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Supporting Information

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A Core/Shell Nanoparticle Approach for Photoreversible Fluorescence Modulation of Hydrophobic Dye in Aqueous Media

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Supporting Information

1. Characterizations:

Figure S1. ^1H NMR spectrum of SPCOOH. ^1H NMR (400 MHz, deuterated DMSO, 25°C, TMS) (ppm): 1.0 – 1.3 (2 CH_3), 2.6 (CH_2COO), 3.4 – 3.5 (CH_2N), 5.9 – 6.0 (olefinic protons, 2H), 6.6 – 8.2 (aromatic protons), 12.0 (COOH , hydrogen bonding).

Figure S2. ¹H NMR spectrum of spiropyran-linked methacrylate (SPMA) monomer.

¹H NMR (400 MHz, CDCl₃, 25°C, TMS) (ppm): 1.0 – 1.3 (**CH**₃ of spiropyran, 6H), 1.8 – 1.9 (**CH**₃ of HEMA, connected to olefinic carbon, 3H), 2.6 – 2.7 (**CH**₂COO of spiropyran, 2H), 3.5 – 3.6 (**CH**₂N of spiropyran, 2H), 4.2 (**CH**₂O of HEMA, 4H), 5.5 – 6.0 (olefinic protons, **CH**₂ and two **CH**, 4H), 6.6 – 8.1 (aromatic protons).

Figure S3. Excitation spectrum for NBD/nanoparticle complex in water ($\lambda_{\text{em}}=530\text{nm}$) .

2. Change in appearance of NBD/nanoparticle dispersion upon UV or visible light irradiation

Figure S4. Photograph for the NBD/spiropyran-containing nanoparticle complex in water after visible light irradiation (a) and UV irradiation (b). The appearance of (a) is the combined effect of absorption of NBD, emission of NBD (excited by the environmental light) as well as the absorption of spiropyran (in SP state); and the appearance of (b) is the combined effect of the absorption of NBD as well as the adsorption and emission of spiropyran (in McH state).

3. Calculation of Förster radii (R_0)^[1,3,4] and some other parameters

Determination of fluorescence quantum yield of the donor NBD

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 area of fluorescence intensity of the donor and the standard at the same excitation wavelength, respectively; A_D and A_S are the absorbance of the donor and the standard at the defined excitation wavelength, respectively; n_S and n_D are the refractive index at 25°C of the solvent of standard (ethanol) and the matrix of donor (PMMA), respectively.

Figure S5. Absorption spectrum for dispersion of spiropyran-free nanoparticles and dispersion of NBD/ spiropyran-free nanoparticles.

To determine the quantum yield of NBD in nanoparticle system, we first need to measure the

actual absorbance of NBD (at 490 nm) in nanoparticle system. Since the NBD/nanoparticle complex dispersion exhibits relatively strong light scattering effect (as shown in Figure S5), to eliminate the error caused by light scattering effect, we also measured the absorption spectrum for the neat nanoparticles (with neither NBD nor spiropyran), and the actual absorbance value for NBD at 490nm can be obtained by the deduction of the absorbance of neat nanoparticle dispersion at 490nm from the apparent absorbance value of NBD/neat nanoparticle dispersion.

The Φ_D of NBD in nanoparticle system was calculated to be 0.68.

Calculation of the Förster radii (R_0)^[1, 3, 4] and determination of experimental energy transfer efficiency

The Förster's distance or critical distance R_0 is the characteristic distance, at which the efficiency of energy transfer is 50%. The magnitude of R_0 is dependent on the spectral properties of the donor and the 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 Forster distance, R_0 in angstroms ($\text{\AA}$), is expressed as follows [Eq. (1)]:

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

κ^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 S6) [Eq. (2)].

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

$F_D(\lambda)$ is the fluorescence intensity of the donor in the absence of acceptor normalized so that $\int_0^\infty F_D(\lambda) d\lambda = 1$; $\varepsilon_A(\lambda)$ is molar extinction coefficient of the acceptor, λ is wavelength. In current

experimental conditions, for sample NP-A1, the $J(\lambda)$ was calculated to be $7.62 \times 10^{14} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$. The Förster distance (R_0) has been calculated assuming random orientation of the donor and acceptor molecules taking $K^2 = 2/3$, $n = 1.49$ (PMMA), and $\Phi_D = 0.68$.

For NBD (donor) and McH form of spiropyran (acceptor) in current experimental situation, by using a commercial software Origin 7.0 as the integral tool, we calculated $R_0 = 43 \text{ Å}$, 42 Å and 42 Å for sample NP-A1, NP-A3 and NP-A4. Energy transfer will be effective within the range $R_0 \pm 50\%$ R_0 [5].

Figure S6. Fluorescence spectrum of NBD in nanoparticle system (donor), and absorption spectrum of spiropyran-containing nanopartilces (acceptor, sample NP-A1) in water (with the light scattering effect eliminated).

Experimental energy transfer efficiencies (E) given in Table 2 (main text) were calculated from $E = 1 - I/I_0$, where I_0 is the fluorescence intensity of NBD/spiropyran-containing nanoparticle complex upon visible light irradiation; I is that upon UV irradiation.

Calculation of the average distance between spiropyran moieties

Assuming that the distribution of spiropyran moieties in the whole nanoparticle core is homogeneous, a sphere occupied by a spiropyran molecule can be defined by its diameter D_{SP} , which corresponds to the distance between two spiropyran moieties. As the volume occupied by the spiropyran molecules contained in polymer matrix is the volume of one nanoparticle, one can write [1].

$$D_{SP} = 2 \left(\frac{3 \times V_{NP}}{4\pi \times N_{SP/NP}} \right)^{1/3}$$

where V_{NP} is the particle's volume and $N_{SP/NP}$ is the number of spiropyran moieties per nanoparticle.

This calculation assumes all monomers are polymerized and the density of PMMA core is 1.19g/cm³. The calculated values are given in Table 2 (main text).

References

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4. Fluorescence intensities recorded upon UV and visible light irradiation for repeated cycles.

Table S1. List of fluorescence intensities for NBD/nanoparticle complex (NBD concentration: 1.07×10^{-5} M, $\lambda_{\text{ex}} = 490\text{nm}$) recorded at 533 nm upon UV illumination and visible light irradiation cycles.

Cycles	Intensity (a.u.)	
	Upon UV	Upon Vis.
0	-	2721.2
1	191.6	2652.3
2	183.2	2527.6
3	185.3	2520.1
4	198.2	2496.9
5	203.8	2461.2
10	215.7	2375.8
20	227.6	2319.9
30	230.1	2288.4