

Supporting Information

Ultralong-lived room temperature phosphorescence from N and P codoped self-protective carbonized polymer dots toward confidential information encryption and decryption

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Experimental Section

Materials: Diethylenetriamine was bought from Aladdin Chemicals Co. Ltd (Shanghai, China). Phosphoric acid was 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 pattern was measured by an X-ray diffraction using Cu-K α 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 FT-IR spectrum was measured using a Nicolet 380 spectrograph. The XPS spectrum was measured with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The Raman spectrum was measured using laser confocal Micro-Raman spectroscopy (LabRAM Aramis). NMR spectra were recorded in Bruker DRX500. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker NMR spectrometer. TGA was recorded from a TA Instruments Q50 thermal analyzer (New Castle, DE, USA) under a stream of nitrogen (N₂) gas with a heating rate of 5 °C min⁻¹. Differential scanning calorimetry (DSC) was studied using a TA Q20 differential scanning calorimeter with a scan rate of 5 °C min⁻¹. Inks were printed using a printer (BroadJET L3000pro, China).

Synthesis of NP-CPDs: In a typical process, diethylenetriamine (3.0 mL) and phosphoric acid (1.0 mL) 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 °C for 5.0 h, and then naturally cooled down to room temperature. Finally, the NP-CPDs were obtained by dialyzing with a dialysis membrane (MWCO: 500 Da) for 2 days and heat-drying, respectively.

Synthesis of the PS-CPDs, PP-CPDs and DS-CPDs: Control experiments were performed by using 1,5-pentanediol to replace diethylenetriamine or using sulphuric acid to replace phosphoric acid under the same reaction conditions as that for the NP-CPDs. The products that obtained from 1,5-pentanediol and sulphuric acid was named as PS-CPDs, from 1,5-

pentanediol and phosphoric acid was named as PP-CPDs, and from diethylenetriamine and sulphuric acid was named as DS-CPDs, respectively.

Preparation of the security ink: The NP-CPDs aqueous dispersion (5.0 mg/mL) can be directly used as security ink for anti-counterfeiting.

Synthesis of the interference ink: Urea (1.0 g) and citric acid (1.0 g) were dissolved in water (20 mL), and the dispersion was then transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (50 mL) and heated at 200 °C for 6 h. After the reaction, the reactor was cooled to room temperature naturally. The excess precursors and resulting small molecules were removed by dialyzing against water through a dialysis membrane (MWCO: 500 Da) for 2 days. The resultant B-CDs were dispersed in water (3.0 mg/mL) and employed as the interference fluorescent ink.

Table S1. Fitting parameters of the FL decay curves of NP-CPDs.

Sample	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ_3 (ns)	B_3 (%)	τ_{avg} (ns)	ϕ
NP-CPDs	3.74	70.88	0.85	3.41	10.03	9.17	3.60	0.99

Table S2. Comparisons of RTP lifetime and delay time of recently reported CDs.

The name of CDs	RTP lifetime	Delay time	References
CDs@MnAPO-CJ50	10.94 ms	119 ms	[20]
TA-CDs	183.6 ms	2.5 s	[22]
FNCDs	1.21 s	-	[23]
CD-CA	187 ms	-	[24]
URTP CDs	1.51 s	12 s	[29]
URTP CDs	1.46 s	10 s	[32]
F-CDs	1.39 s	10 s	[33]
GQD	783 ms	4 s	[34]
M-CDs	664 ms	2 s	[35]
MP-CDs	880 ms	8 s	[36]
CPDs	320 ms	7 s	[37]
NP-CPDs	1.48 s	23 s	This work

