Supplementary Information

Supramolecular recognition control of polyethylene glycol modified N doped graphene quantum dots: tunable selectivity for alkali and alkaline-earth metal ions

Siwei Yang, Jing Sun, Chong Zhu, Peng He, Zeng Peng and Guqiao Ding,*

State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Science, Shanghai, P. R. China

* Corresponding authors: Guqiao Ding, gqding@mail.sim.ac.cn

Experiment details

Synthesis of PN-GQD-2

Synthesis progress of PN-GQD-2 is shown in Figure 1a and as follows: 16.8 mg (0.1 mM) 1-Chloro-2-(2-methoxymethoxy-ethoxy)-ethane was added into 9.0 mL, 1.0 mg mL^{-1} N-GQDs aqueous solution. The mixture were transferred to a Teflon-lined autoclave (10 mL) and heated at 180 ^{o}C for 24 h. The obtained aqueous solution was dialysed in a 3500 Da dialysis bag for a week to remove small molecules.

Synthesis of PN-GQD-3

Synthesis progress of PN-GQD-3 is shown in Figure 1a and as follows: 22.6 mg (0.1 mM) 1-Chloro-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethane was added into 9.0 mL, 1.0 mg mL^{-1} N-GQDs aqueous solution. The mixture were transferred to a Teflon-lined autoclave (10 mL) and heated at 180 ^{o}C for 36 h. The obtained aqueous solution was dialysed in a 3500 Da dialysis bag for a week to remove small molecules.

Synthesis of PN-GQD-4

Synthesis progress of PN-GQD-4 is shown in Figure 1a and as follows: 27.1 mg (0.1 mM) 1-Chloro-2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethane was added into 9.0 mL, 1.0 mg mL^{-1} N-GQDs aqueous solution. The mixture were transferred to a Teflon-lined autoclave (10 mL) and heated at 180 ^{o}C for 36 h. The obtained aqueous solution was dialysed in a 3500 Da dialysis bag for a week to remove small molecules.

Synthesis of PN-GQD-5

Synthesis progress of PN-GQD-5 is shown in Figure 1a and as follows: 31.5 mg (0.1 mM) 1-Chloro-2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethane was added into 9.0 mL, 1.0 mg mL^{-1} N-GQDs aqueous solution. The mixture were transferred to a Teflon-lined autoclave (10 mL) and heated at 180 ^{o}C for 48 h. The obtained aqueous solution was dialysed in a 3500 Da dialysis bag for a week to remove small molecules.

Synthesis of PN-GQD-6

Synthesis progress of PN-GQD-6 is shown in Figure 1a and as follows: 35.8 mg (0.1 mM) 1-Chloro-2-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-ethane was added into 9.0 mL, 1.0 mg mL^{-1} N-GQDs aqueous solution. The mixture were transferred to a Teflon-lined autoclave (10 mL) and heated at 180 ^{o}C for 48 h. The obtained aqueous solution was dialysed in a 3500 Da dialysis bag for a week to remove small molecules.

Synthesis of PN-GQD-1B

Synthesis progress of PN-GQD-1B is shown in Figure 1a and as follows: 18.2 mg (0.1 mM) 1-Chloro-2-(2-ethoxymethoxy-ethoxy)-ethane was added into 9.0 mL, 1.0 mg mL^{-1} N-GQDs aqueous solution. The mixture were transferred to a Teflon-lined autoclave (10 mL) and heated at 180 ^{o}C for 36 h. The obtained aqueous solution was dialysed in a 3500 Da dialysis bag for a week to remove small molecules.

Synthesis of PN-GQD-1C

Synthesis progress of PN-GQD-1C is shown in Figure 1a and as follows: 19.6 mg (0.1 mM) 2-[2-(2-Chloro-ethoxy)-ethoxymethoxy]-propane was added into 9.0 mL, 1.0 mg mL^{-1} N-GQDs aqueous solution. The mixture were transferred to a Teflon-lined autoclave (10 mL) and heated at

180 ^{o}C for 48 h. The obtained aqueous solution was dialysed in a 3500 Da dialysis bag for a week to remove small molecules.

