Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Material

Facile synthesis of multicolor photoluminescent polymer carbon dots with surface-state energy gap-controlled emission

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Fluorescence quantum yield measurements. The fluorescence quantum yields (QYs) were tested using a widely accepted relative method.[1,2] Especially, quinine sulfate (QYs = 54% in 0.1 M H_2SO_4) was chosen as the reference for y-PCDs and b-PCDs. Fluorescein (QYs = 95% in 0.1M NaOH) was used as a reference for g-PCDs. The QYs of PCDs was then calculated according to the following equation:

$$\varphi_x = \varphi_{st}\,(K_x / K_{st})(\eta_x / \eta_{st})^2 \qquad (1)$$

where φ is the QYs of the testing sample, K is the slope determined by the curves and η is the refractive index (1.33 for water and 1.558 for DMF). The subscript "st" denotes the referenced fluorescence dyes of known QYs and "x" denotes the PCDs of unknown QYs. The fluorescence spectra were measured at optimal excitation wavelengths of the three types of PCDs (355, 410, and 380 nm for y-PCDs, g-PCDs, and b-PCDs, respectively). Moreover, the fluorescence intensity was integrated. QYs were determined by comparison of the integrated fluorescence intensity and absorbance curves. To minimize reabsorption effects, absorbance was always kept below 0.1 at the excitation wavelength.

pH response experiments of three types of PCDs. For the pH response of three types of PCDs, 20 μL of y-PCDs, 10 μL of g-PCDs, and 10 μL of b-PCDs solutions were added to a 1.5 mL microcentrifuge tubes, respectively, and then the solutions were diluted to 1.0 mL by BR buffers with different pH values. The as-obtained solutions were mixed and incubated for 10 min at room temperature before subjecting to the fluorescence measurement. The excitation wavelengths were 355, 380, and 410 nm for y-PCDs, g-PCDs, and b-PCDs, respectively.

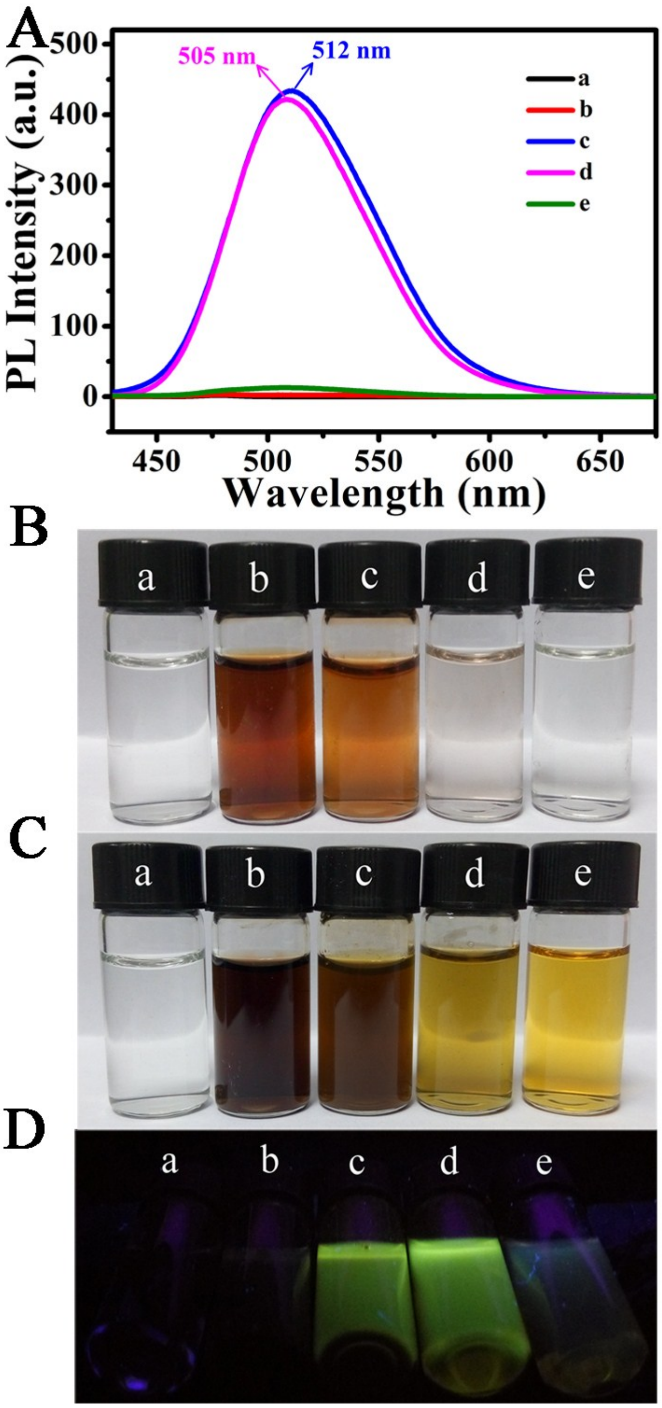

Fig. S1 (A) PL spectra of as-prepared reaction mixtures after hydrothermal treatment. The photographs of as-prepared reaction mixtures (B) before hydrothermal treatment and (C) after hydrothermal treatment, under visible light. (D) The photographs of as-prepared reaction mixtures after hydrothermal treatment, under 365-nm UV light. From left to right, these samples were mixtures of (a) hydroquinone (3 mL, 0.1 M) with an adequate amount of sodium dithionite (0.0613 g) and ethylenediamine (150 μL, 1 M), (b) hydroquinone (3 mL, 0.1 M) with NaOH (150 μL, 1 M), (c) hydroquinone (3 mL, 0.1 M) with ethylenediamine (150 μL, 1 M), (d) catechol (3 mL, 0.1 M) with ethylenediamine (150 μL, 1 M), (e) resorcinol (3 mL, 0.1 M) with ethylenediamine (150 μL, 1 M).

