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Supporting information

Aggregation-Induced Room Temperature Phosphorescent Carbonized Polymer Dots with Wide-Range Tunable Lifetime for Optical Multiplexing

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Experimental Section

Materials: Triethylenetetramine was bought from Aladdin Chemicals Co. Ltd (Shanghai, China). Phosphoric acid and boric acid were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All chemicals were used as received without further purification unless otherwise specified. Deionized water was used throughout this study.

Characterization Method: A JEOL JEM 2100 TEM was used to examine the morphologies of NP-CPDs. The XRD patterns were measured by an X-ray diffraction using Cu-Kα radiation (PANalytical X'Pert Pro MPD). Optical absorption spectra were recorded on an UV-2600 spectrophotometer. The FL/RTP spectra and time-resolved FL/RTP decay data were obtained using a spectrometer (FLS1000) from Edinburgh Instruments. The absolute QY was obtained using Edinburgh FLS1000 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe900) and an integrating sphere, respectively. The photographs were taken with camera (Nikon, D7200) under UV lamp illumination working at 365 nm (UV lamp: SPECTROLINE, ENF-280C/FBE, 8W). The FTIR spectra were measured using a Nicolet 380 spectrograph. The XPS spectra were measured with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. TGA was recorded from a TA Instruments Q50 thermal analyzer (New Castle, DE, USA) under a stream of nitrogen (N_2) gas with a heating rate of 5 ℃ min^{-1}. Differential scanning calorimetry (DSC) was studied using a TA Q20 differential scanning calorimeter with a scan rate of 5 ℃ min^{-1}. Inks were printed using a printer (HP DesKJet 1110).

Synthesis of CPDs: In a typical process, triethylenetetramine (0.8 mL), phosphoric acid (0.8, 1.0, 1.3, 1.6 mL) and boric acid (1.5 g) were dissolved in deionized water (20 mL) to form a clear dispersion. The resultant dispersion was transferred to a Teflon-inlet stainless steel autoclave (50 mL), heated at 200 ℃ for 6.0 h, and then natually cooled down to room temperature. The obtained solution was heated at 200 ℃ for 3.0 h to get powder samples. Finally, the CPDs-0.8, CPDs-1.0, CPDs-1.3, and CPDs-1.6 were obtained.

Preparation of the security ink: The CPDs aqueous dispersion (50 mg/mL) can be directly used as security inks for anti-counterfeiting.

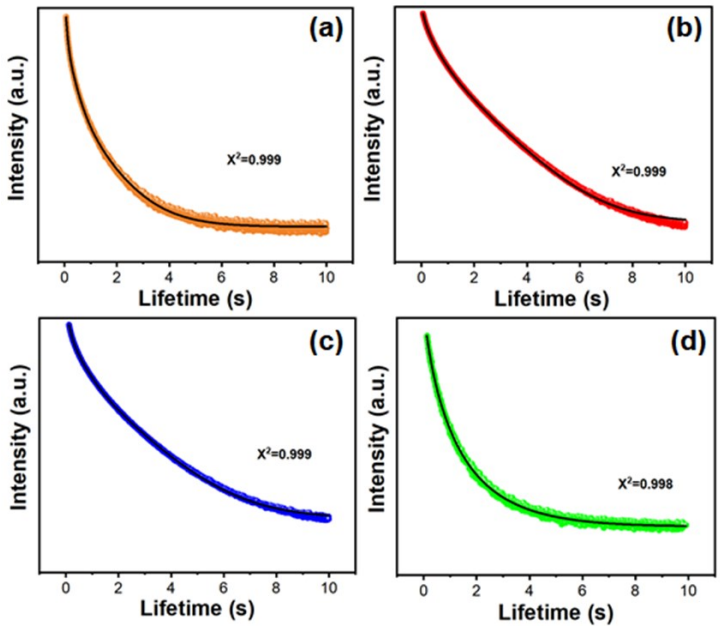

Figure S1. The fitting curves of RTP lifetime decay with CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d).

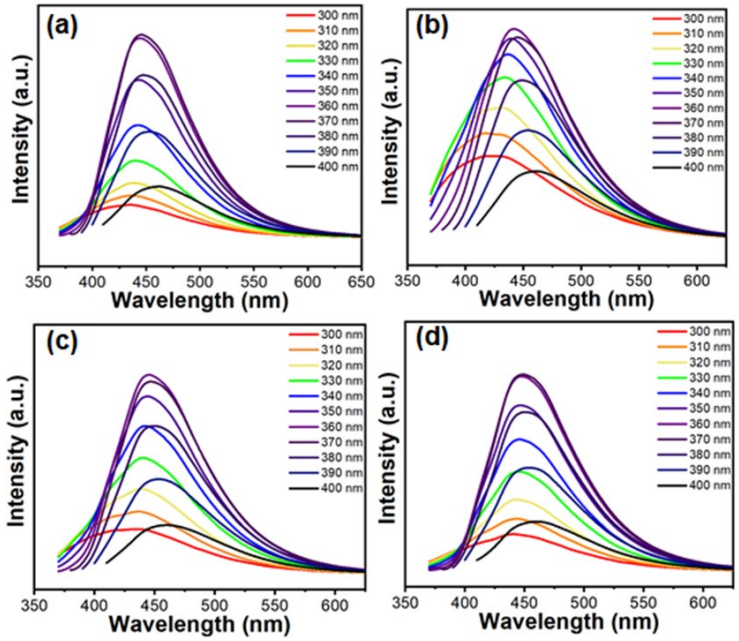

Figure S2. Evolution of the FL spectra with the variation of the excitation wavelength for the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d) aqueous solution, respectively.