Synthesis of PN-GQD-1D

Synthesis progress of PN-GQD-1D is shown in Figure 1a and as follows: 2.10 mg (0.1 mM) 2-[2-(2-Chloro-ethoxy)-ethoxymethoxy]-2-methyl-propane was added into 9.0 mL, 1.0 mg mL^{-1} N-GQDs aqueous solution. The mixture were transferred to a Teflon-lined autoclave (10 mL) and heated at 180 ^{o}C for 72 h. The obtained aqueous solution was dialysed in a 3500 Da dialysis bag for a week to remove small molecules.

Quantum yield measurement

As the most direct and important index, the quantum yield (φ) was calculated according to equation 1:

$$\varphi = \varphi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2} \qquad (1)$$

where I is the measured integrated emission intensity, η is the refractive index of the solvent, A is the optical density, and the subscript R refers to the reference standard with a known φ (quininesulfate, φ_R=0.55). In order to minimize reabsorption effects, absorbance was kept under 0.1 at 345 nm excitation wavelength in 10×10 mm fluorescence cuvette.

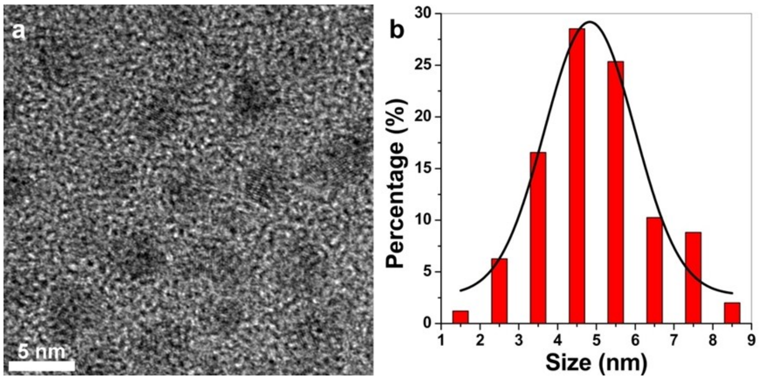

Fig. S1 (a) TEM image of N-GQDs, (b) corresponding size distribution histogram of PN-GQD-1, the black curve is the Gaussian fitting curve.

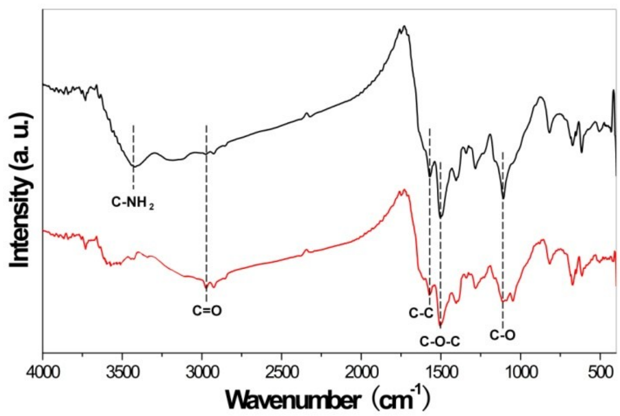

Fig. S2 FT-IR spectra of N-GQDs (black curve) and PN-GQD-1 (red curve).

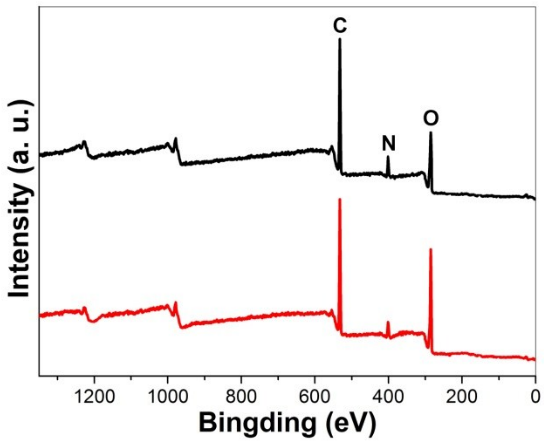

Fig. S3 XPS spectra of N-GQDs (black curve) and PN-GQD-1 (red curve).