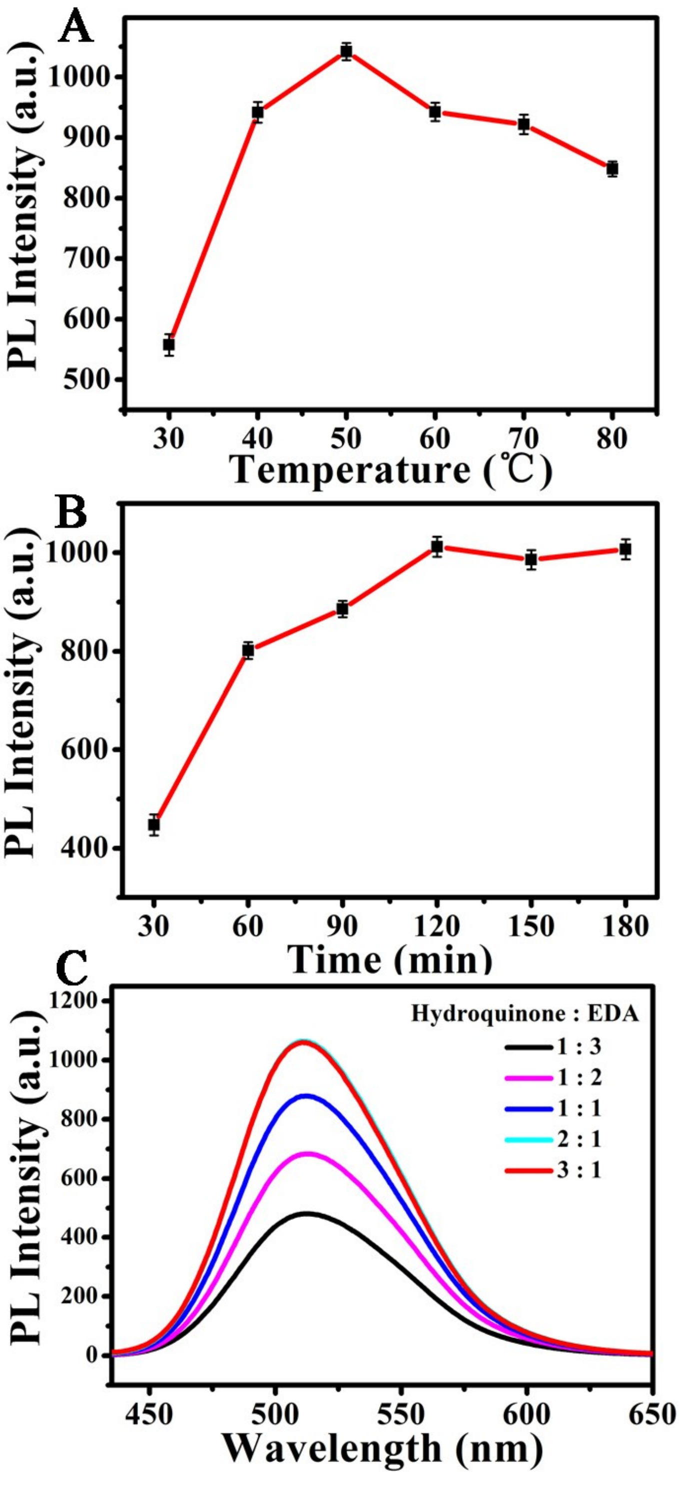

Fig. S2 (A) PL intensity of reaction mixtures prepared at an identical molar ratio of 2.0 (hydroquinone versus ethylenediamine (EDA)), same reaction time (2 h) but different reaction temperatures. (B) PL intensity of reaction mixtures prepared at an identical molar ratio of 2.0 (hydroquinone versus EDA), same reaction temperature (50 °C) but different reaction time. (C) PL spectra of reaction mixtures prepared at the identical reaction temperature (50 °C), same reaction time (2 h) but different molar ratios.

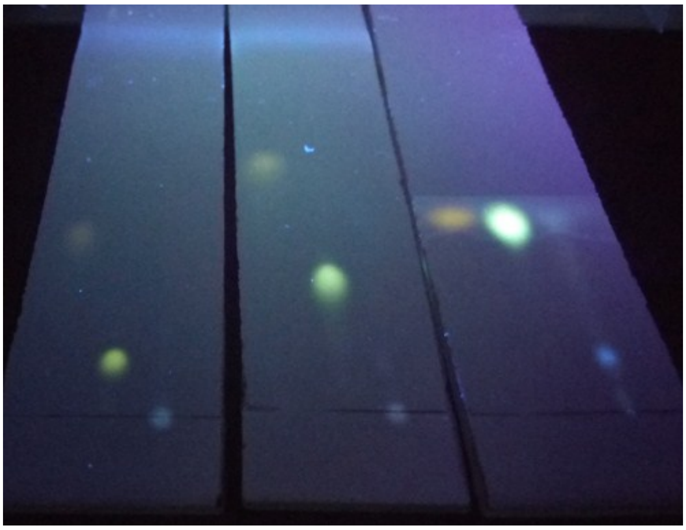

Fig. S3 Thin layer chromatogram of the purified PCDs in the different eluents. From left to right, the eluents are a mixture petroleum ether with ethyl acetate (6:4), ethyl acetate, and 75% ethanol (V/V), respectively.

