

Supporting Information

Deep-Blue Thermally Activated Delayed Fluorescence Carbon Dots with Ultralong lifetime

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Materials: Citric acid, boric acid and diethanol amine were purchased from Aladdin Reagent Corporation (Shanghai, China). All of the reagents were used directly without further purification. The deionized water used throughout all the experiments was purified through Water Purifier Nanopure water system (18.25 M.cm).

Experimental Section

Synthesis of BCDs: Typically, 3 g of boric acid (BA) and 50 mg of citric acid (CA) were dissolved in 40 mL of deionized water in a 100 mL beaker. Meanwhile, the beaker was covered with foil to keep the water evaporating slowly. And then, the beaker heated to 180 °C for 5 h in a draught drying cabinet. After cooled down to room temperature naturally, finally, BCDs were obtained by grinding.

Synthesis of BNCDS: Firstly, 3 g of boric acid (BA) , 50 mg of citric acid (CA) and x ml diethanol amine (DEA, x=0.1,0.2,0.3)were dissolved in 40 mL of deionized water in a 100mL beaker. Meanwhile, the beaker was covered with foil to keep the water evaporating slowly. And then, the beaker heated to 180 °C for 5 h in a draught drying cabinet. After cooled down to room temperature naturally, finally, BCDs-xN(0.1,0.2,0.3) (BNCDS) were obtained by grinding.

Synthesis of CDs-1: Firstly, 50 mg of citric acid (CA) was dissolved in 40 mL of deionized water in a 100 mL beaker. Meanwhile, the beaker was covered with foil to keep the water evaporating slowly. And then, the beaker heated to 180 °C for 5 h in a draught drying cabinet. CDs-1 were obtained after cooled down to room temperature naturally.

Synthesis of CDs-2: 50 mg of citric acid (CA) and 0. 1 ml DEA were dissolved in 40 mL of deionized water in a 100 mL beaker. Meanwhile, the beaker was covered with foil to keep the water evaporating slowly. And then, the beaker heated to 180 °C for 5 h in a draught drying

cabinet. CDs-2 were obtained after cooled down to room temperature naturally.

Purify of CDs: The BCDs-0.1N were dissolved in deionized water, purified by centrifugation at 7000 rpm and were further dialyzed with 1000 Da dialysis membrane for 24 hours. The CDs powder were harvested after freeze-dried for 48 hours.

In vitro cellular imaging

HuH-7 cells were plated with 2×10^5 cells/dishes in a 20 mm glass bottom cell culture dish and cultured in 2 ml Dulbecco's modified Eagle's medium (DMEM) mixed with 10% of fetal bovine serum (FBS) and 1% penicillin-streptomycin for 12 h (37 °C, 5% CO₂). Next, the cells were washed with phosphate buffered saline (PBS) buffer, and were incubated with 25 mg/mL BNCDs in 2 ml DMEM medium for 6 h. After that, the excess BCDs-0.1N were removed by washing three times with PBS buffer.

Characterization

The transmission electron microscopy (TEM) was recorded on FEI Tecnai G2 F20 S-TWIN system operating at 200 kV (America). XRD patterns were obtained with a Smart Lab 9 kW using Cu Ka radiation (Japan). Fourier transform infrared (FT-IR) spectrum of BNCDs were recorded on a Bruker Vertex-22 spectrometer from 4000 to 500 cm⁻¹. X-Ray photoelectron spectroscopy (XPS) were obtained on a Thermo Fisher(USA) ESCALAB 250Xi Multitechnique Surface Analysis. The UV-visible absorption spectra of BNCDs were recorded by using a Cary 5000 (America). Fluorescence spectrophotometry F7100 (Japan) was recorded on fluorescence and phosphorescence spectra of BNCDs. Edinburgh FLS980 measured low temperature fluorescence and afterglow from 78-297 K. Transient Fluorescence Spectrometre FLS1000 was recorded on phosphorescence lifetime of BNCDs. Quantum Efficiency

Measurement System C9920-02G was recorded on phosphorescence quantum yield. The cells images were obtained using a confocal laser scanning microscope (Leica TCS SP8, Germany) at 405 nm excitation. The digital photos was recorded on the iPhone XR.