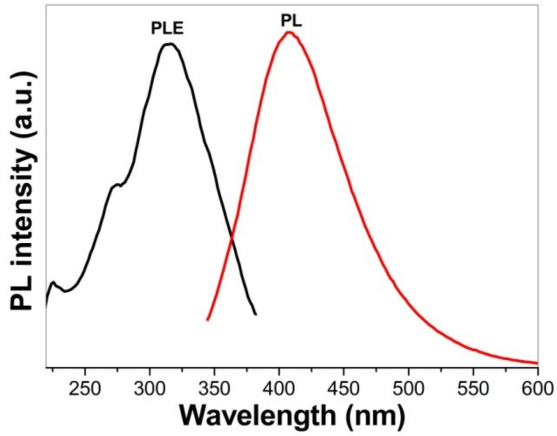

Fig. S4 PL (red curve) and PLE (black curve) spectra of N-GQDs.

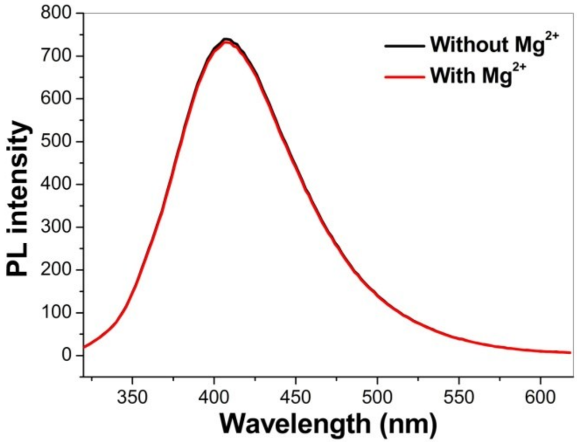

Fig. S5 PL spectra of N-GQDs with (red curve) and without (black curve) Mg^{2+}.

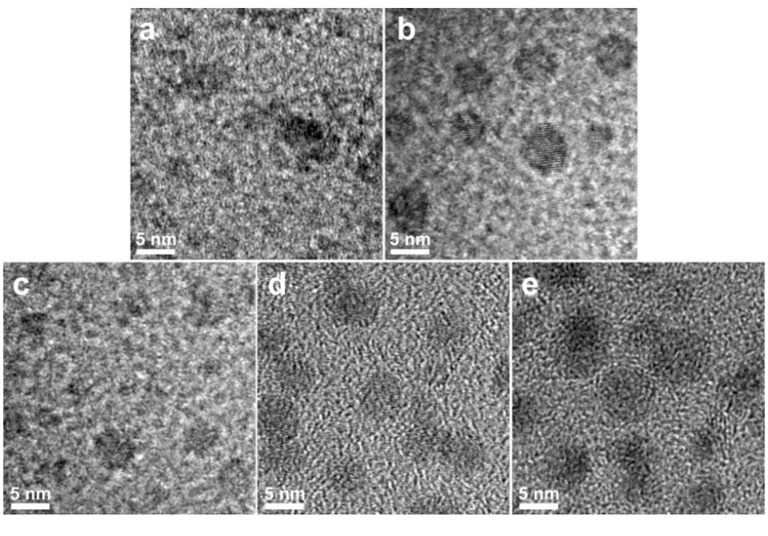

Fig. S6 TEM images of (a) PN-GQD-2, (b) PN-GQD-3, (c) PN-GQD-4, (d) PN-GQD-5 and (e) PN-GQD-6.