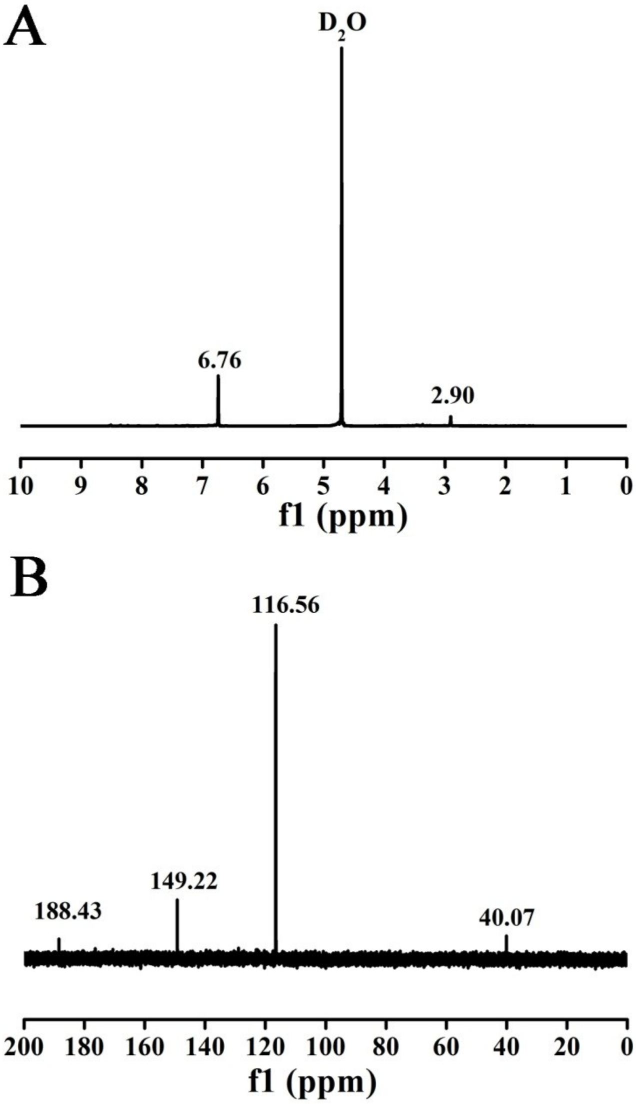

Fig. S4 (A) ^{1}H NMR and (B) ^{13}C NMR spectra (D_2O, 600 MHz) of PCDs before silica-gel column chromatography.

Table S1 Fluorescence lifetimes of y-PCDs, g-PCDs, and b-PCDs in water solutions.

	λ_{ex} (nm)	λ_{em} (nm)	τ (ns)	Percentage (%)	χ^2
y-PCDs	355	550	0.89	100	1.181
g-PCDs	410	510	4.01	100	1.071
b-PCDs	380	465	2.83	100	1.142

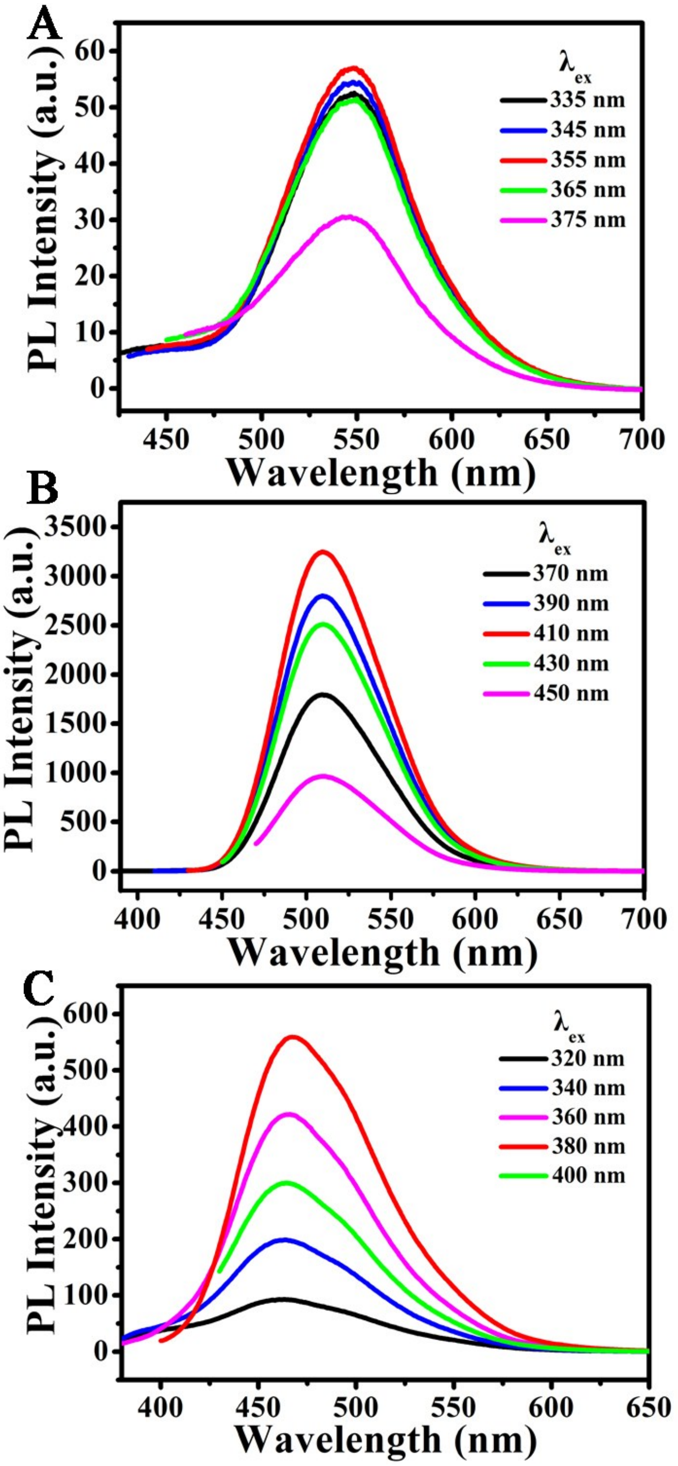

Fig. S5 PL emission spectra of (A) y-PCDs, (B) g-PCDs, and (C) b-PCDs under different excitation wavelengths.