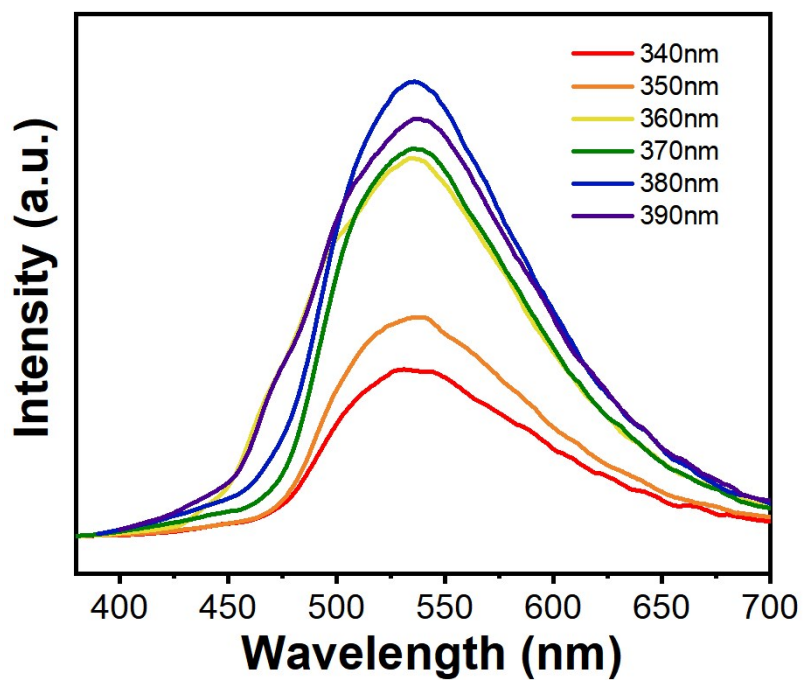


Fig. S1. Evolution of the URTP spectra with the excitation wavelength for the NP-CPDs.

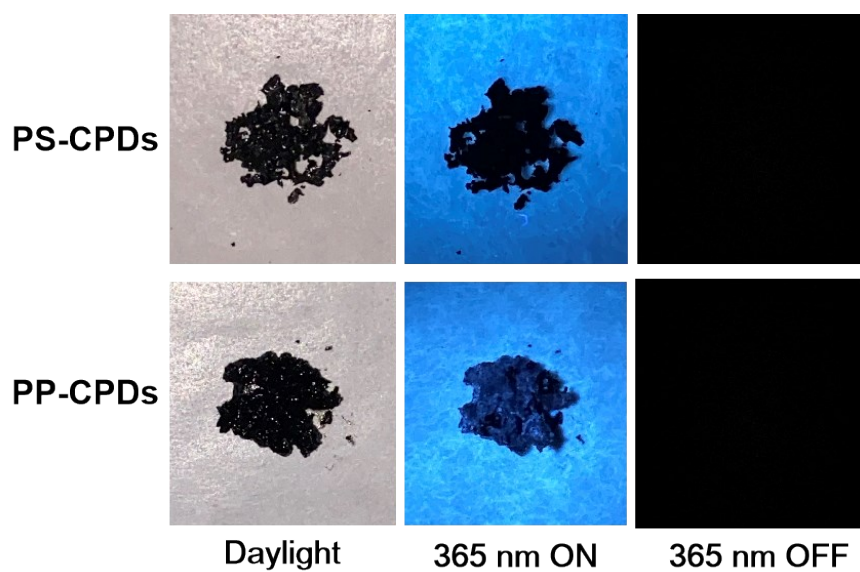


Fig. S2. Photographs of PS-CPDs and PP-CPDs powder captured under daylight and a UV lamp (365 nm) ON and OFF, respectively.

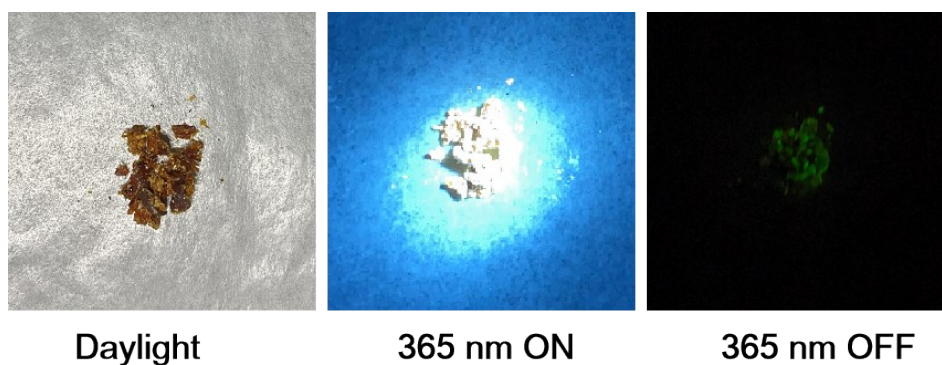


Fig. S3. Photographs of DS-CPDs powder captured under daylight and a UV lamp (365 nm) ON and OFF, respectively.