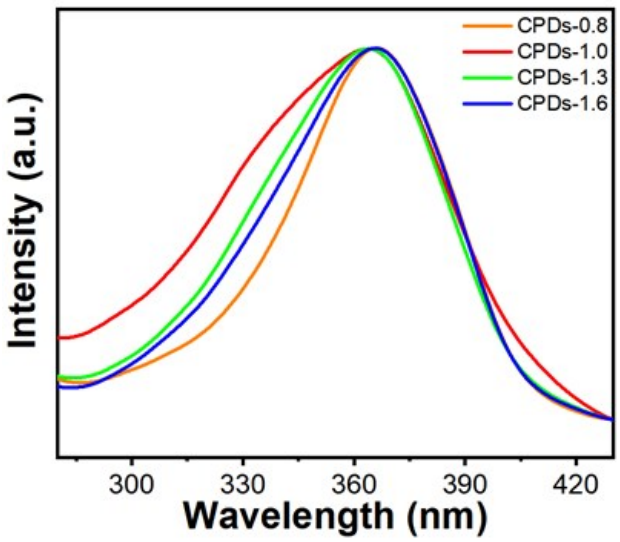

Figure S3. Excitation spectra of the FL of CPDs-0.8, CPDs-1.0, CPDs-1.3 and CPDs-1.6 aqueous solution, respectively.

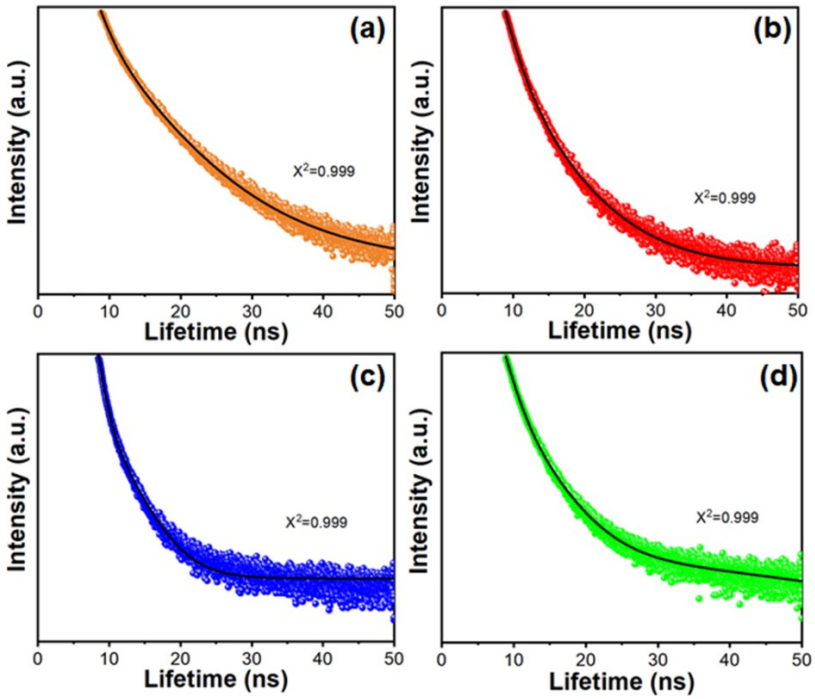

Figure S4. The fitting curves of FL lifetime decay with CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d).

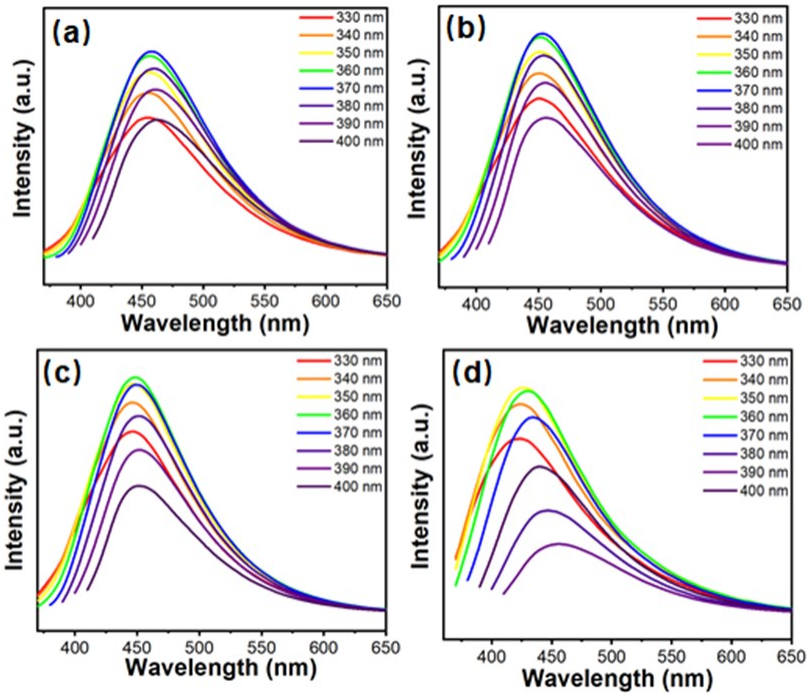

Figure S5. Evolution of the FL spectra with the variation of excitation wavelength for the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d), respectively.