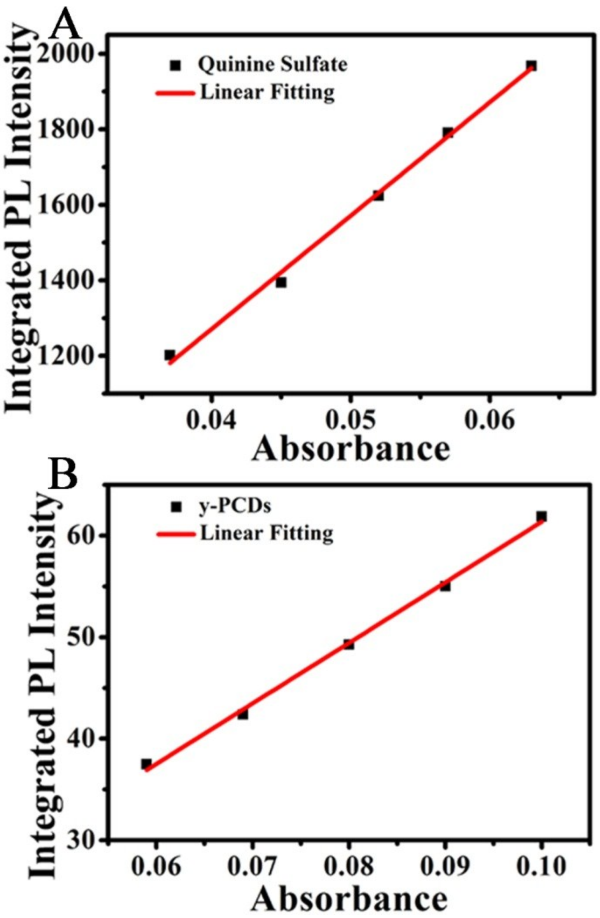

Fig. S6 Plots of integrated PL intensity of (A) quinolone sulfate in 0.1 M H_2SO_4 and (B) y-PCDs in DMF as a function of optical absorbance at 355 nm.

Table S2 QYs data of y-PCDs.

	Quinine Sulfate	y-PCDs in Water	y-PCDs in DMF
Slope	30011.25	—	596.91
QYs (%)	54	—	1.47

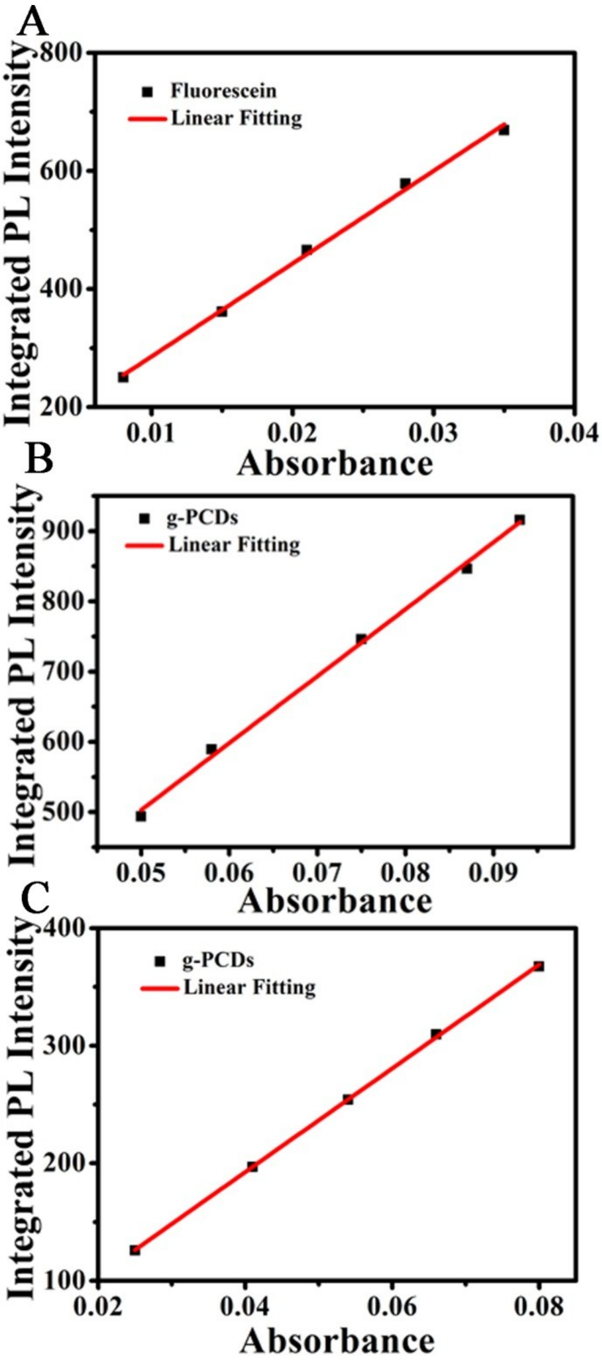

Fig. S7 Plots of integrated PL intensity of (A) fluorescein in 0.1 M NaOH, (B) g-PCDs in DMF, and (C) g-PCDs in water as a function of optical absorbance at 410 nm.