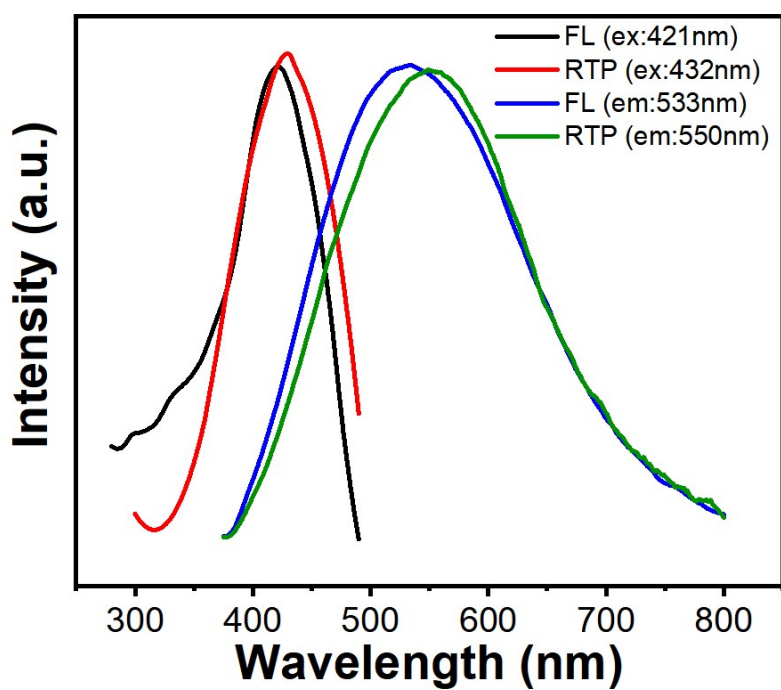


Fig. S4. Normalized excitation and emission spectra of DS-CPDs for FL (black and blue lines) and RTP (red and green lines).

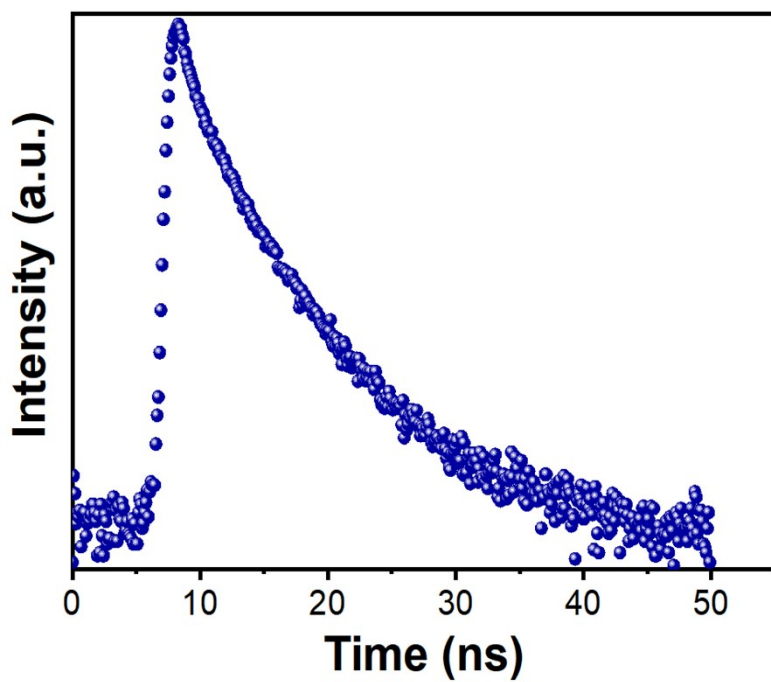


Fig. S5. FL decay spectrum of the NP-CPDs.

