Supporting Information

One-pot fabrication of polymer nanoparticle-based chemosensor for Cu^{2+} detection in aqueous media

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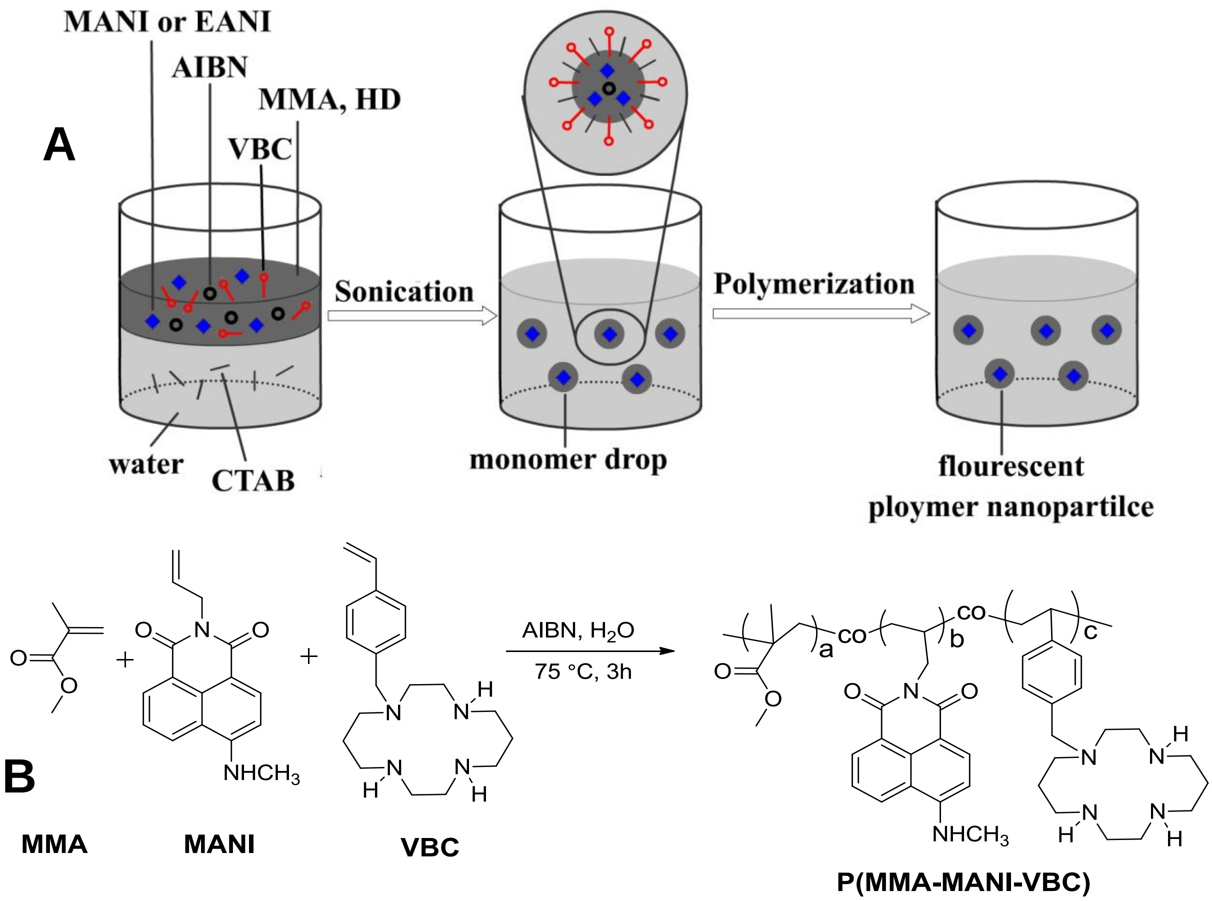


Scheme S1 A) Schematic illustration for preparation of fluorescent polymeric nanoparticle via miniemulsion polymerization; B) Synthetic Schemes Employed for the Preparation of P(MMA-MANI-VBC).

Table S1. List of Some Data and Parameters of Several Nanoparticle Samples

Sample[a]	MANI[mg] Feed	VBC[mg] Feed	D_{NP}[b] [nm]
NP-0	—	—	87.82
NP-M1	0.4	—	82.27
NP-M2	0.8	—	89.72
NP-M3	1.2	—	95.21
NP-M4	1.6	—	83.81
NP-M5	2.0	—	81.61
NP-V1	—	70	77.03

a: The MMA/HD/CTAB/AIBN feed is 0.5/0.05/0.05/0.025g, respectively;

b: Average nanoparticle diameter, determined from DLS data;

