

Supporting Information

PVP-templated highly luminescent copper nanoclusters for sensing trinitrophenol and living cell imaging

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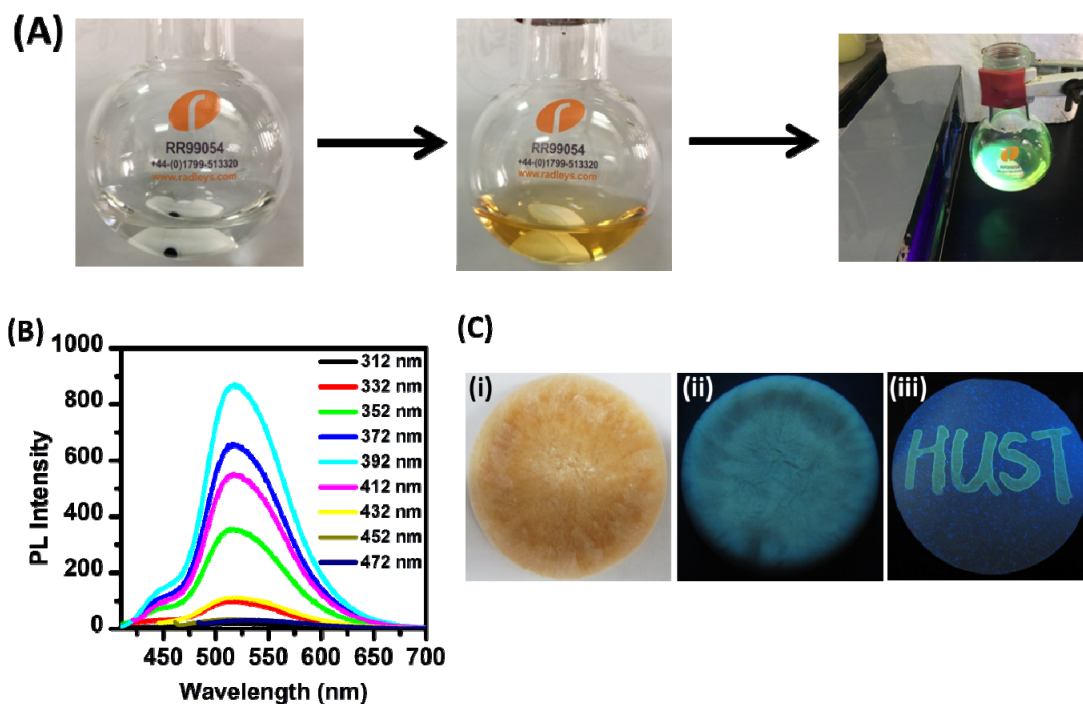


Fig. S1. (A) The color of the solution before and after reaction, and the fluorescence under the hand-held UV lamp irradiation at 365 nm during daytime, (B) Emission spectra of aqueous CuNCs at various excitation wavelengths. (C) Photograph of the freeze-dried CuNCs powder under day light (i) and UV light (ii), and the photography of aqueous CuNCs@PVP used as ink to write a word of “HUST” on filter paper, after completely drying under 365 nm UV lamp (iii).