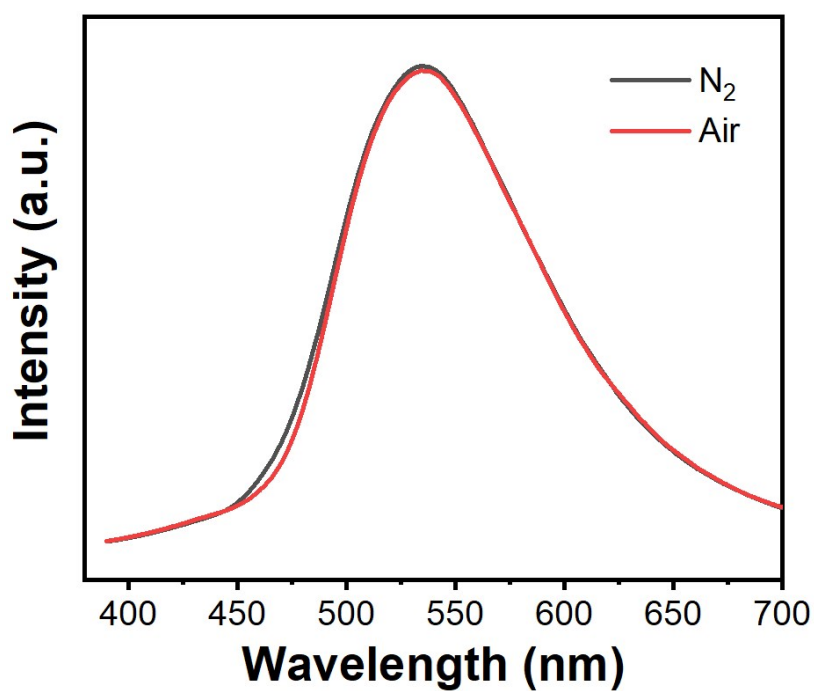


Fig. S6. URTP emission spectra of NP-CPDs in air and N₂.

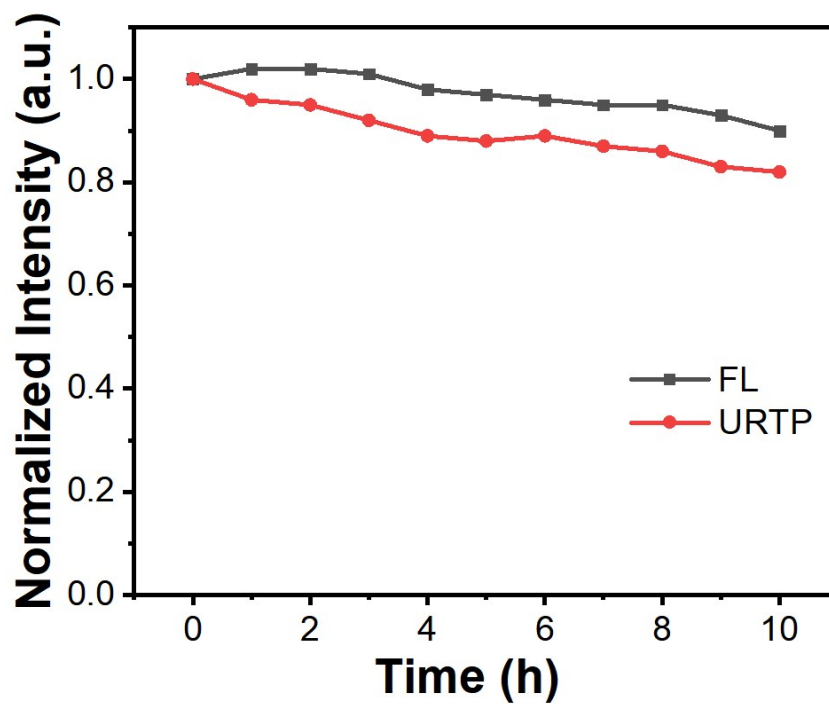


Fig. S7. Photostability of NP-CPDs under continuous illumination with an UV (365 nm) beam for 10 h.



Fig. S8. Photographs of the NP-CPDs dispersion under daylight (left) and 365 nm UV lamp (right).