Table S3 QYs data of g-PCDs.

	Fluorescein	g-PCDs in Water	g-PCDs in DMF
Slope	15719.83	4413.17	9530.62
QYs (%)	95	26.67	78.68

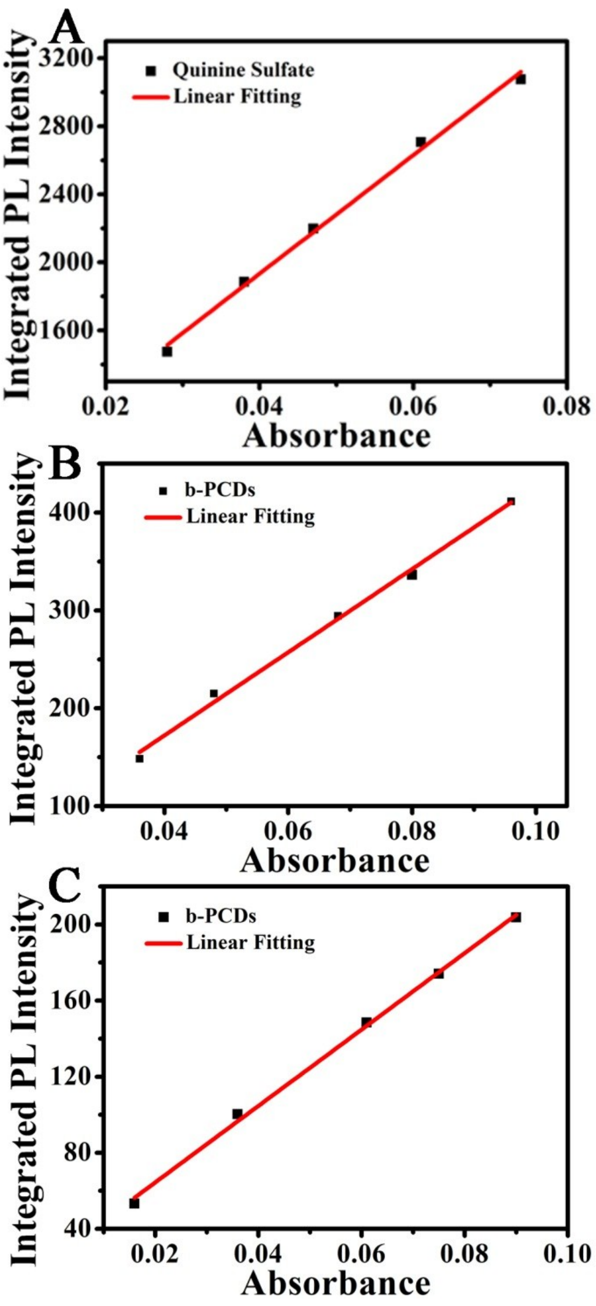

Fig. S8 Plots of integrated PL intensity of (A) quinolone sulfate in 0.1 M H_2SO_4, (B) b-PCDs in DMF, and (C) b-PCDs in water as a function of optical absorbance at 380 nm

Table S4 QYs data of b-PCDs.

	Quinine Sulfate	b-PCDs in Water	b-PCDs in DMF
Slope	34867.40	2008.79	4407.50
QYs (%)	54	3.11	9.32

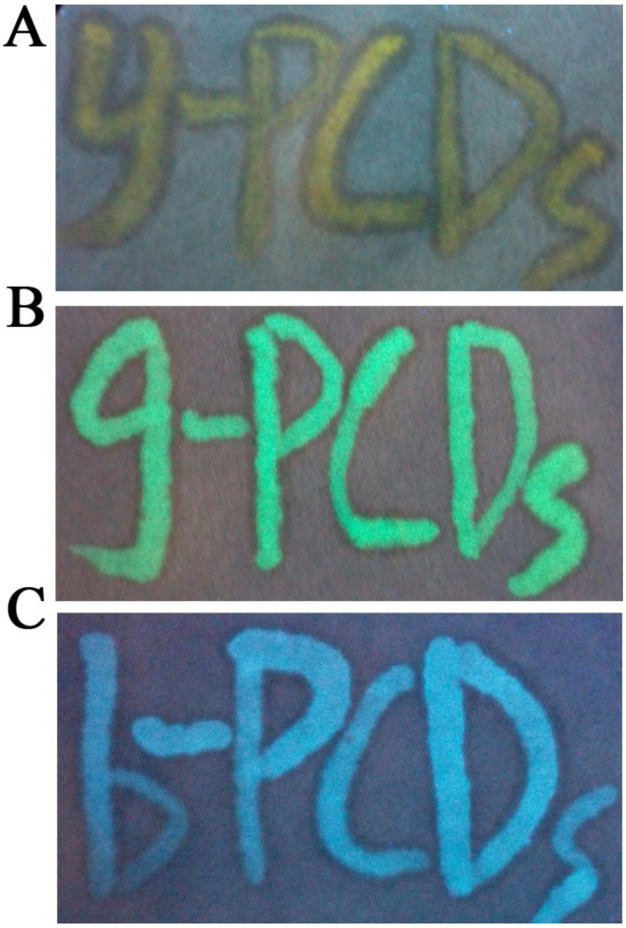

Fig. S9 The pictures obtained by handwriting them with the fluorescent ink of (A) y-PCDs, (B) g-PCDs, and (C) b-PCDs on a filter paper, under 365-nm UV light irradiation.