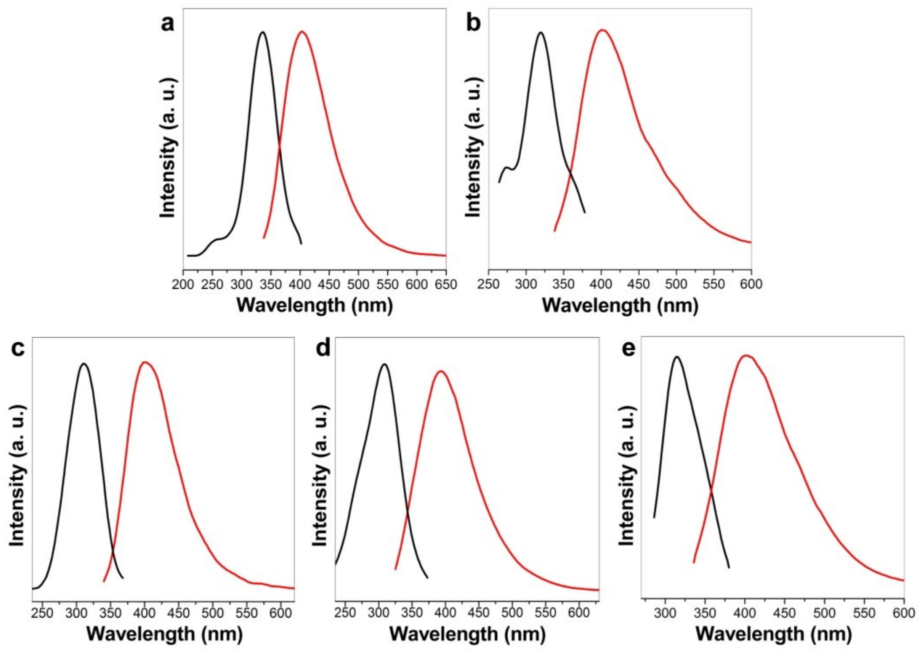

Fig. S7 PL (red curve) and PLE (black curve) spectra of (a) PN-GQD-2, (b) PN-GQD-3, (c) PN-GQD-4, (d) PN-GQD-5 and (e) PN-GQD-6.