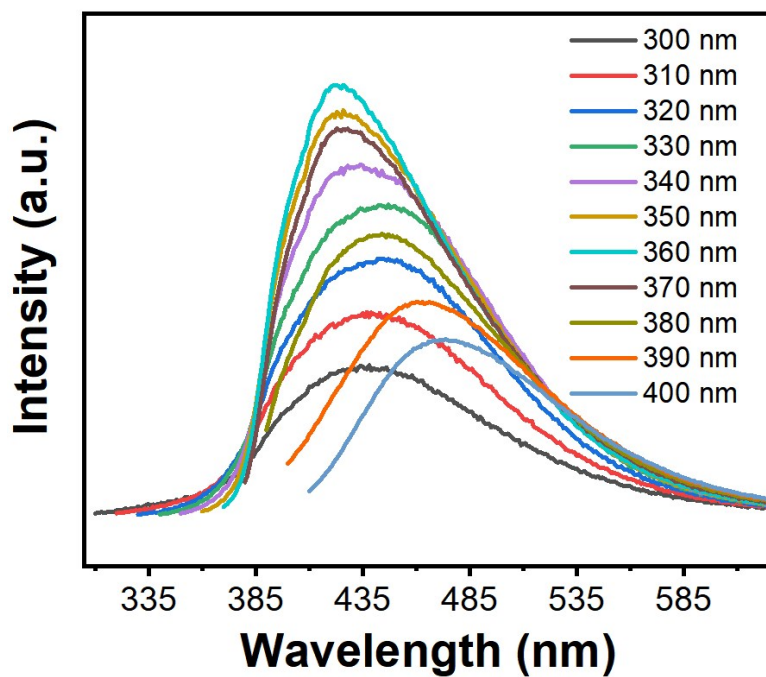


Fig. S9. Evolution of the FL spectra with the excitation wavelength for the NP-CPDs dispersion.

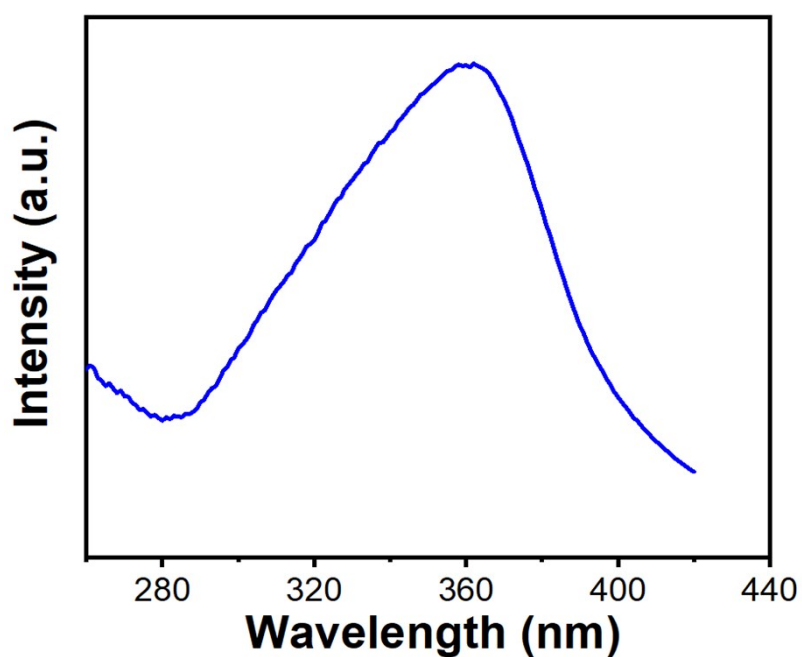


Fig. S10. Excitation spectrum of the FL of the NP-CPDs dispersion. The FL spectrum is monitored at 426 nm.

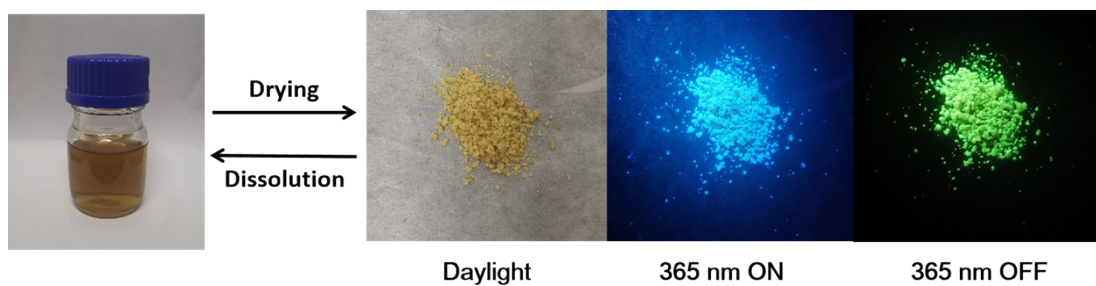


Fig. S11. Liquid-solid reversibility of NP-CPDs after 10 cycles.

