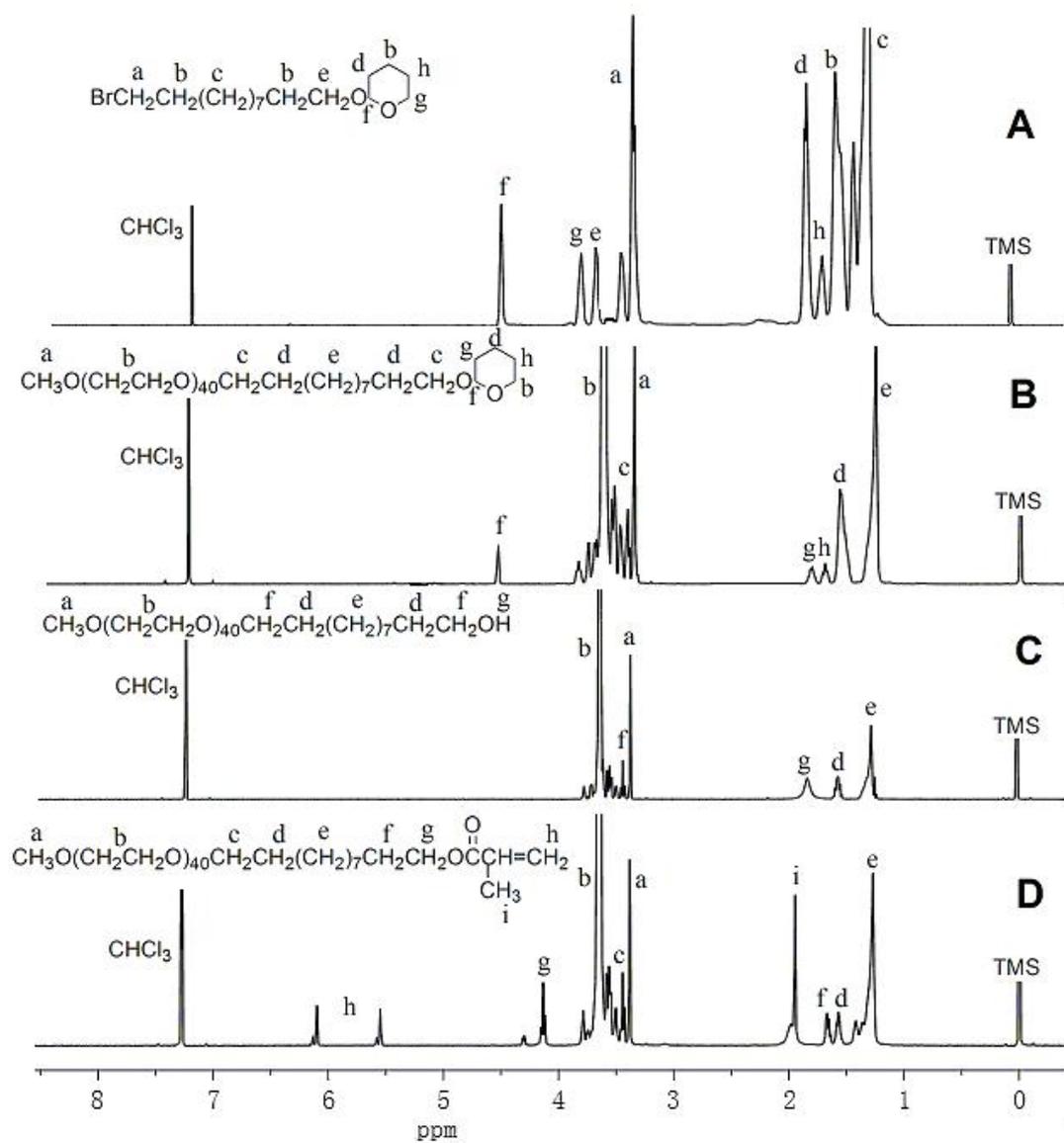


Fig. S1 ^1H NMR spectrum of the intermediate compounds and PEO-R-MA-40.