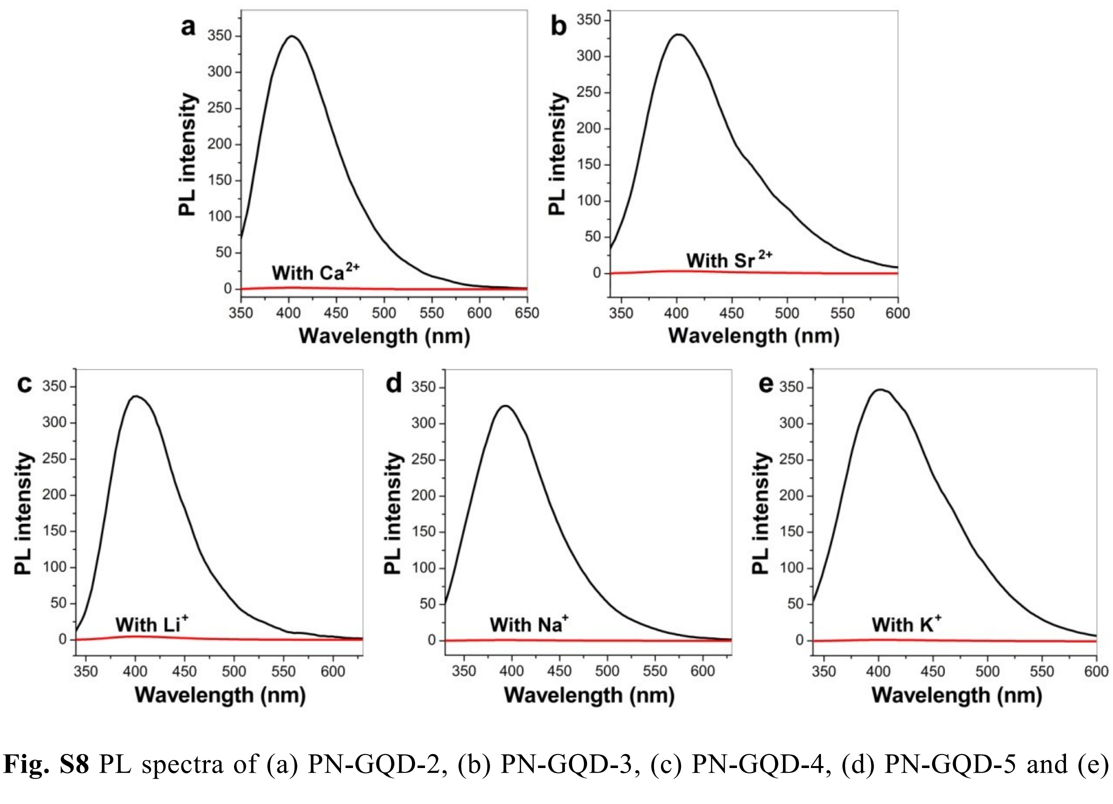

Fig. S8 PL spectra of (a) PN-GQD-2, (b) PN-GQD-3, (c) PN-GQD-4, (d) PN-GQD-5 and (e) PN-GQD-6 with (red curve) and without (black curve) ions.

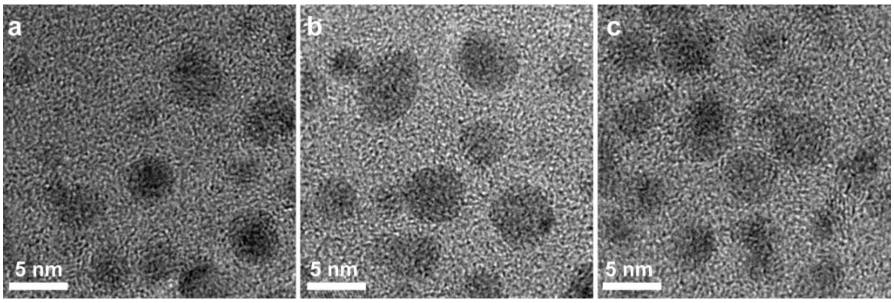

Fig. S9 TEM images of (a) PN-GQD-1B, (b) PN-GQD-1C and (c) PN-GQD-1D.

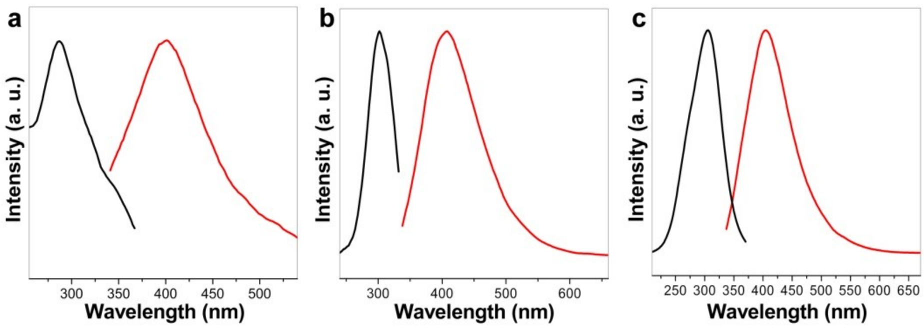

Fig. S10 PL (red curve) and PLE (black curve) spectra of (a) PN-GQD-1B, (b) PN-GQD-1C and (c) PN-GQD-1D.

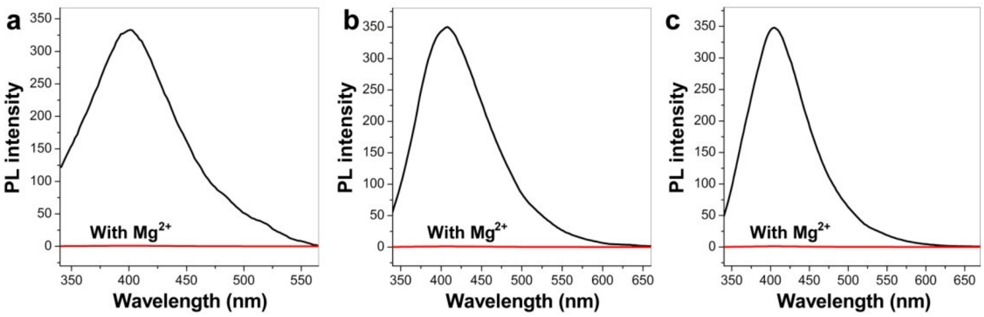

Fig. S11 PL spectra of (a) PN-GQD-1B, (b) PN-GQD-1C and (c) PN-GQD-1D with (red curve) and without (black curve) Mg^{2+}.