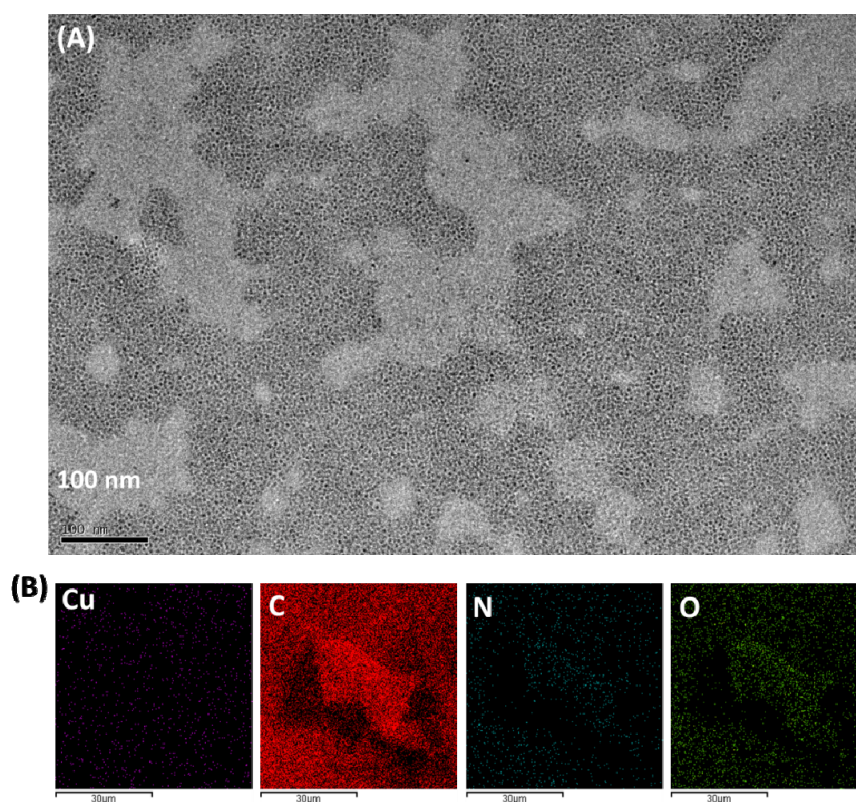


Fig. S2. (A) TEM image of CuNCs on 100 nm scale bar. (B) SEM-mapping results.

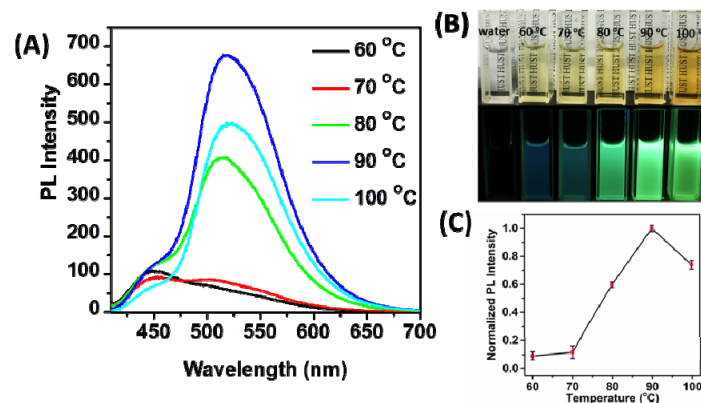


Fig. S3. (A) The emission spectra of CuNCs prepared at different temperatures. (B) Corresponding photographs of CuNCs prepared at 5 different temperatures under daylight (up) and 365 nm UV lamp (down), with water as a reference. (C) The trendline.

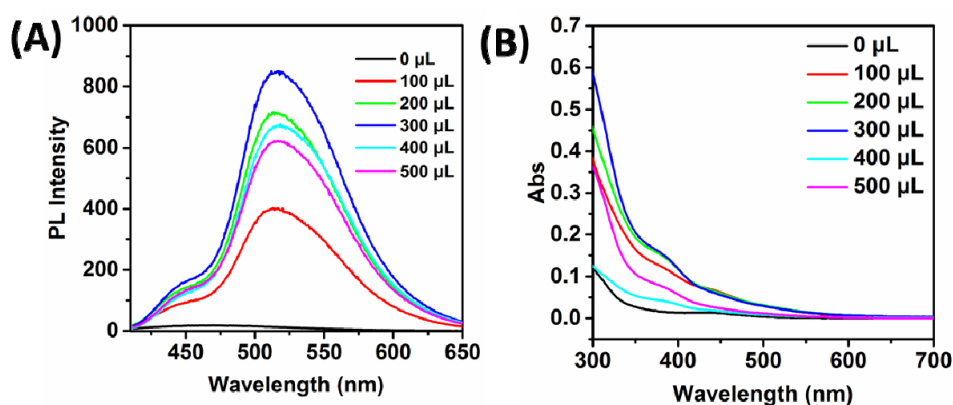


Fig. S4. (A) and (B) The emission and UV-vis absorption spectra of CuNCs obtained by the addition of different amount of AA, respectively.