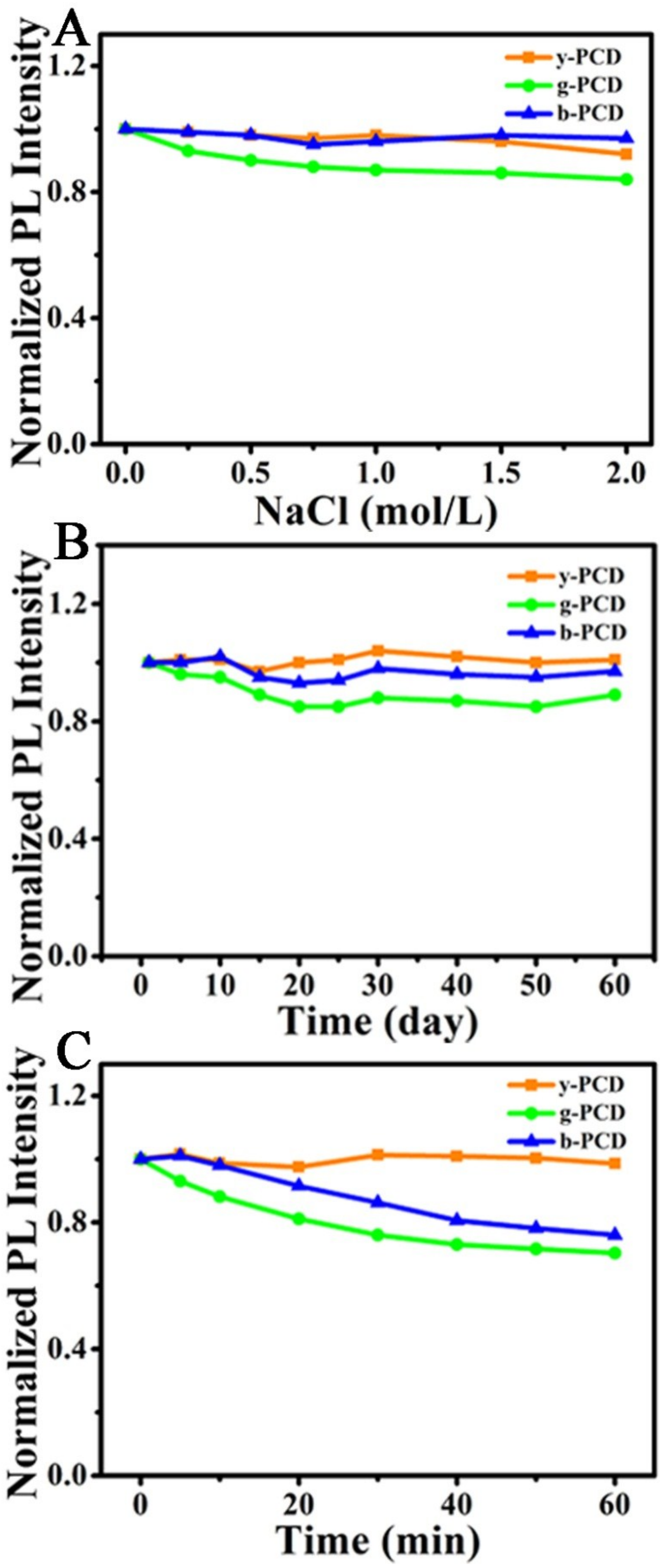

Fig. S10 (A) Effect of ionic strengths on the PL intensity of the three types of PCDs. (B) The normalized PL intensity of the three types of PCDs stored in ambient conditions two months. (C) Photostability for three types of PCDs in water under continuous irradiation with a 365-nm UV light for one hour.