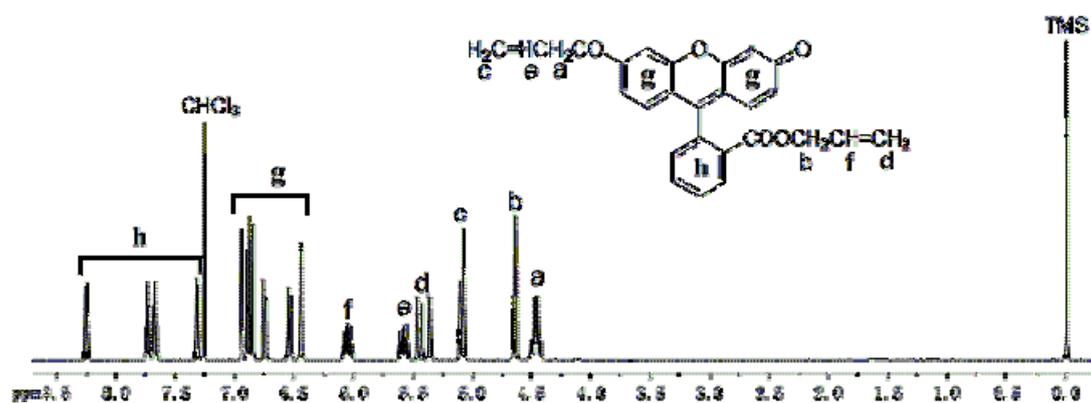


Fig. S2 ¹H NMR spectrum of FBP monomer.

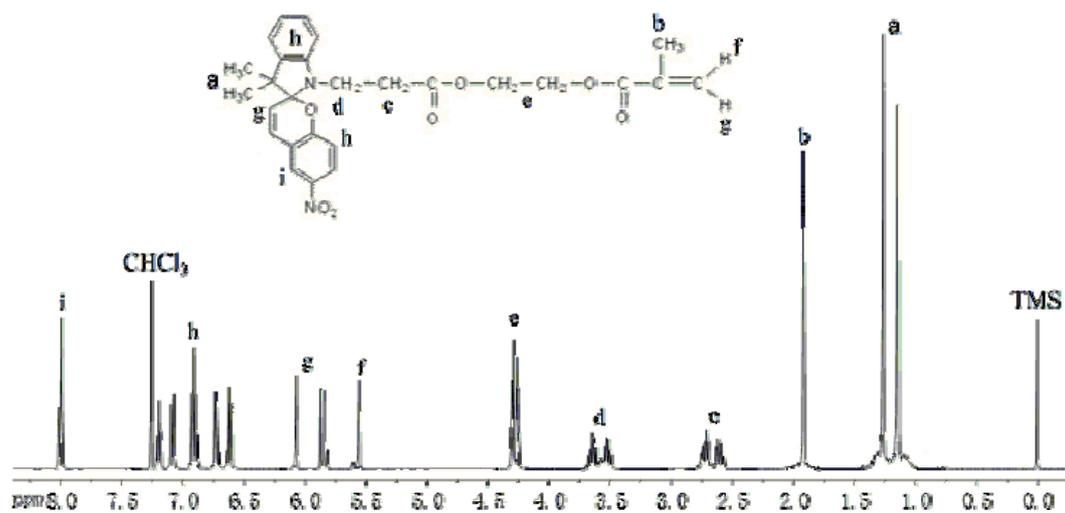


Fig. S3 ¹H NMR spectrum of SPMA monomer

Table S1. List of FBP-containing nanoparticle samples prepared with various content of PEO-R-MA-40 in this work.

Sample ^a	PEO-R-MA-40 Feed	Average diameter ^c
	[g]	[nm]
NP-F1	0.050	238.7
NP-F2	0.063	215.3
NP-F3	0.084	201.8
NP-F4	0.125	177.9

a: All experiments were carried out at 60°C, using 0.5g of MMA, 0.05g of HD, 0.002g of FBP,

0.007g KPS and 11.5g of water; b: Determined by dynamic light scattering (DLS) method.