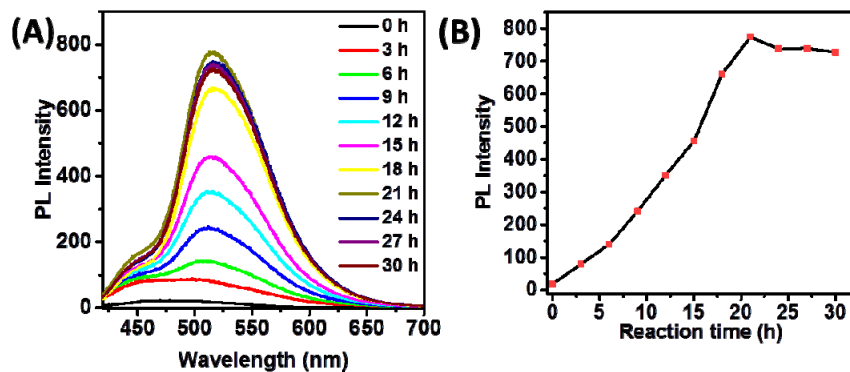


Fig. S5. (A) Fluorescence emission spectra of CuNCs prepared at different reaction time, (B) the trendline.

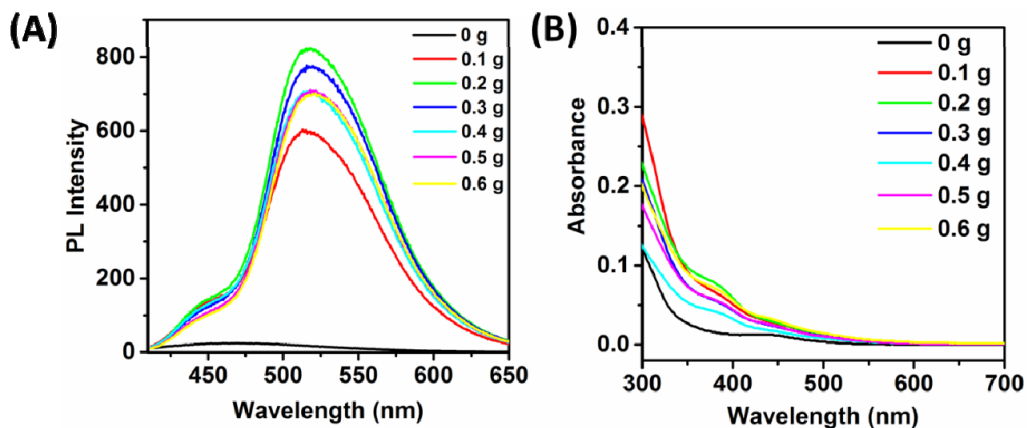


Fig. S6. (A) and (B) The emission and UV-vis absorption spectra of CuNCs obtained by the addition of different amount of PVP, respectively.

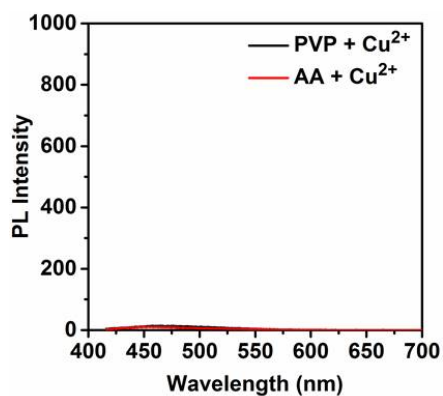


Fig. S7. Emission spectra of the mixtures of PVP/Cu²⁺ and AA/Cu²⁺.