Supplementary Figures

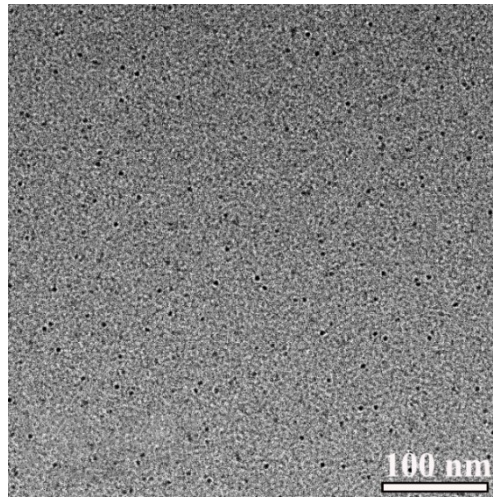


Figure S1. TEM images of BCDs-0.1N.

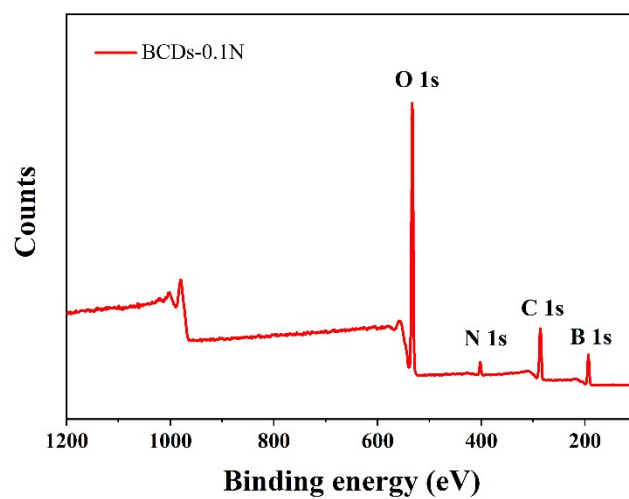


Figure S2. XPS full-survey spectra of the BCDs-0.1N.

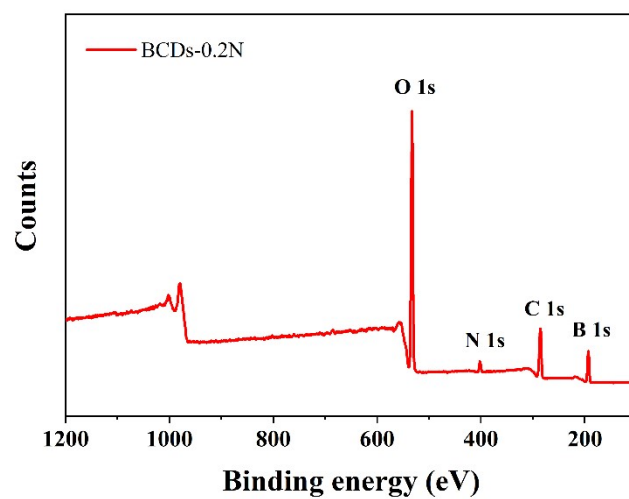


Figure S3. XPS full-survey spectra of the BCDs-0.2N.

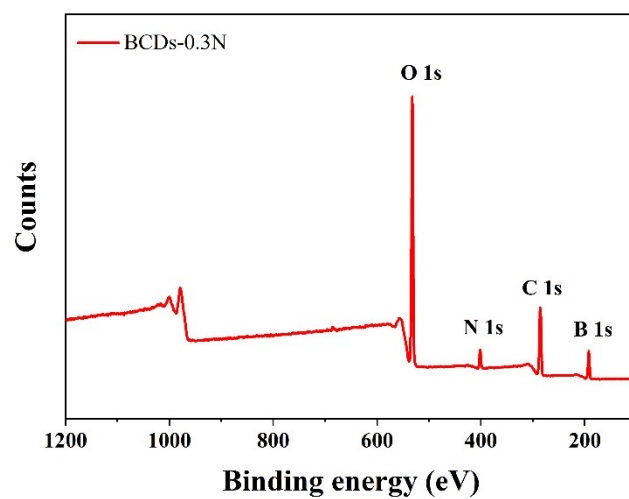


Figure S4. XPS full-survey spectra of the BCDs-0.3N.