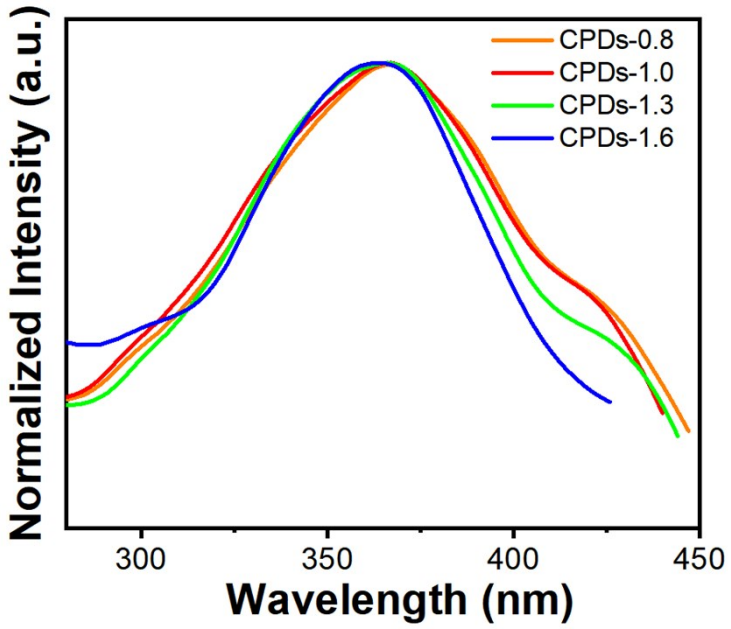

Figure S6. Excitation spectra of the FL of CPDs-0.8, CPDs-1.0, CPDs-1.3 and CPDs-1.6, respectively.

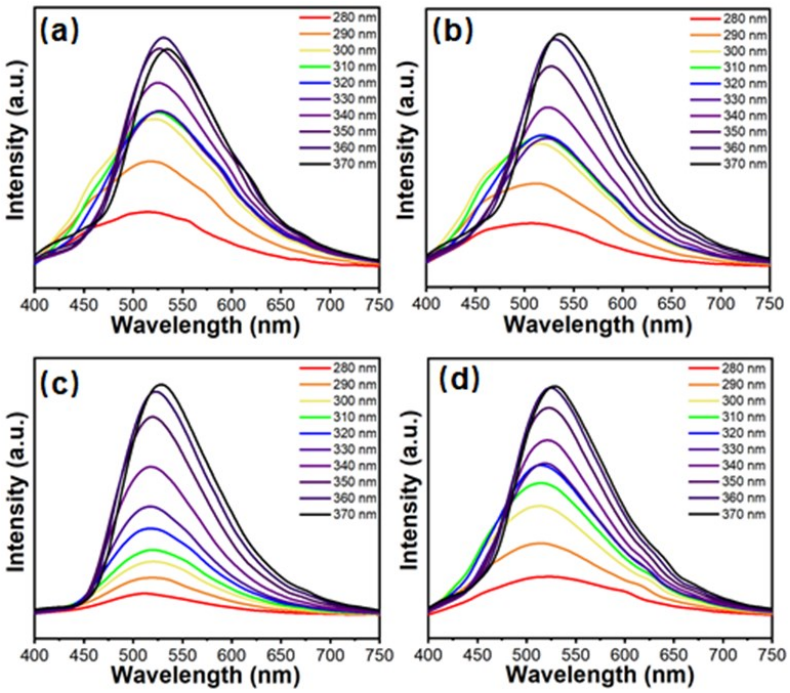

Figure S7. Evolution of the RTP spectra with the variation of excitation wavelength for the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d), respectively.

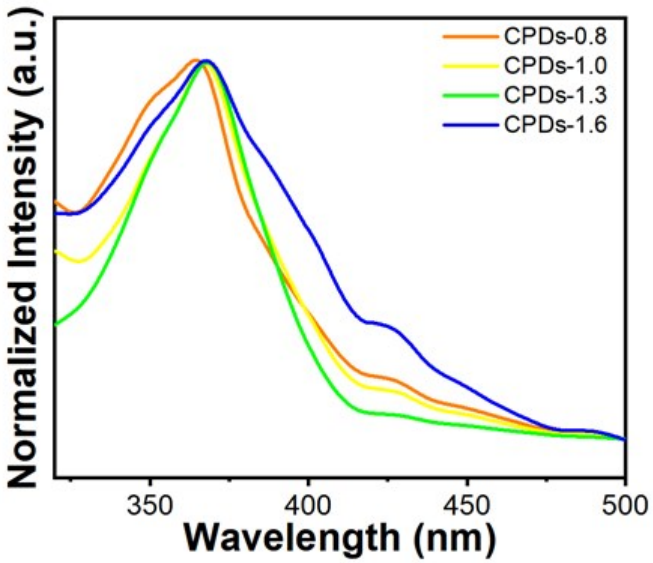

Figure S8. Excitation spectra of the RTP of CPDs-0.8, CPDs-1.0, CPDs-1.3 and CPDs-1.6, respectively.