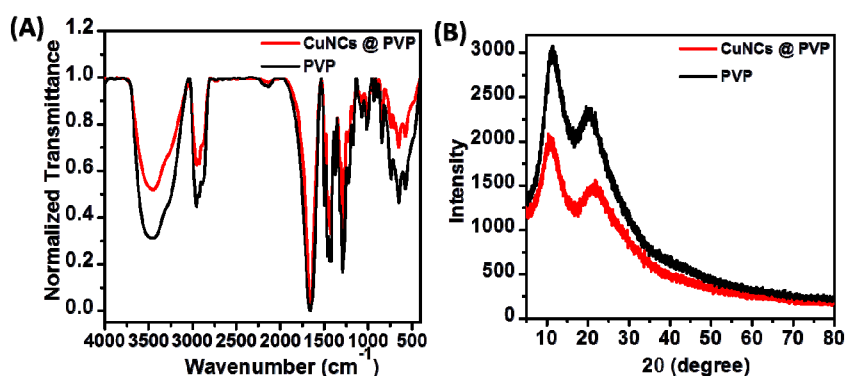


Fig. S8. (A) and (B) The FT-IR and XRD spectra of CuNCs@PVP, as well as PVP polymer, respectively.

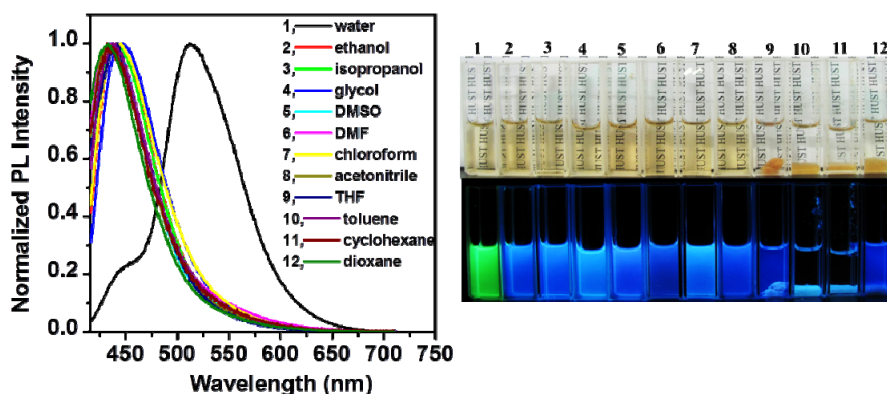


Fig. S9. (A) Normalized fluorescence emission spectra of freeze-dried CuNCs powder re-dissolved in water and another eleven kinds of organic solvents, the concentrations were about 5 mg/mL. (B) Photographs of CuNCs powder in water and organic solvents under daylight (upper) and 365 nm UV lamp (down).

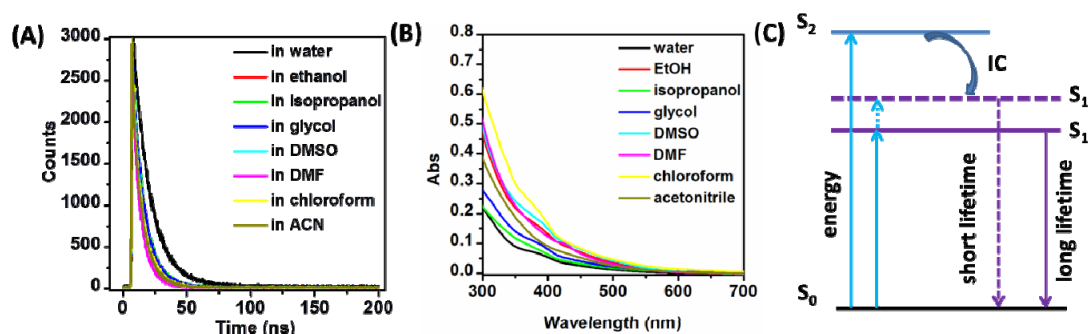


Fig. S10. (A) and (B) are the PL decay traces and UV-vis absorption spectra of CuNCs dissolved in water and different organic good solvents. (C) The schematic illustration for solvatochromic effect on energy level difference. S_0 , S_2 and IC represent the ground state, the second singlet excited state, and the internal conversion process, respectively. S_1 and S_1' represent the first singlet excited state of CuNCs dissolved in water and organic solvents respectively.