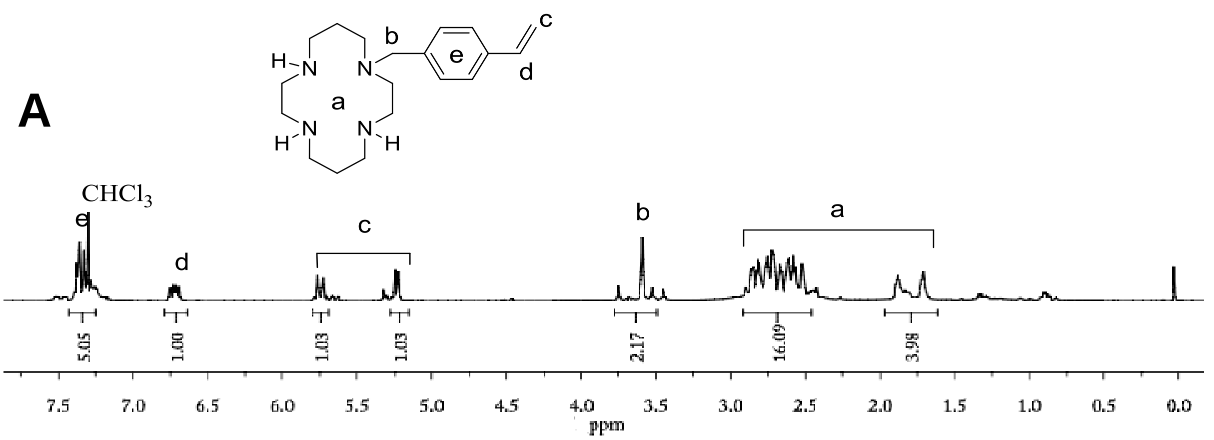


Figure S1. ^{1}H NMR spectra of the VBC.

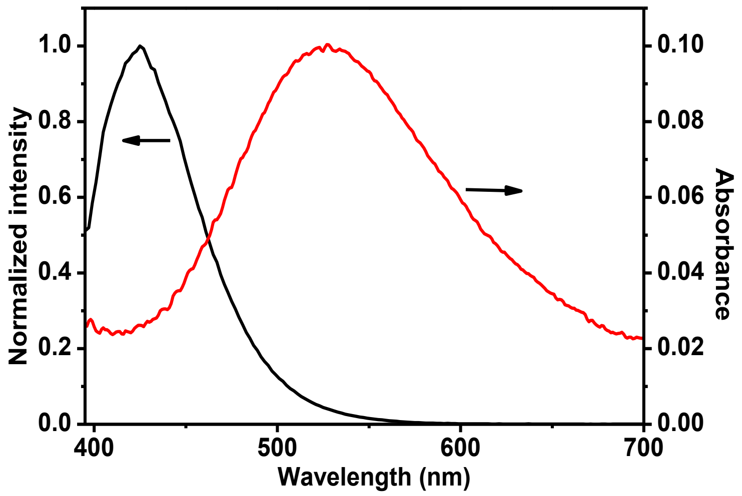


Figure S2. Normalized fluorescence emission spectrum of EANI (black curve) and absorption spectrum of the Cu^{2+}/cyclam complex (red curve).

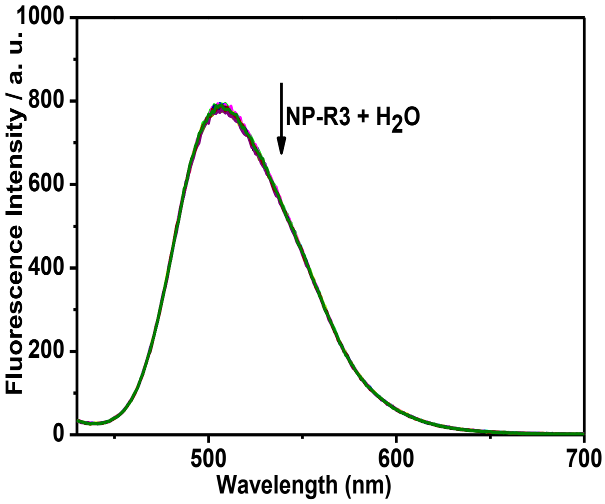


Figure S3. Fluorescence titration of a nanoparticle sample (NP-R3. solid content: 0.03 wt%) with water.