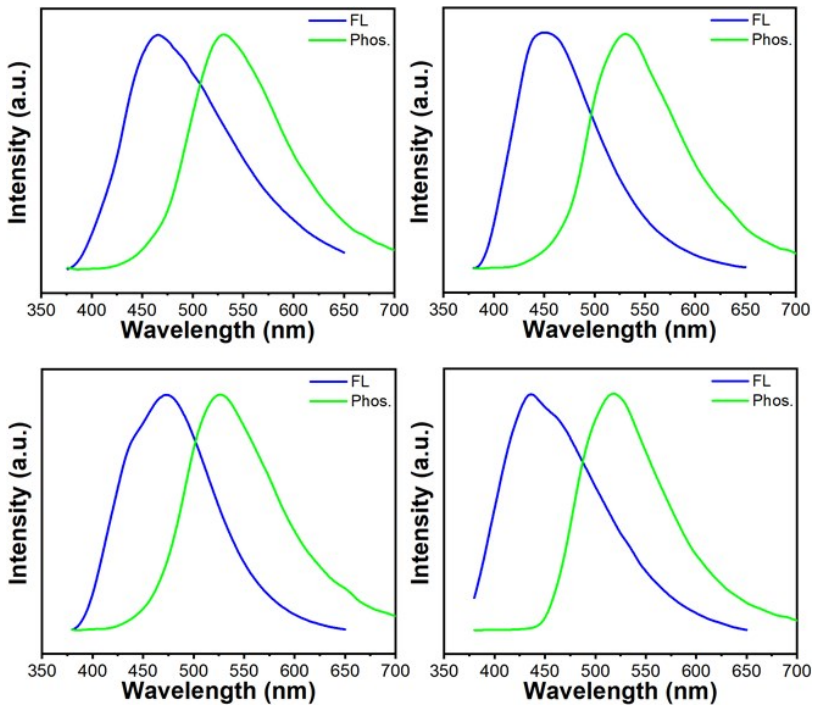

Figure S9. FL and RTP spectra of the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d) measured at 77 K upon excitation at 365 nm, respectively.

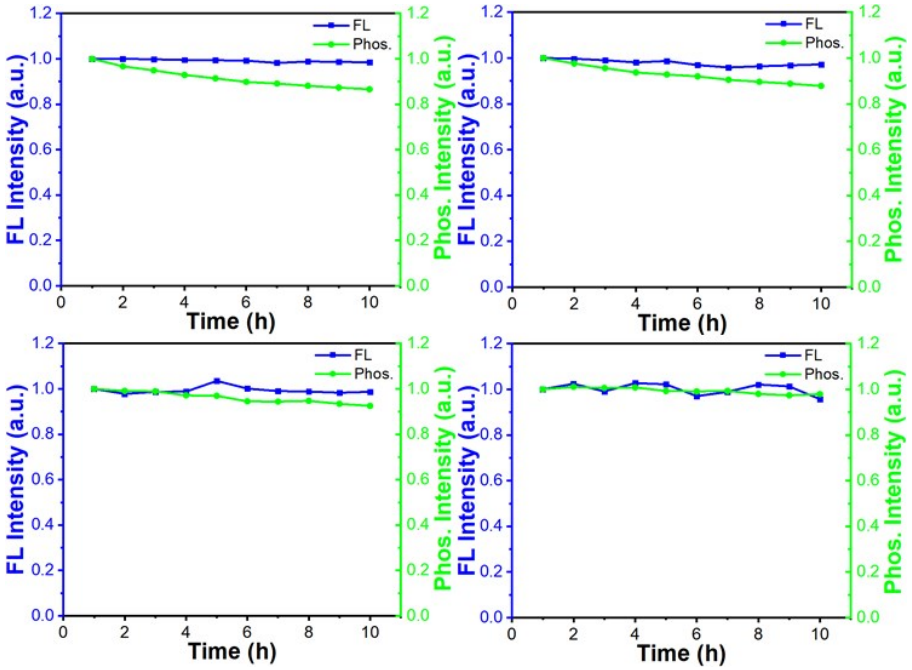

Figure S10. Photostability of CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d) under continuous illumination with an UV (365 nm) beam for 10 h.

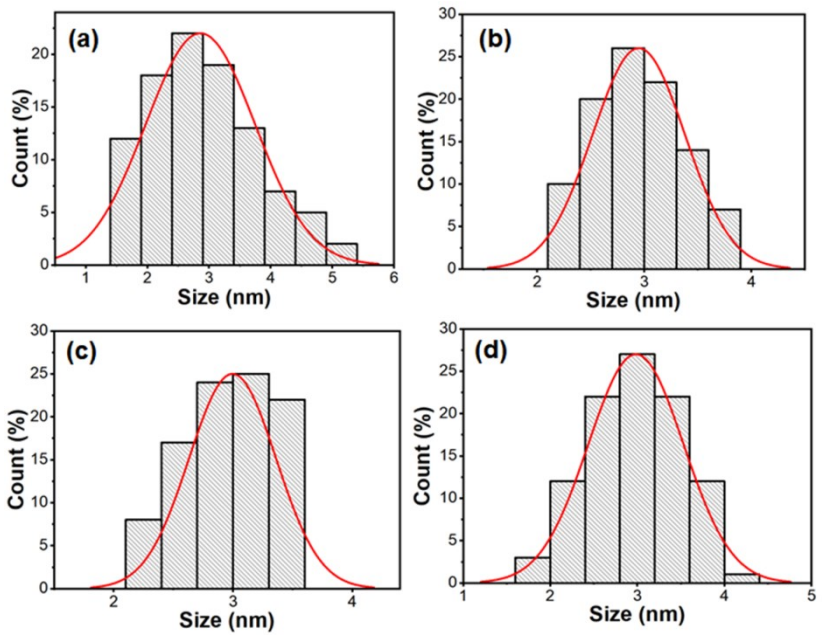

Figure S11. The size distributions of CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d).