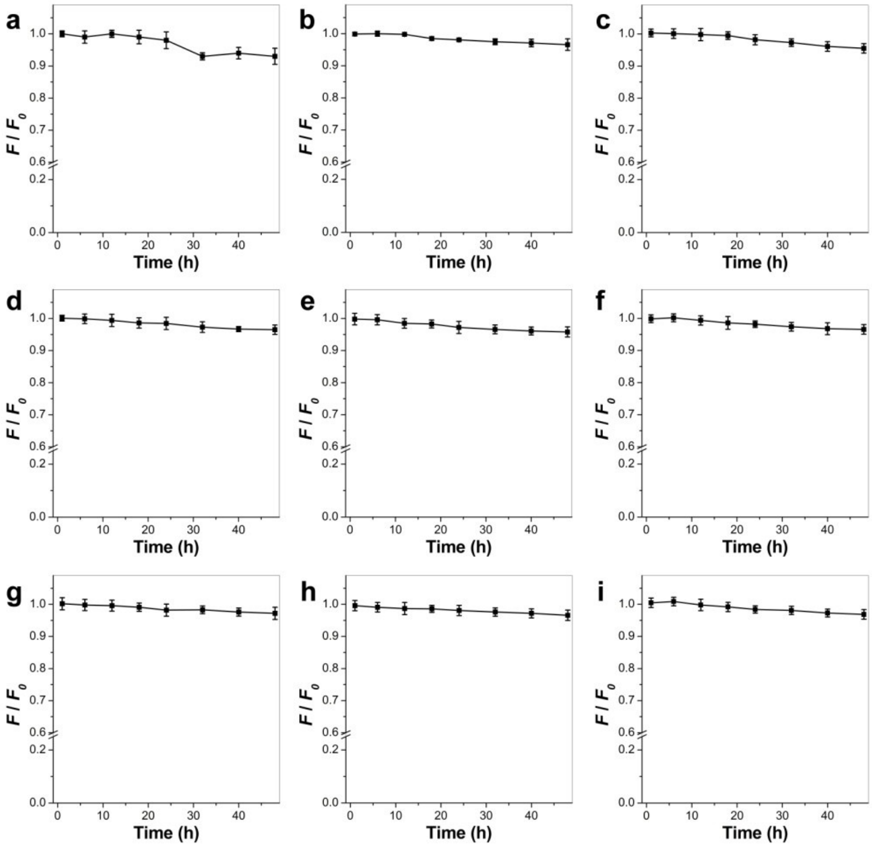

Fig. S13 photostability of PN-GQDs under 365 nm UV light (100 W) at room temperature. (a) PN-GQD-1, (b) PN-GQD-2, (c) PN-GQD-3, (d) PN-GQD-4, (e) PN-GQD-5, (f) PN-GQD-6, (g) PN-GQD-1B, (h) PN-GQD-1C, (i) PN-GQD-1D. The concentration of PN-GQDs is 0.1 mg/mL. F_0 is PL intensity of PN-GQDs, F is PL intensitie of PN-GQDs under different time.