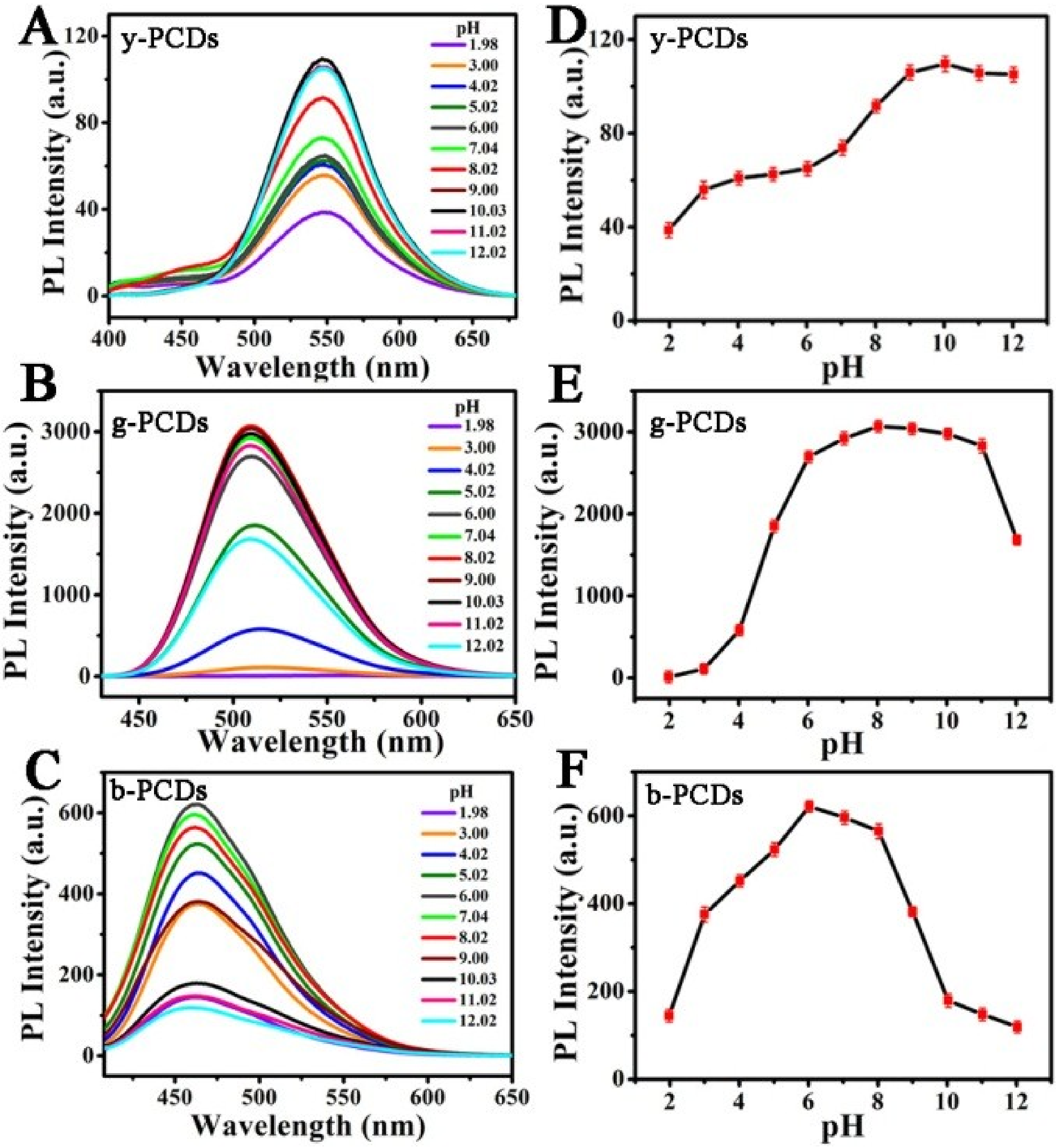

Fig. S11 PL spectra of (A) y-PCDs, (B) g-PCDs, and (C) b-PCDs in BR buffer solution with different pH values. The plot of PL intensities of (D) y-PCDs, (E) g-PCDs, and (F) b-PCDs versus different pH values.