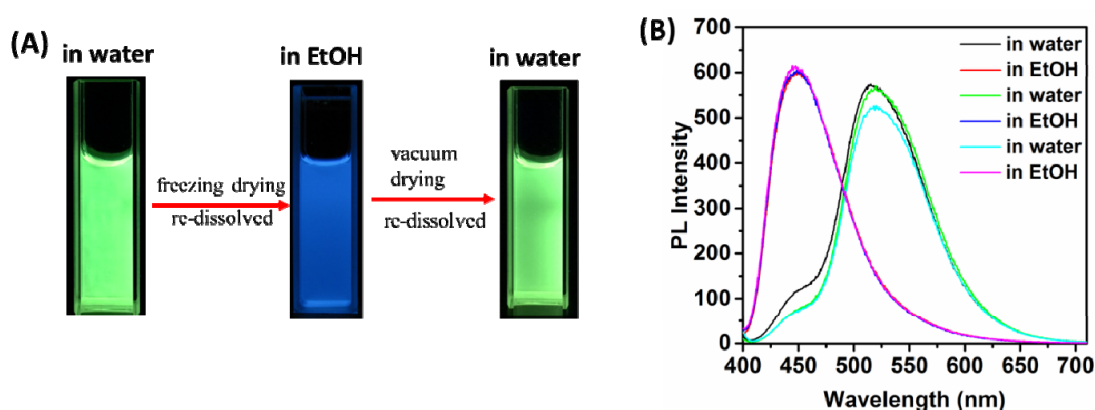


Fig. S11. The photographs of CuNCs@PVP powder re-dissolved in water and ethanol under 365 nm UV lamp (A), the PL intensity of CuNCs powder dissolved in water and ethanol for repeatedly three cycles (B).

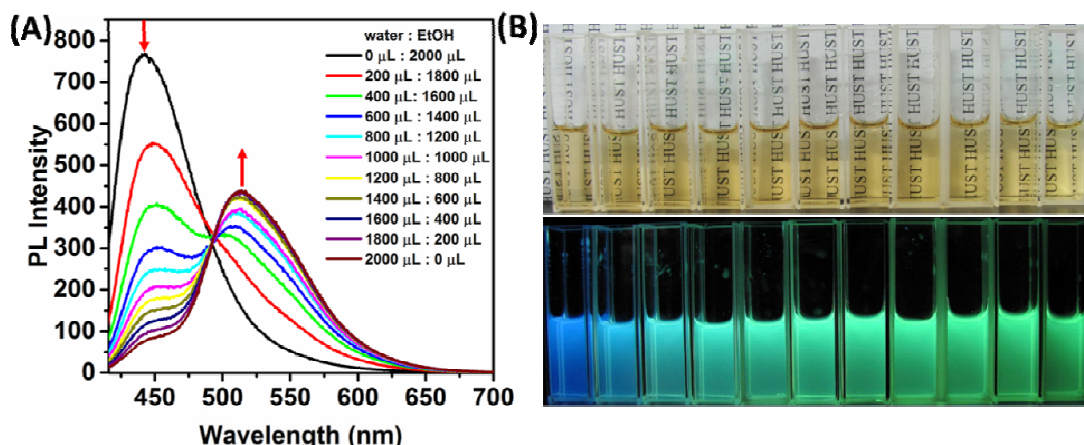
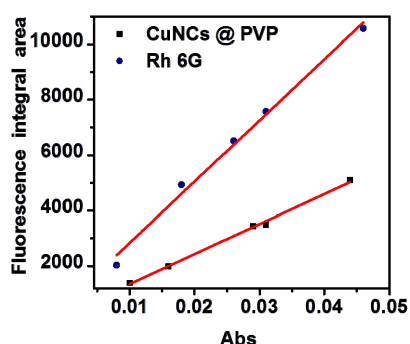


Fig. S12. (A) The emission spectra of CuNCs in the mixed solvents (water/ethanol), with different volume ratios. (B) Corresponding photographs under day light and 365 nm UV lamp.