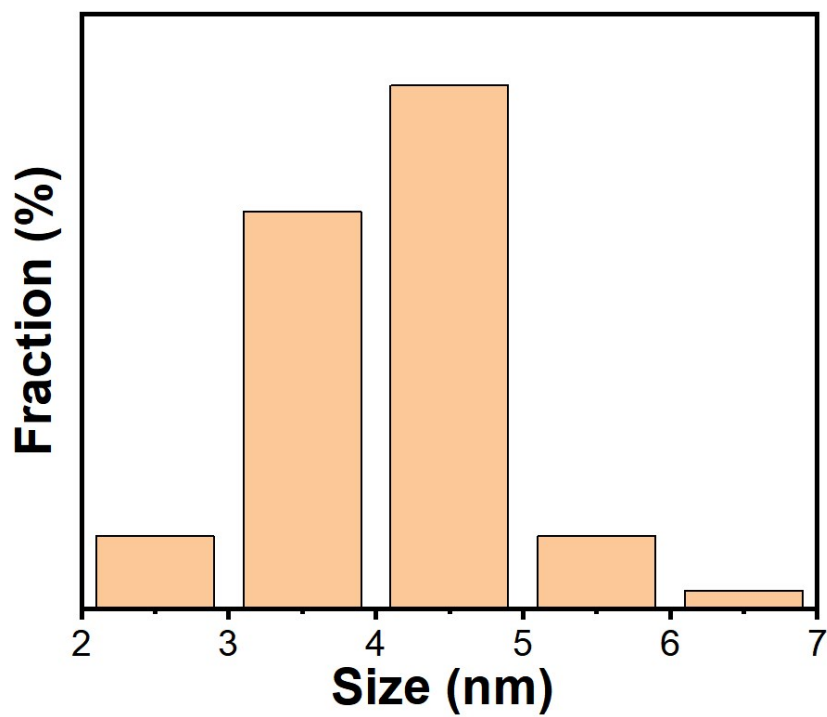


Fig. S12. Size distribution of NP-CPDs.

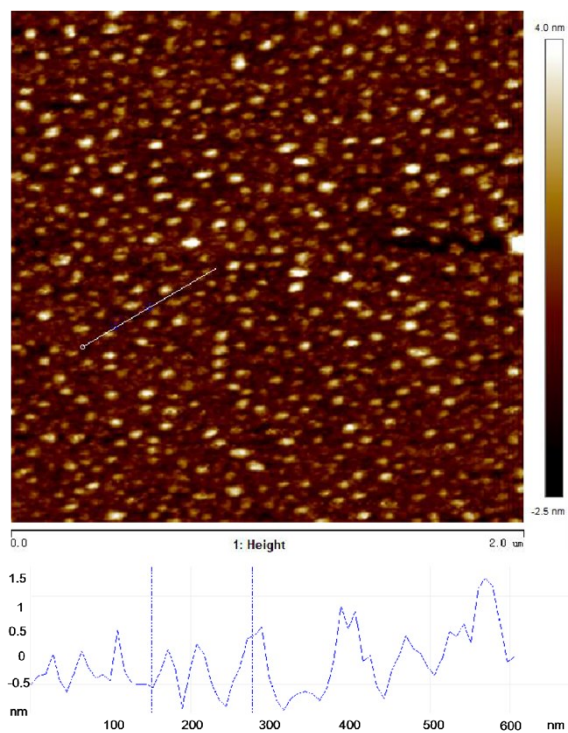


Fig. S13. AFM image and height profiles of NP-CPDs.