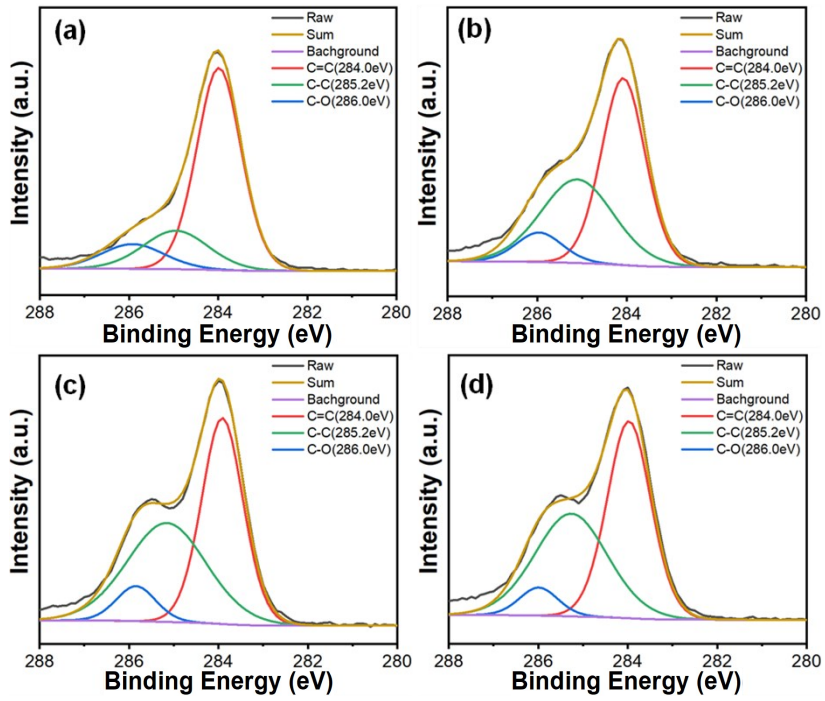

Figure S12. High-resolution C 1s spectra of the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d).

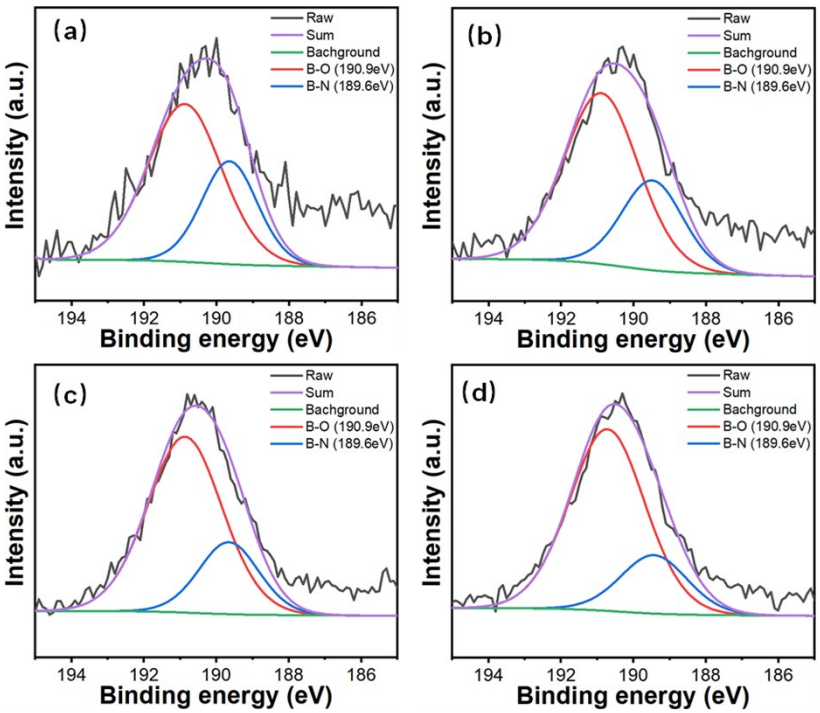

Figure S13. High-resolution B 1s spectra of the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d).