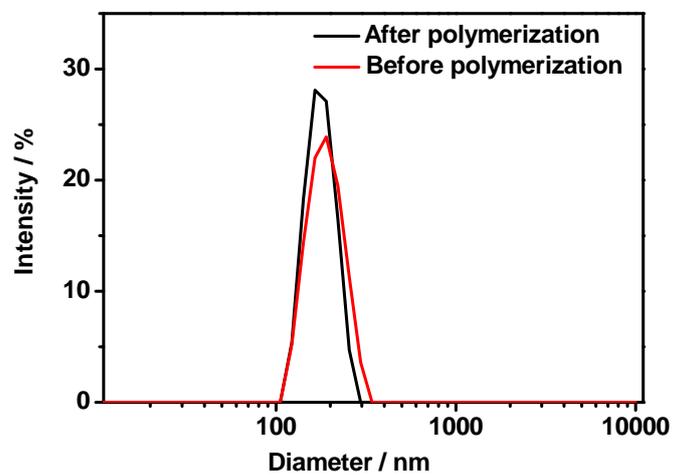


Fig. S4 Size distribution for the sample NP-F4 before and after polymerization, determined by DLS.

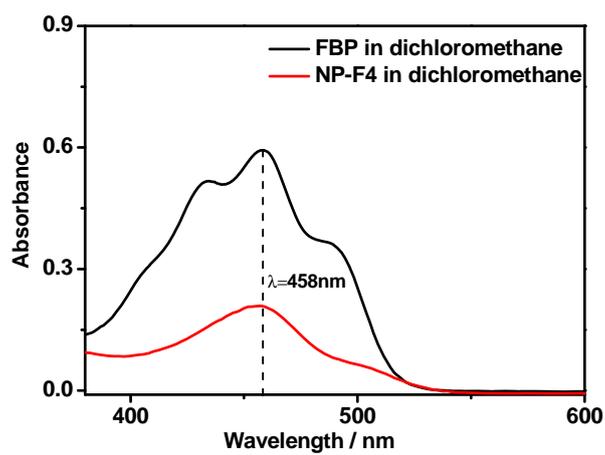


Fig. S5 Absorption spectra for the purified FBP contained polymer and FBP monomer in dichloromethane solution.

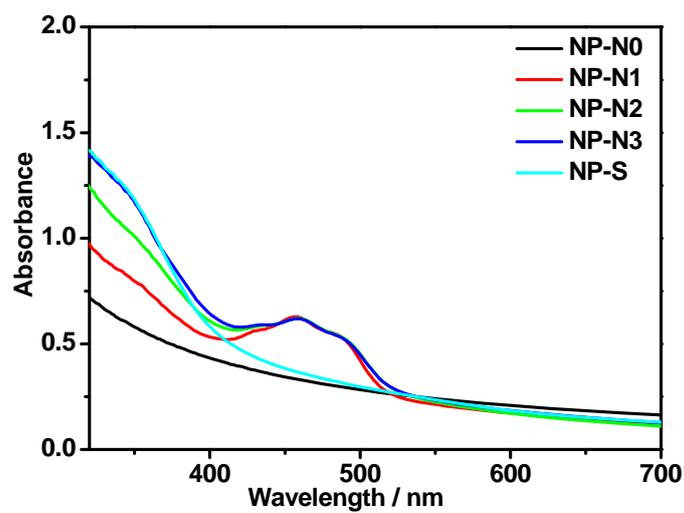


Fig. S6 Absorption spectra for three nanoparticle samples with the same FBP feed and different spiropyran feeds (from sample NP-N1 to NP-N3, the spiropyran feed increasing by a certain value), as well as blank sample (NP-0) and SPMA-contained nanoparticles sample (NP-S).

1. Calculation of the fluorescence quantum yield of donor

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

Where Φ_S defined the fluorescence quantum yield of reference standard (Fluorescein, 0.97, 25 °C) (in reference 2 and 3), F_D and F_S are the integral area of fluorescence intensity of donor and standard at the same excitation wavelength, respectively, A_D and A_S are the absorbance of the donor and standard at the defined excitation wavelength, n_S and n_D are the refractive index at 25 °C of the solvent of standard (ethanol) and the matrix of donor (mainly PMMA), respectively.

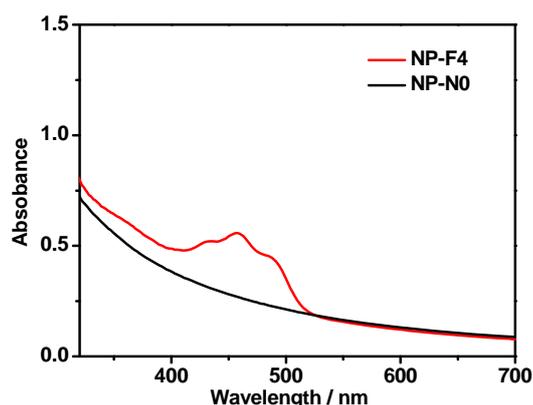


Fig. S7 Absorption spectrum for dispersion of neat nanoparticles (NP-N0) and dispersion of FBP contained nanoparticles (NP-F4).