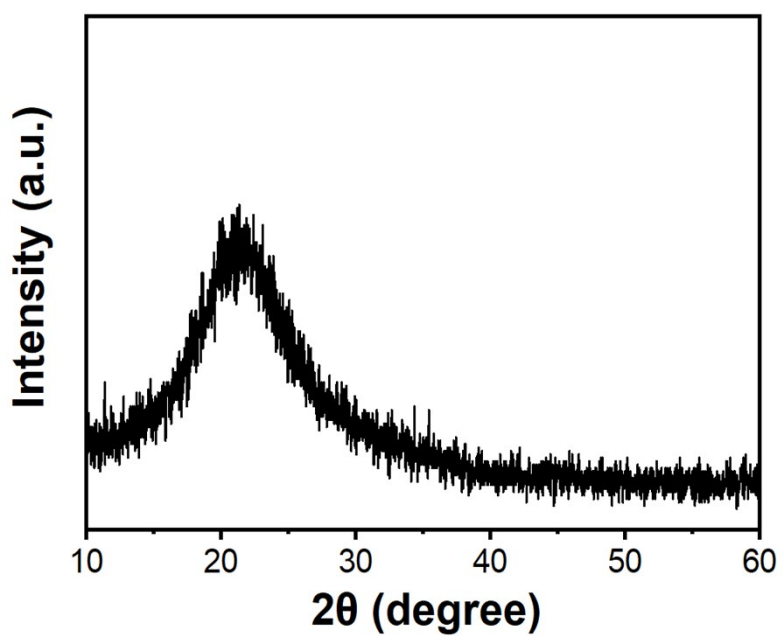


Fig. S14. XRD pattern of NP-CPDs.

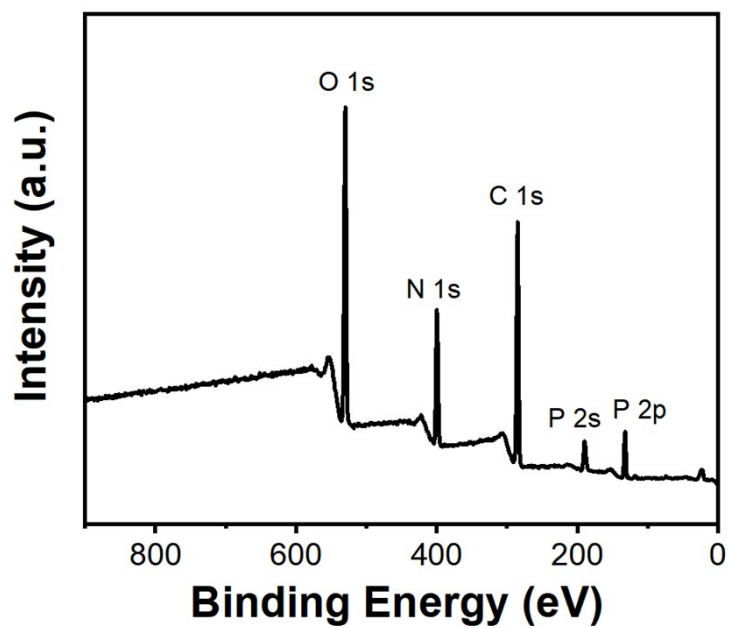


Fig. S15. XPS survey spectrum of NP-CPDs.