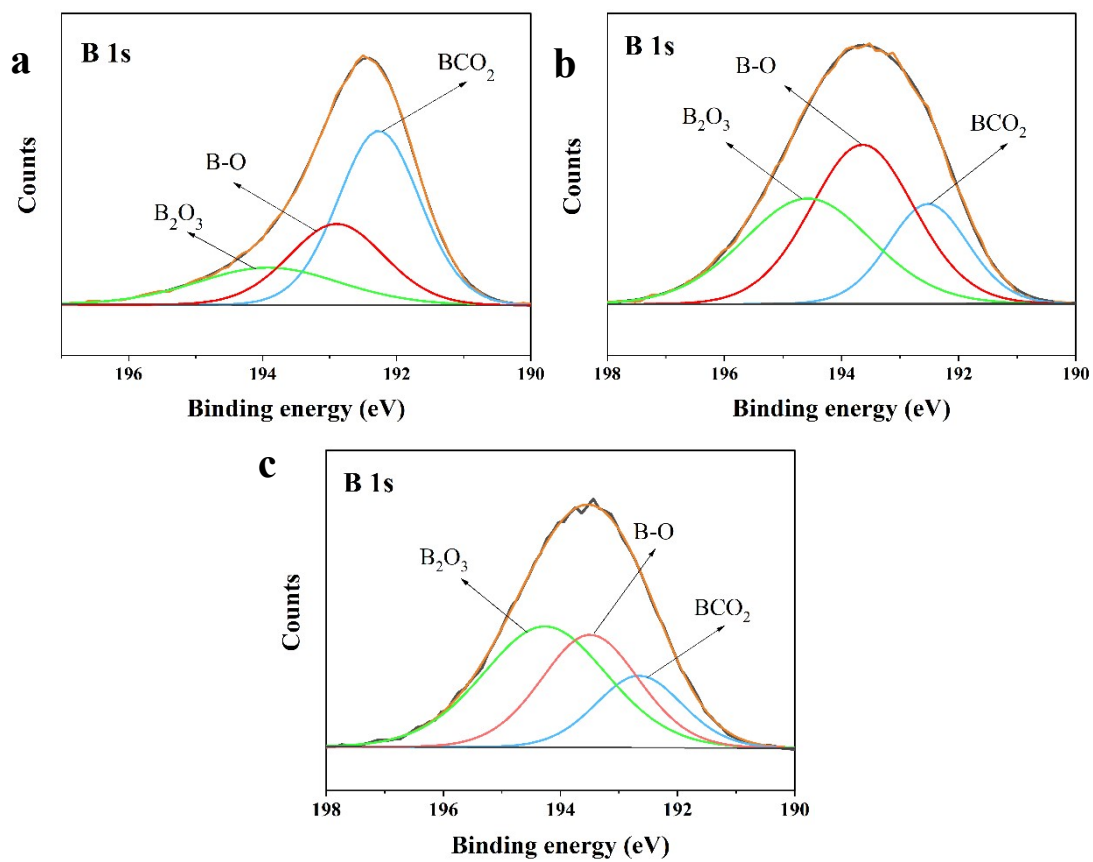


Figure S5. High-resolution XPS of the B1s (a) BCDs-0.1N (b) BCDs-0.2N (c) BCDs-0.3N.