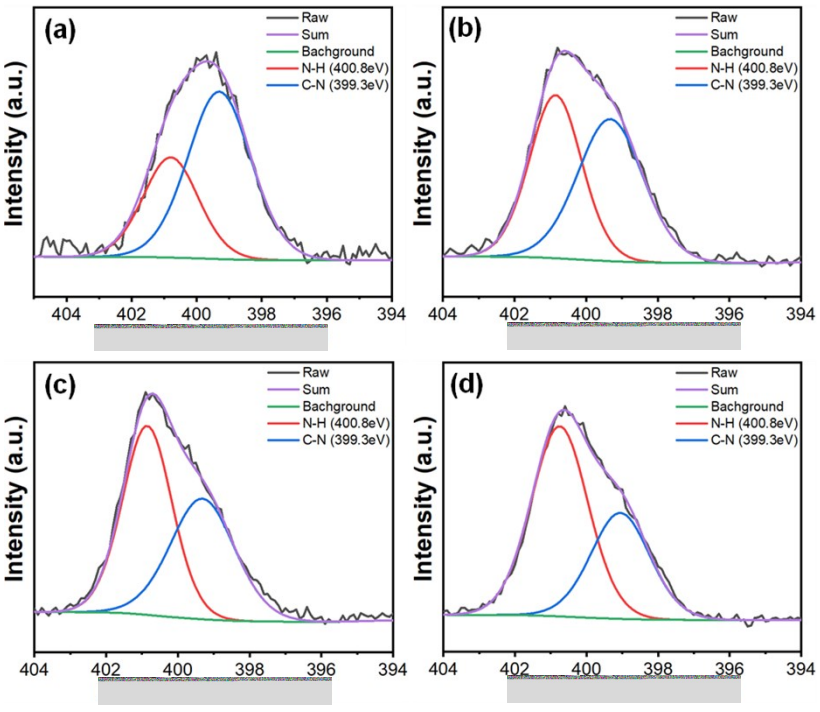

Figure S14. High-resolution N 1s spectra of the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d).

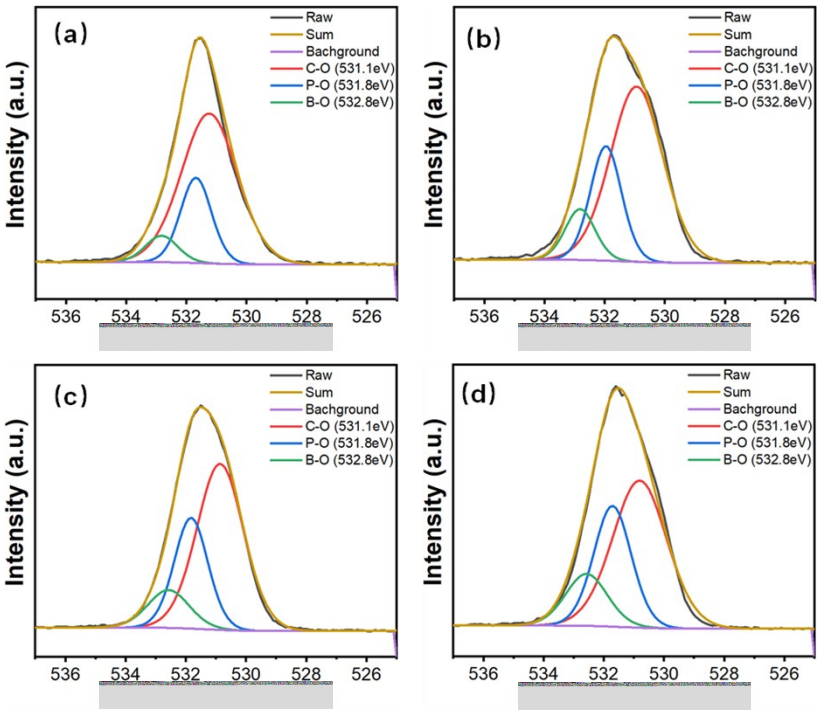

Figure S15. High-resolution O 1s spectra of the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d).

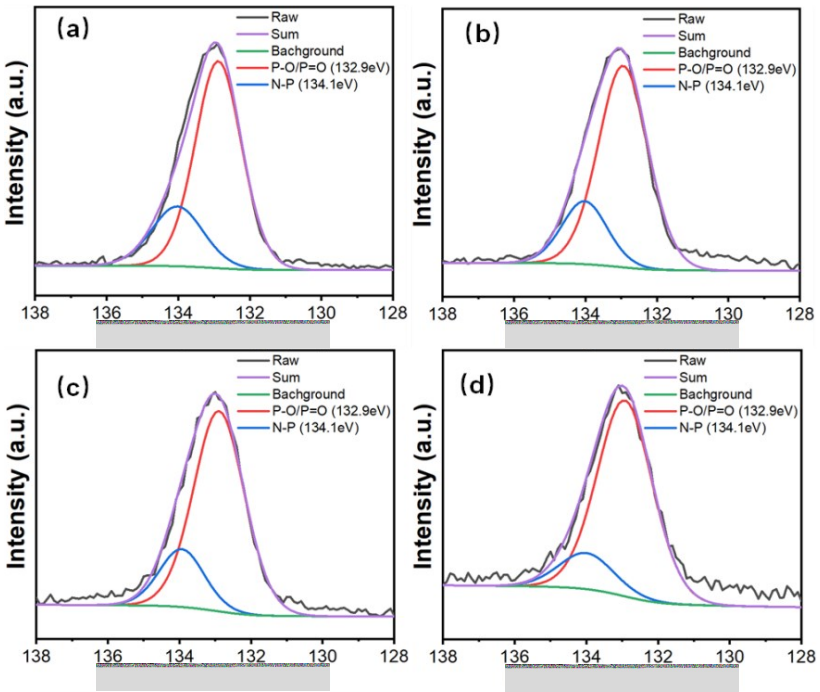

Figure S16. High-resolution P 2p spectra of the CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d).