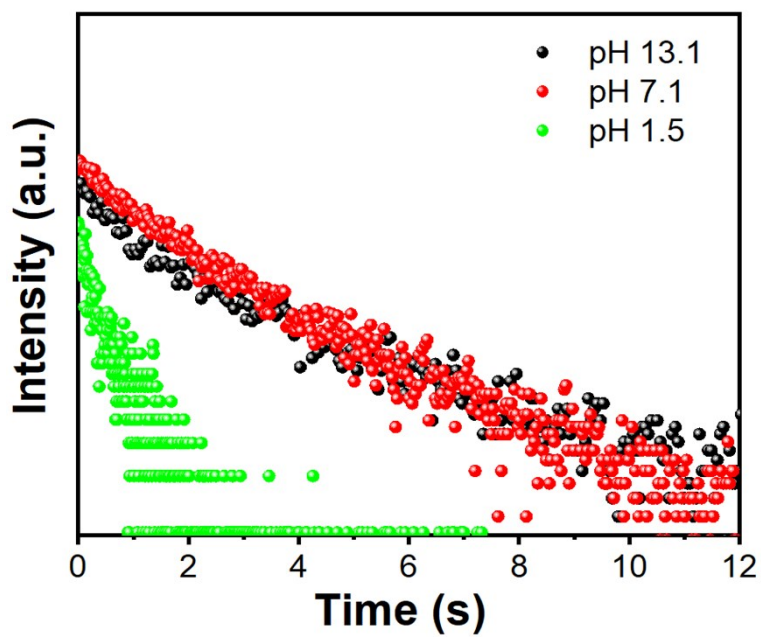


Fig. S16. RTP lifetime decay curves of NP-CPDs at pH 13.1, 7.1 and 1.5.

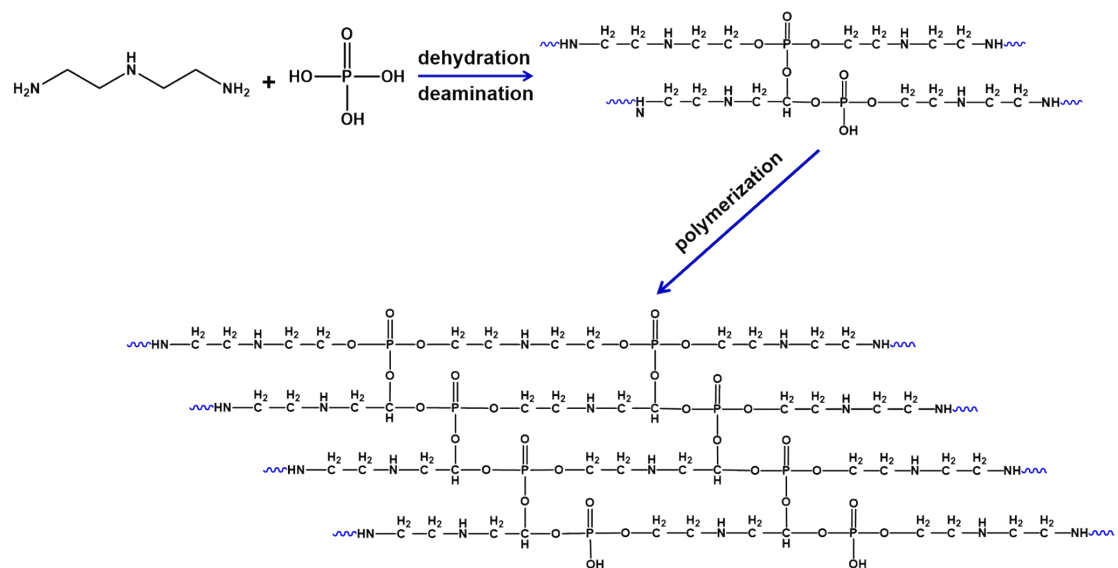


Fig. S17. Illustration of the growth mechanism of NP-CPDs.

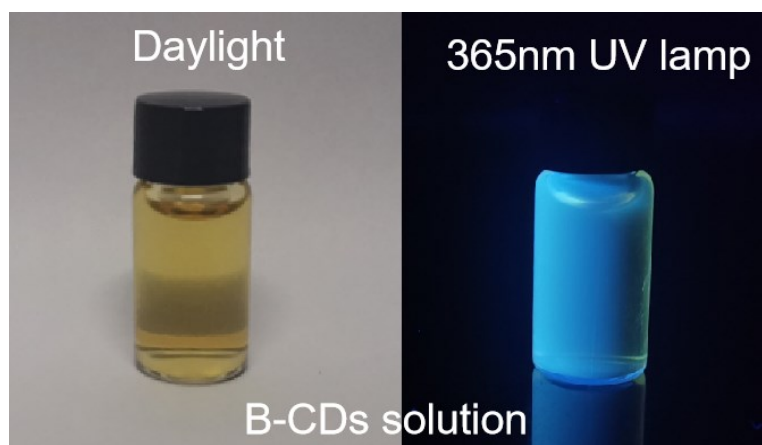


Fig. S18. Photographs of the B-CDs dispersion under daylight (left) and 365 nm UV lamp (right).