Table S1. The optimal excitation and emission wavelengths of freshly prepared CuNCs@PVP, and freeze-dried CuNCs powder dissolved organic good solvents, as well as corresponding Stokes shift, lifetime and quantum yield (QY, calculated as Fig S13).

Solvent	Ex (nm)	Em (nm)	Stokes shift (nm)	τ_{ave} (ns)	QY (%)
water	392	518	126	13.58	44.67
ethanol	390	444	54	9.15	40.61
isopropanol	388	442	54	9.20	46.99
glycol	388	446	58	9.20	46.78
DMSO	390	440	50	7.97	51.20
DMF	388	433	45	7.17	44.14
chloroform	388	444	56	8.37	45.99
ACN	388	435	47	8.08	38.95



	m	n
CuNCs@PVP	108315	1.333
Rh 6G	220820	1.3614

Fig. S13. Right is the relationship between fluorescence curve integral areas (in the range of 412 – 700 nm) and corresponding optical density of CuNCs and Rhodamine 6G, respectively. The relationship between the fluorescence integral area and optical absorption (Abs) for CuNCs@PVP, Rh 6G were $Y=108315X+256$ and $Y=220820X+628$ respectively. And the left table is the value for m obtained from the slope of the fitting line and n (refractive index of solvent). Therefore, with Rh 6G as a reference ($Q_R=0.95$, in ethanol) and based on $Q=Q_R [m/m_R] [n^2/n_R^2]$, the relative QY for CuNCs is, $QY = 0.95 \times [108315/220820] \times [1.333/1.3614]^2 = 44.67\%$.

Table S2. Comparison of fluorescent copper nanoclusters from different synthesis methods and here the “-” represents no data provided in the literature or the ligand as both reducing agent. And QY was obtained in the mentioning solvent. And the corresponding abbreviations, poly(ethylene glycol)-*block*-poly(propylene sulfide) (PEG-*b*-PPS), Polyethyleneimine (PEI), Glutathione (GSH), Bovine serum albumin (BSA), 2-mercapto-5-n-propylpyrimidine (MPP), hydrazine hydrate (N₂H₄).

Ligand	Reducing agent	Solvent	Ex (nm)	Em (nm)	QY (%)	Size (nm)	Ref
PVP	formaldehyde	water	310 - 390	398 - 457	13	3.3 ± 0.4	1
PVP/GSH	ascorbic acid	water	380	423	27	around 3	2
PVP/DHLA	ascorbic acid	water	365	435, 650	10.8	1.9 ± 0.6	3
PVP	ascorbic acid	water	380	425	12	3.3 ± 0.8	4
PVP/citrate	ascorbic acid	water	380	425	14	3	5
PEG- <i>b</i> -PPS	-	water	530	620	30	1.5 ± 0.6	
		THF	-	583	67		6
BSA	-	water	325	410	15	2.8 ± 0.5	7
GSH	-	water	410	610	5	2.3	8
lysozyme	N ₂ H ₄	water	360	450	18	0.96 ± 0.25	9
GSH	-	water	340	430	6	around 2.2	10
papain	N ₂ H ₄	water	370	620	14.3	2.3 ± 0.7	11
cysteine	-	water	360	490	5.6	3.5	12
cysteine	-	water	375	480	14.3	2 - 3	13
PEI	ascorbic acid	water	360	430	2.1	2.5	14
peptide	ascorbic acid	water	373	454	7.3	1.7 ± 0.4	15
dopamine	-	water	320	390	9.6	around 8	16
4-fluorothiophenol	-	-	316	548	15.6	1.7 ± 0.5	17
1-dodecanethiol	-	CHCl ₃	370	550	15.4	1.9	18
1-dodecanethiol	-	-	-	607	23.5	1.8 ± 0.2	19
4-bromothiophenol	-	-	440	649	18.9	0.4 ± 0.1	20
MPP	NaBH ₄	-	283, 364	425, 593	4.4	-	21
GSH	-	DMSO	340	627	1.9	2 - 5	22
1-dodecanethiol	-	-	365	490	6.5	1.9 ± 0.2	23
PEI	N ₂ H ₄	THF	-	-	21	around 1.8	24
GSH	ascorbic acid	80% EtOH	345	620	6.6	1.3 ± 0.4	25
PVP	ascorbic acid	water	392	518	44.67	2.28 ± 0.92	This work