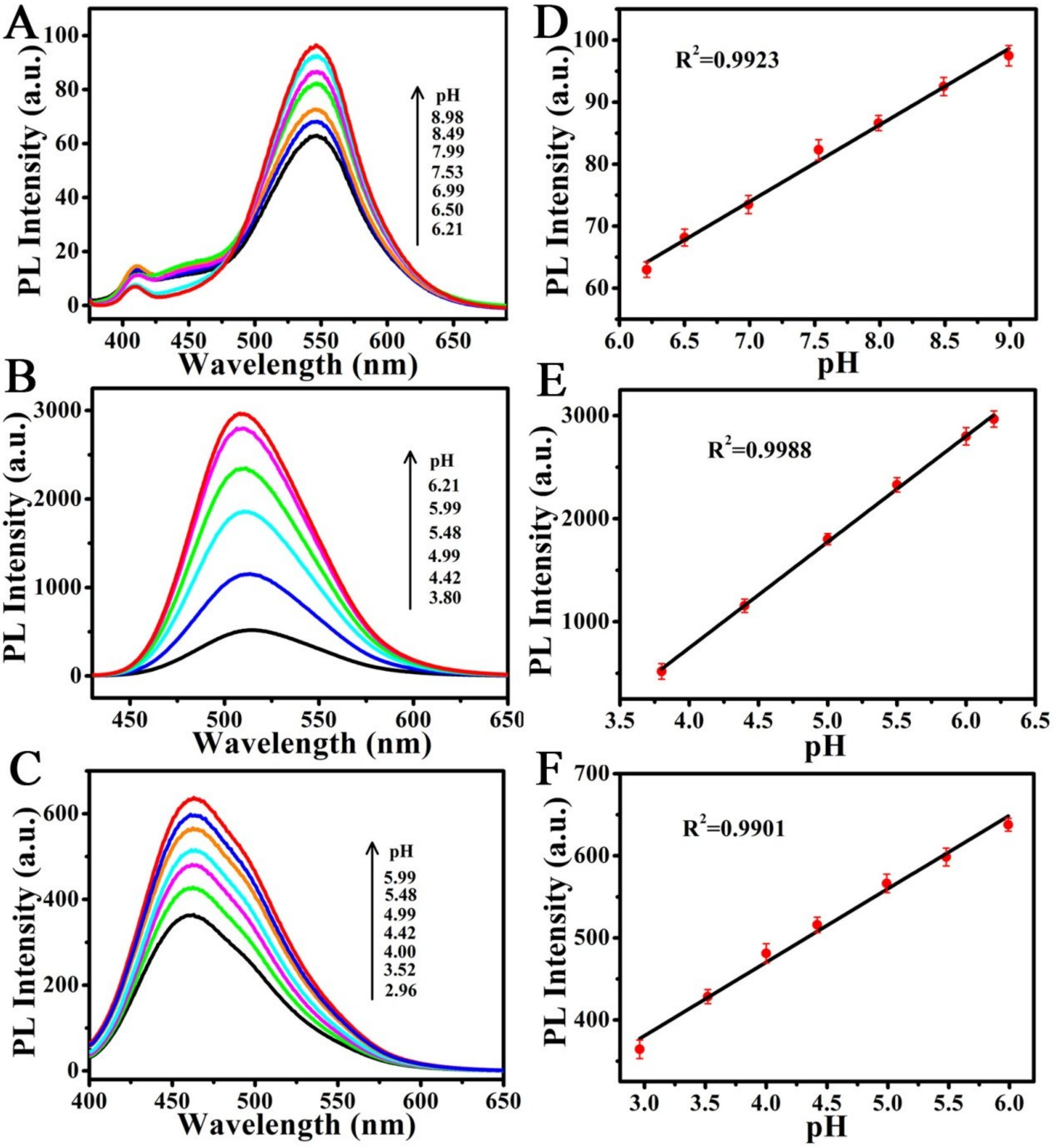

Fig. S12 PL spectra of (A) y-PCDs, (B) g-PCDs, and (C) b-PCDs in BR buffer solution with different pH values. The corresponding linear responses of (D) y-PCDs, (E) g-PCDs, and (F) b-PCDs versus pH values.

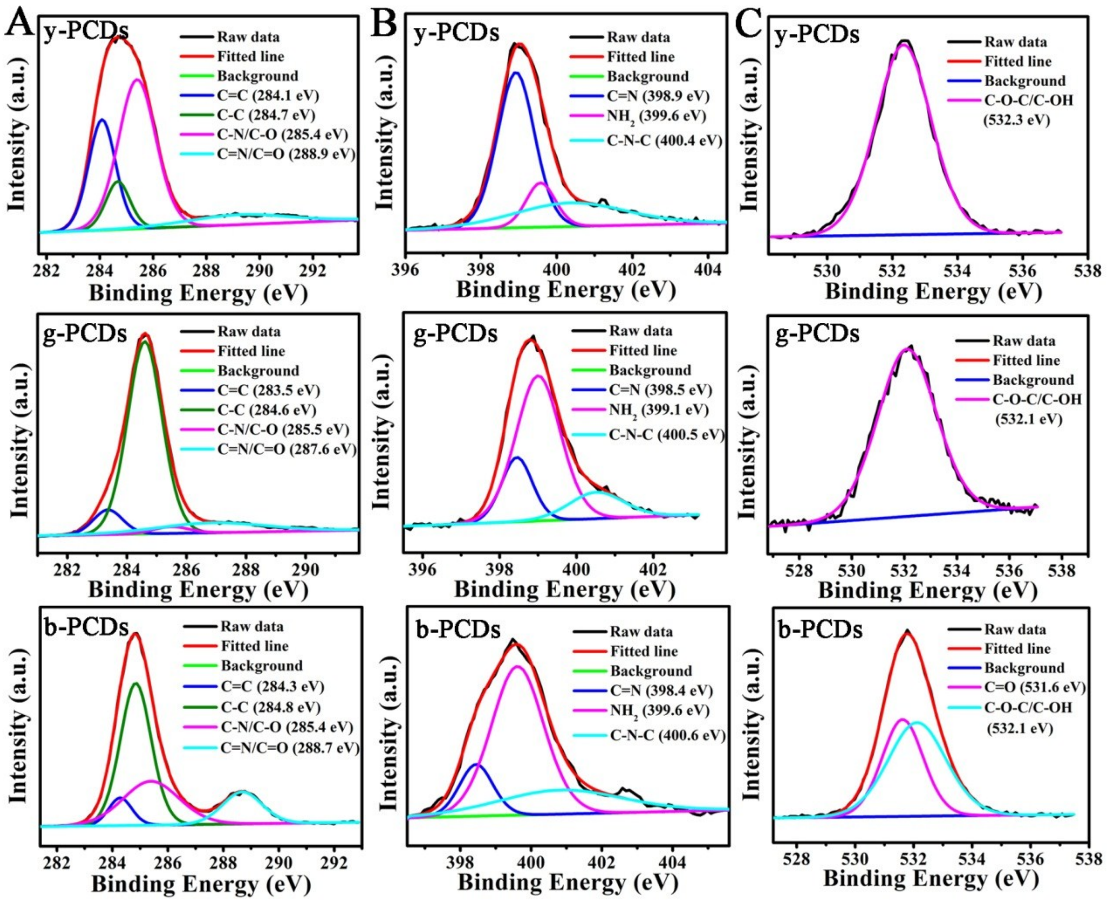

Fig. S13 Deconvoluted high-resolution XPS spectra of (A) C1s, (B) N1s, and (C) O1s for three types of PCDs.

Table S5 The relative contents of C, N, and O atoms for three types of PCDs were determined by XPS.

Sample	C (%)	N (%)	O (%)
y-PCDs	73.29	12.13	14.58
g-PCDs	78.45	14.36	7.19
b-PCDs	72.93	3.55	23.51

Table S6 XPS analysis of the C1s spectra of the three types of PCDs.

Sample	C=C	C–C	C–N/C–O	C=N/C=O
y-PCDs	27.72%	10.83%	52.03%	9.41%
g-PCDs	8.33%	76.58%	2.75%	12.34%
b-PCDs	7.36%	50.17%	28.14%	14.33%

Table S7 XPS analysis of the O1s spectra of the three types of PCDs.

Sample	C=O	C–O–C/C–OH
y-PCDs	—	100%
g-PCDs	—	100%
b-PCDs	42.41%	57.59%

References

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2 K. Jiang, S. Sun, L. Zhang, Y. Lu, A. G. Wu, C. Z. Cai and H. W. Lin, *Angew. Chem. Int. Ed.*, 2015, **54**, 5360–5363.