To determine the quantum yield of FBP in NP system, we first need to measure the actual absorbance of FBP (at 480 nm) in NP system. Since the FBP/NP complex dispersion exhibits light scattering effect (as indicated in Fig. S6), to eliminate the error caused by light scattering effect, we also measured the absorption spectrum for the neat NP dispersion (without FBP), and the actual absorbance value for FBP at 480 nm can be obtained by the deduction of the absorbance of neat NP dispersion at 480 nm from the apparent absorbance

value of FBP/NP dispersion. The calculated Φ_D for FBP in nanoparticle system is 0.46.

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 (in reference 3 and 4) [Eq. (1)]:

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

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 (Fig. 5) [Eq. (2)].

$$J(\lambda) = \int_0^\infty F_D(\lambda) \times \epsilon_A(\lambda) \times \lambda^4 \times d\lambda \quad [\text{Eq. (2)}]$$

where $F_D(\lambda)$ is the fluorescence intensity of the donor in the absence of acceptor, $\epsilon_A(\lambda)$ is molar extinction coefficient of the acceptor MC (35,000 $mol^{-1}.L.cm^{-1}$ for polar solution was used for the calculation), λ is wavelength. In current experimental conditions, the Förster distances (R_0) have been calculated assuming random orientation of the donor and acceptor molecules taking $K^2 = 2/3$, $n = 1.49$ (PMMA), and are listed in Table S2. For FBP (donor) and SPMA (acceptor) in current experimental situation, we calculated $R_0 = 45.1 \text{ \AA}$. Energy transfer will be effective for $d \leq 67.6 \text{ \AA}$ (upper limit: $R_0 + 50\% R_0$) (in reference 5).

Table S2. Calculated R_0 of the Donor-Acceptor pair

Donor	Acceptor	Φ_D	$J(\lambda)$ ($M^{-1}cm^{-1}nm^4$)	R_0	$D_{\text{effective}}^a$ (nm)
FBP	MC	0.46	1.53×10^{15}	4.51	6.76

[a]: Effective energy transfer distance ($R_0 + 50\% R_0$).

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

According to the Förster non-radiative energy transfer theory, the energy transfer efficiency E depends not only on the distance (r) between the donor (FBP) and the acceptor (SPMA), but also on the critical energy transfer distance (R_0) expressed by the following equation (eq 3):

$$E = \frac{R_0^6}{R_0^6 + r^6} \quad [\text{Eq. (3)}]$$

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

$$E = 1 - \frac{F_{DA}}{F_D} \quad [\text{Eq. (4)}]$$

where F_{DA} and F_D is the maximum fluorescence intensity of the donor (FBP in nanoparticles dispersion) in the presence of the acceptor (at MC form of SPMA moieties) or absence of acceptor (at SP form of SPMA moieties), respectively.

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.

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

The calculated data are listed in Table 2 in the main text.

4. Estimation of N_A (number of spiropyrans residing around one donor within the effective energy transfer distance)

For the core-shell amphiphilic nanoparticles, we cannot access to small-angle neutron scattering approach for the determination of the core radius. However, based on the average overall diameter (D_{NP} , Table 2) of amphiphilic nanoparticles in dried state obtained by AFM, the weight ratio of hydrophilic PEO part to hydrophobic PMMA part in every nanoparticle (assuming all MMA monomers are polymerized), as well as the density of PEO and PMMA, we estimated the averaged core diameter (D_{core} , Table 2) by assuming the hydrophobic PMMA were densely packed in water.

Moreover, we need to assume that the distribution of spiropyran moieties or FBP molecules in the whole nanoparticle core is homogeneous, and the existence or the distribution of the donor (FBP) 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 (67.6 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 (67.6 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, the N_A was estimated via the following equation:

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

Where V_N is the PMMA core's volume, V_d is the volume of the sphere with its radius

equivalent to the effective energy transfer distance (67.6 Å) and $N_{SP/NP}$ is the number of spiropyran moieties per particle core.

Reference

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