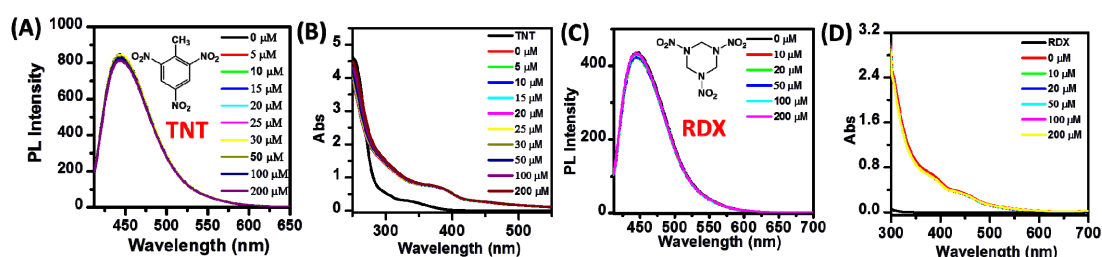


Fig. S14. (A) and (C) the emission spectra of CuNCs@PVP incubated with different concentrations of trinitrotoluene (TNT) and RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) in ethanol/ACN mixed solvents. (B) and (D) the corresponding UV-vis absorption spectra.

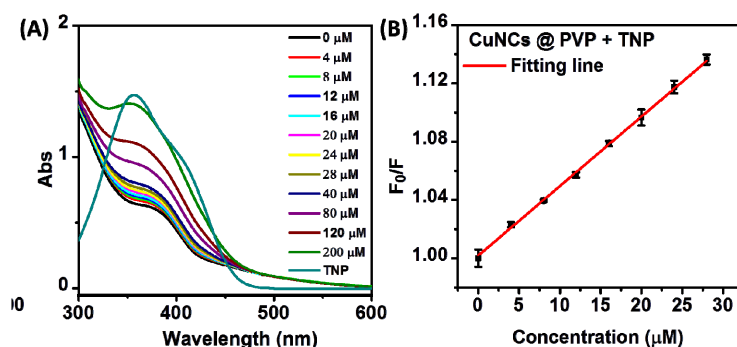


Fig. S15. (A) The UV-vis absorption spectra of CuNCs incubated with increasing concentrations of TNP in water. (B) The Stern-Volmer plots of CuNCs incubated with TNP in water. F_0 is the initial PL intensity, F stands for the PL intensity after adding the TNP, and the linear regression equation of the fitting line can be expressed as $F_0/F=0.00477[c]+1.00191$.