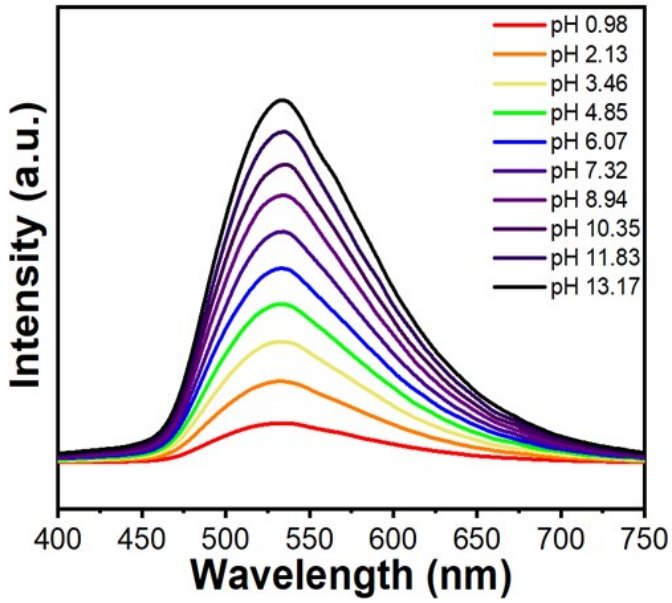

Figure S17. RTP spectra of CPDs-1.6 for various pH values.

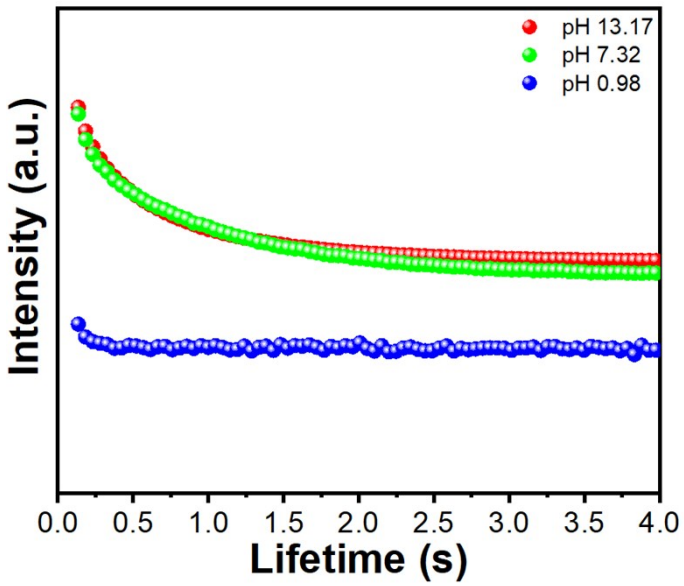

Figure S18. RTP lifetime decay curves of CPDs-1.6 at pH 13.17, 7.32 and 0.98.

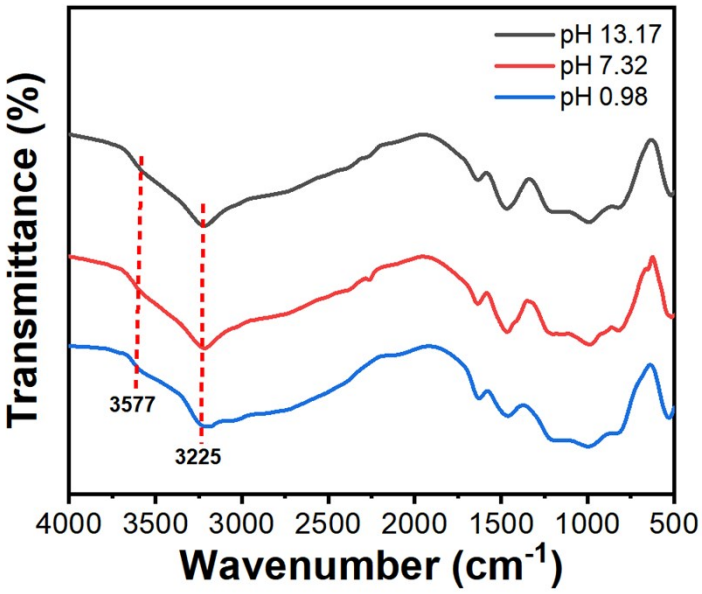

Figure S19. FTIR spectra of FNCDs at certain pH values.

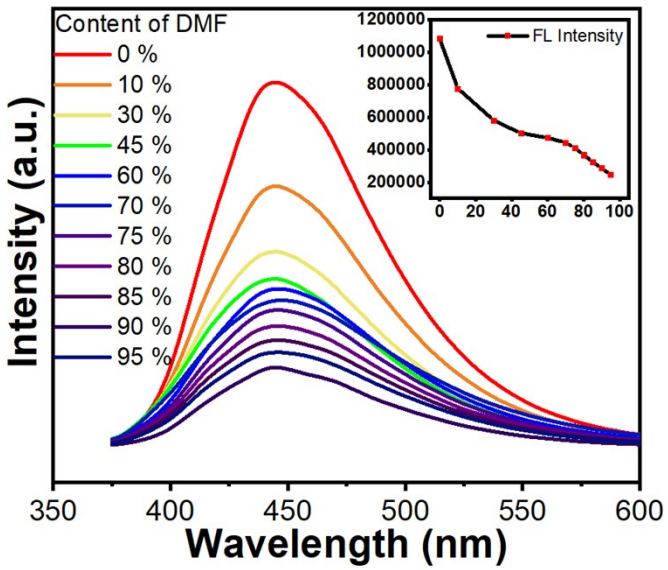

Figure S20. FL emission spectra of the CPDs-1.6 dispersion in water with various amounts of DMF from 0 to 95 % (inset: relationship between FL intensity and DMF content).