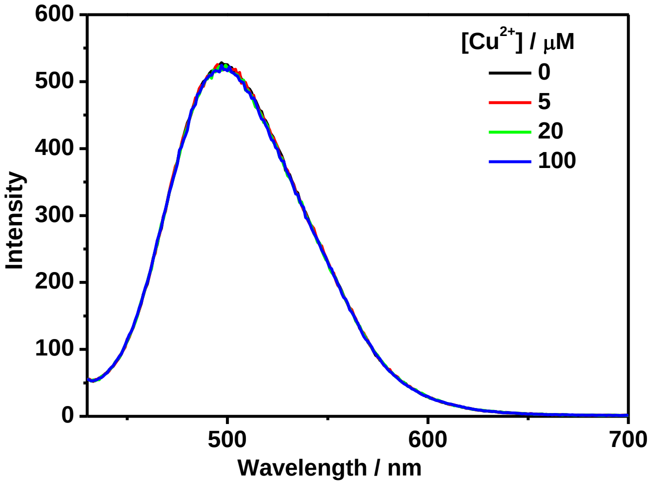


Figure S4. Fluorescence titration of a nanoparticle sample (NP-M4. solid content: 0.03 wt%) with different Cu^{2+} concentration.

1. 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)]:

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

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 (Figure 4 and Figure S4) [Eq. (2)].

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

where $F_D(\lambda)$ is the fluorescence intensity of the donor in the absence of acceptor, $\varepsilon_A(\lambda)$ is molar extinction coefficient of the acceptor, 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 Φ_{MANI}=0.99[4] and Φ_{EANI}=0.74[5] are listed in Table S1.

Table S2. Calculated R_0 of the two Donor-Acceptor pair

Donor	Acceptor	Φ_D	$J(\lambda)$ ($M^{-1}cm^{-1}nm^4$)	R_0	$D_{effective}$[a](nm)
MANI	Cu^{2+}/cyclam complex	0.99	4.12×10^{14}	4.11	6.17
EANI	Cu^{2+}/cyclam complex	0.74	1.09×10^{14}	3.14	4.71

[a]: Effective energy transfer distance (R_0 + 50% R_0).[6]

2. 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 and the acceptor, but also on the critical energy transfer distance (R_0) expressed by the following equation (eq 3):

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

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

$$E = 1 - \frac{F_{DA}}{F_D} = 1 - \frac{I}{I_0} \qquad \text{[Eq. (4)]}$$

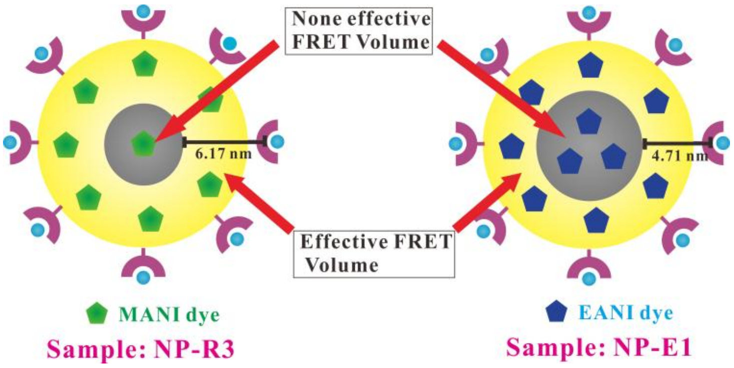
where F_{DA} (or I) and F_{D} (or I_0) is the maximum fluorescence intensity of the donor in the presence of the acceptor or absence of acceptor, respectively. [3]

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.

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

The calculated data are listed in Table 1 in the main text.

3. Schematic illustrations for the effect of donor type on the energy transfer efficiency (quenching efficiency).



Scheme S1. Illustration for effective and noneffective FRET volume in MANI-contained and EANI-contained polymeric nanoparticle.

Compared to the EANI-contained polymeric nanoparticles, the MANI-contained polymeric nanoparticles with the same diameter have the longer Förster critical distance R_0 and the upper effective energy transfer distance $D_{effective}$, as shown in Table S2. As illustrated above, the ratio of the non-effective FRET volume, in which the MANI cannot transfer its excited energy to the Cu^{2+}/Cyclam complex, to the overall volume of a MANI-contained nanoparticle, is lower than that for EANI-contained nanoparticle system, hence for EANI-contained particle system, the number of the donors which cannot be quenched is more than that in MANI-contained system, and thus the quenching efficiency for EANI-contained system is lower than that for MANI-contained one.

Reference

[1]. F. Gouanvé, T. Schuster, E. Allard, R. Méallet-Renault, C. Larpent, *Adv. Funct. Mater.* **2007**, *17*, 2746-2756
[2]. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*; Plenum: New York, **1999**.
[3]. B. Valeur in *Molecular Fluorescence: principles and applications*, Wiley-VCH, Weinheim, New York, **2002**.
[4]. I. Grabtchev, T. Konstantinov, S. Guittonneau, P. Meallier, *Dyes and Pigments*. **1997**, *35*, 361-366.

[5]. I. Grabtchev, T. Konstantinov. *Dyes and Pigments*. **1997**, *33*, 197-203.
[6]. K. E. Sapsford, L. Berti, I. L. Medintz, *Angew. Chem. Int. Ed.*, **2006**, *45*, 4562-4588.