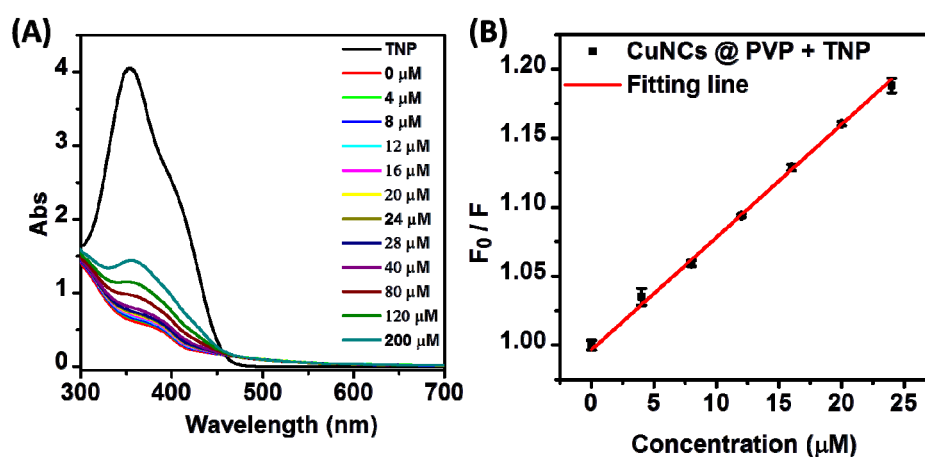


Fig. S16. (A) The UV-vis absorption spectra of CuNCs after the addition of different concentrations of TNP (in ethanol). (B) The Stern-Volmer plots of CuNCs incubated with TNP in ethanol. And the linear regression equation of the fitting line can be expressed as $F_0/F=0.00817[c]+0.99642$.

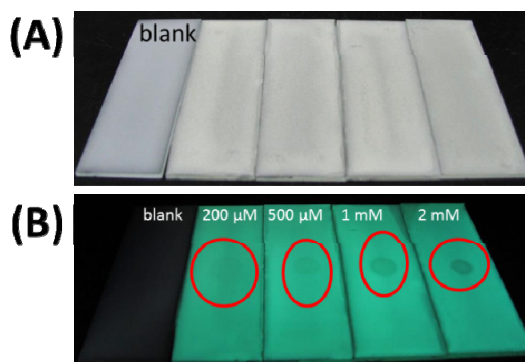


Fig. S17. (A) Photograph of the blank and CuNCs@PVP coated silica gel plate under daylight. (B) The photo of blank and CuNCs@PVP coated silica gel plate under UV lamp (365 nm irradiation), and with their center added a drop of different concentrations of TNP.

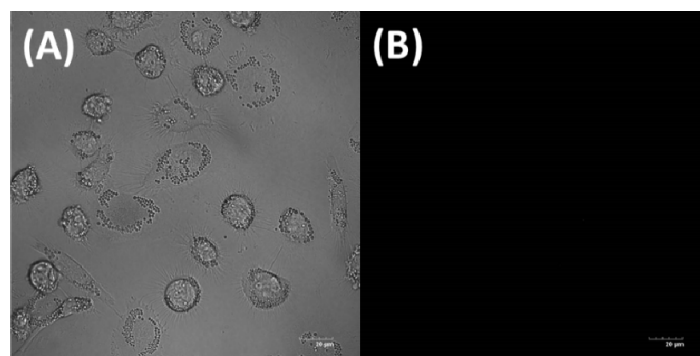


Fig. S18. (A) and (B) The confocal images of THP-1 macrophage without CuNCs@PVP under bright and dark field. The excitation wavelength: 405 nm, scale bar: 20 μm .

Table S3. The maximum tolerant concentration for the as-prepared CuNCs@PVP, as well as the tolerant concentration for other nanoclusters reported.

Item	Ligand	Cell	Maximum tolerant concentration	Incubation time (h)	Ref
CuNCs	BSA	Cal-27	80 $\mu\text{g/mL}$	24	26
AuNCs	MUA	HeLa	100 μM	24	27
AuNCs	DPA	HeLa	300 $\mu\text{g/mL}$	24	28
CuNCs	FA	HeLa/A549	300 $\mu\text{g/mL}$	20	29
CuNC-hydrogel	DHLA/PVP	HeLa	15.7 $\mu\text{g/mL}$	24	3
AgNCs	-	HeLa	250 $\mu\text{g/mL}$	24	30
CuNCs	GSH	HeLa	75 μM	12	10
AgNCs	DNA	HeLa	1 μM	24	31
AuNCs	PA	HeLa	80 μM	-	32
GNCs	dodecanethiol	HepG2	0.4 $\mu\text{g/mL}$	48	33
CuNCs	PVP	THP-1	12 mg/mL (300 μM)		This work

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