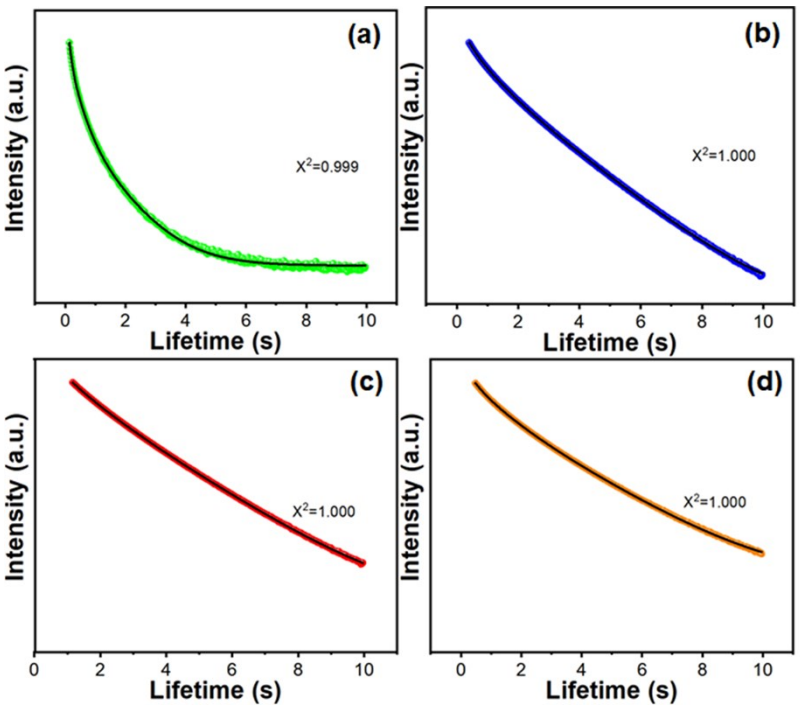

Figure S21. The fitting curves of RTP lifetime decay with CPDs-0.8 (a), CPDs-1.0 (b), CPDs-1.3 (c) and CPDs-1.6 (d) at 77 K.

Table S1. Fitting parameters of the RTP decay curves of CPDs-0.8, CPDs-1.0, CPDs-1.3 and CPDs-1.6 under excitation at 410 nm.

Sample	τ_1 (ms)	B_1 (%)	τ_2 (ms)	B_2 (%)	τ_3 (ms)	B_3 (%)	τ_{avg} (s)	x^2
CPDs-0.8	34.26	11.69	266.67	32.87	1152.23	55.44	0.73	0.999
CPDs-1.0	143.76	5.64	536.01	34.31	1512.72	60.06	1.10	0.999
CPDs-1.3	382.38	6.72	934.14	37.03	1746.56	56.26	1.35	0.999
CPDs-1.6	532.27	5.46	1553.89	35.15	2836.35	59.39	2.26	0.998

Table S2. Fitting parameters of the FL decay curves of CPDs-0.8, CPDs-1.0, CPDs-1.3 and CPDs-1.6 under excitation at 410 nm.

Sample	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ_{avg} (ns)	x^2
CPDs-0.8	2.08	25.99	7.16	74.01	5.58	0.999
CPDs-1.0	1.82	50.40	5.98	49.60	3.88	0.999
CPDs-1.3	1.24	43.49	4.82	56.51	3.26	0.999
CPDs-1.6	1.65	54.06	5.26	45.94	3.31	0.999

Table S3. Relative contents of C, N, O, P and B in the CPDs-0.8, CPDs-1.0, CPDs-1.3 and CPDs-1.6 based on XPS measurements.

Sample	C 1s (%)	N 1s (%)	B 1s (%)	P 2p (%)	O 1s (%)
CPDs-0.8	53.54	5.27	10.67	4.33	26.19
CPDs-1.0	44.77	8.49	14.44	4.92	27.37
CPDs-1.3	38.41	9.18	15.65	6.46	30.30
CPDs-1.6	35.35	9.58	16.28	7.24	31.55

Table S4. Relative contents of different functional groups in the CPDs-0.8, CPDs-1.0, CPDs-1.3 and CPDs-1.6 (based on the fitting results of Figure S10-14).

Sample	C 1s (%)			N 1s (%)		B 1s (%)		P 2p (%)		O 1s (%)		
	C-C	C=C	C-O	C-N	N-H	B-O	B-N	P-O/P=O	N-P	B-O	P-O	C-O
CPDs-0.8	68.5	19.2	12.3	65.8	34.2	67.1	32.9	75.8	24.2	7.1	22.5	70.4
CPDs-1.0	52.4	38.7	8.9	52.1	47.9	69.9	30.1	77.5	22.5	10.1	25.8	64.1
CPDs-1.3	48.1	44.2	7.7	45.4	54.6	75.2	24.8	80.6	19.4	12.9	28.6	59.5
CPDs-1.6	50.3	43.2	6.5	36.7	63.3	78.1	21.9	84.9	15.1	14.7	31.0	54.3

Table S5. Fitting parameters of the RTP decay curves of CPDs-0.8, CPDs-1.0, CPDs-1.3 and CPDs-1.6 at 77 K.

Sample	τ_1 (ms)	B_1 (%)	τ_2 (ms)	B_2 (%)	τ_{avg} (ms)	x^2
CPDs-0.8	663.91	47.99	1060.60	52.01	870.23	0.999
CPDs-1.0	460.21	26.50	1618.52	73.50	1311.56	1.000
CPDs-1.3	492.27	25.22	1802.58	74.78	1472.12	1.000
CPDs-1.6	747.80	15.18	2726.52	84.82	2426.15	1.000