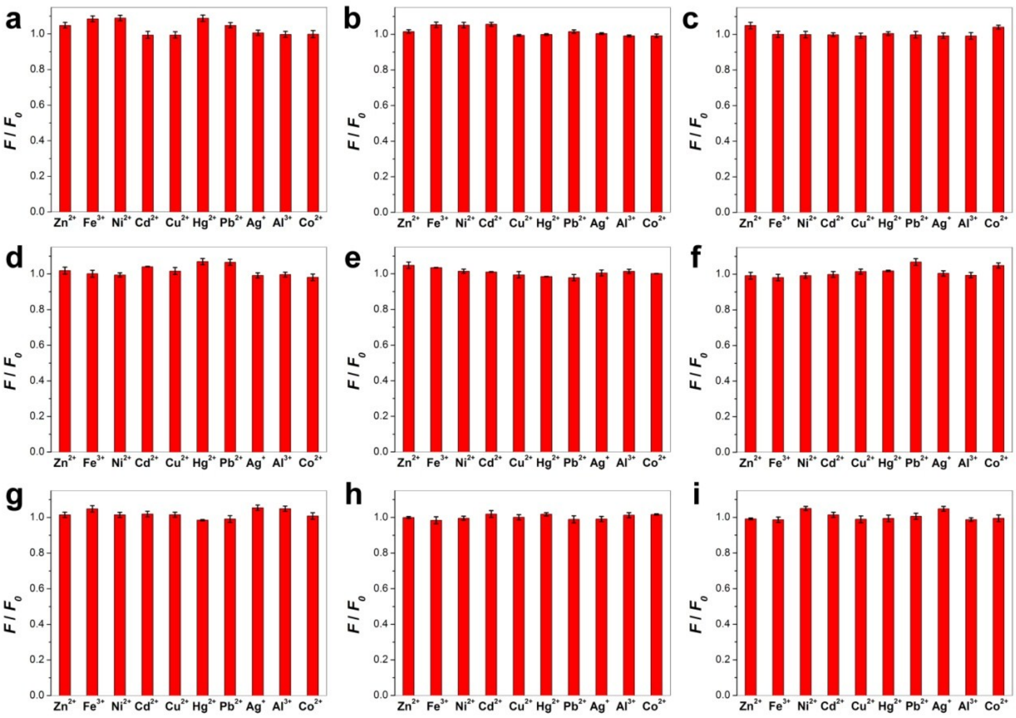

Fig. S13 The difference in PL intensity of PN-GQDs aqueous solution between the blank and solutions containing different common positive ions (F_0 and F are PL intensities in the absence and presence of ions, respectively. The concentrations of all ions are all 0.1 M, the concentrations of PN-GQDs is 0.5 mg mL^{-1}). (a) PN-GQD-1, (b) PN-GQD-2, (c) PN-GQD-3, (d) PN-GQD-4, (e) PN-GQD-5, (f) PN-GQD-6, (g) PN-GQD-1B, (h) PN-GQD-1C, (i) PN-GQD-1D.

Table S1. Optical properties of N-GQDs and PN-GQDs

	λ_{ex} (nm)	λ_{em} (nm)	FWHM (nm)	φ	τ (ns)	κ_r (10^7 S^{-1})	Detection limit (nM)	Linearity range (M)	Ions
-N-GQD	321	408	70	0.74	9.2	8.04	N	N	N
PN-GQD-1	321	402	90	0.71	8.0	8.88	0.2	5×10^{-10}-5×10^{-8}	Mg^{2+}
PN-GQD-2	318	400	70	0.73	7.6	9.61	0.1	3×10^{-10}-1×10^{-8}	Ca^{2+}
PN-GQD-3	322	405	80	0.69	8.8	7.84	0.4	8×10^{-10}-2×10^{-8}	Sr^{2+}
PN-GQD-4	321	399	75	0.72	7.4	9.73	0.5	1×10^{-9}-2×10^{-8}	Li^{+}
PN-GQD-5	322	402	80	0.71	8.2	8.66	0.1	3×10^{-10}-1×10^{-8}	Na^{+}
PN-GQD-6	321	405	95	0.71	7.8	9.10	0.3	8×10^{-10}-4×10^{-8}	K^{+}
PN-GQD-1B	318	402	90	0.70	8.3	8.43	0.4	8×10^{-10}-6×10^{-8}	Mg^{2+}
PN-GQD-1C	316	405	70	0.71	7.6	9.34	0.9	5×10^{-9}-8×10^{-8}	Mg^{2+}
PN-GQD-1D	318	402	65	0.71	7.9	8.98	8.1	2×10^{-8}-2×10^{-6}	Mg^{2+}