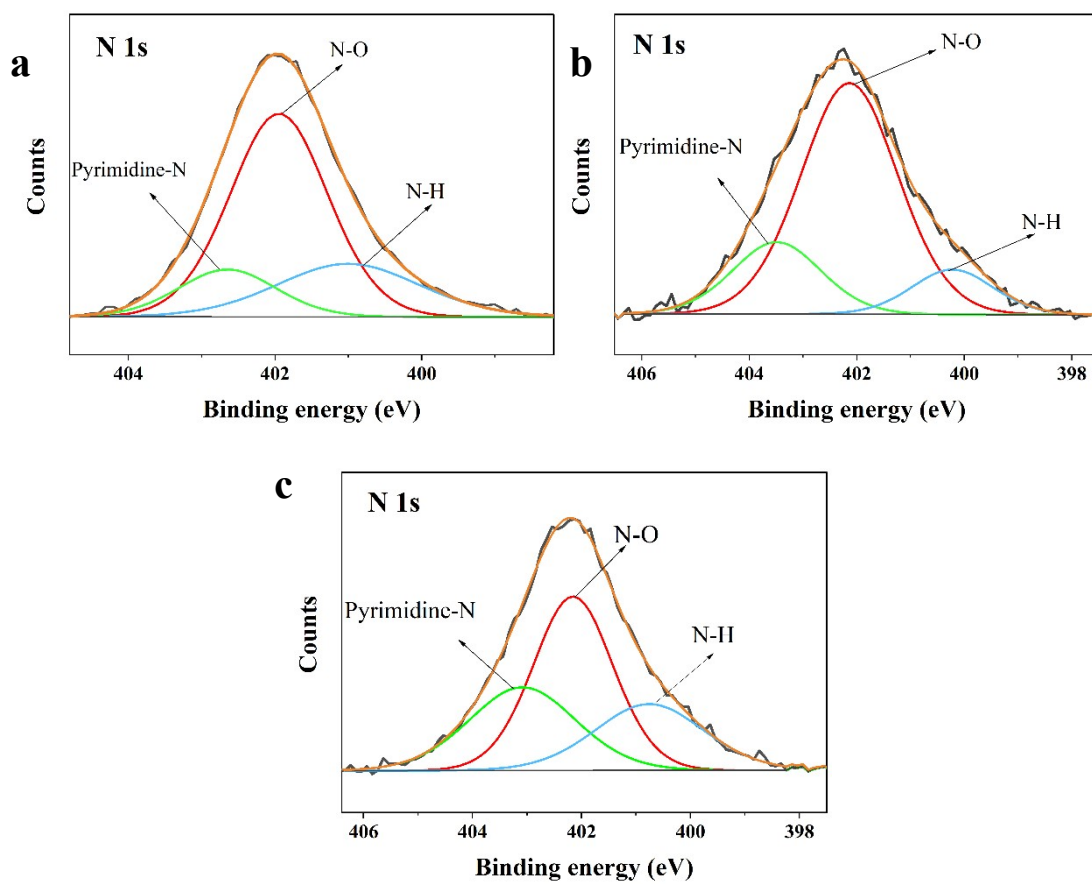


Figure S6. High-resolution of the N1s (a) BCDs-0.1N (b) BCDs-0.2N (c) BCDs-0.3N.

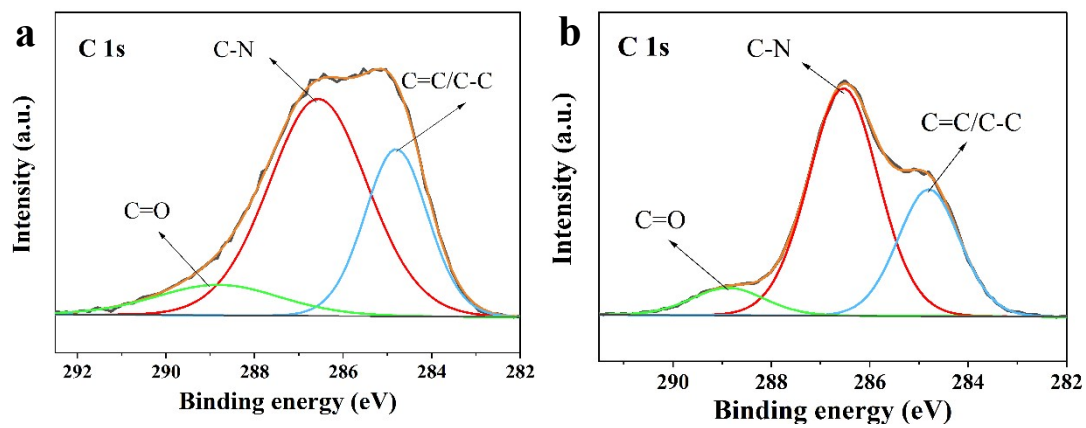


Figure S7. High-resolution of the C1s (a) BCDs-0.2N (b) BCDs-0.3N.

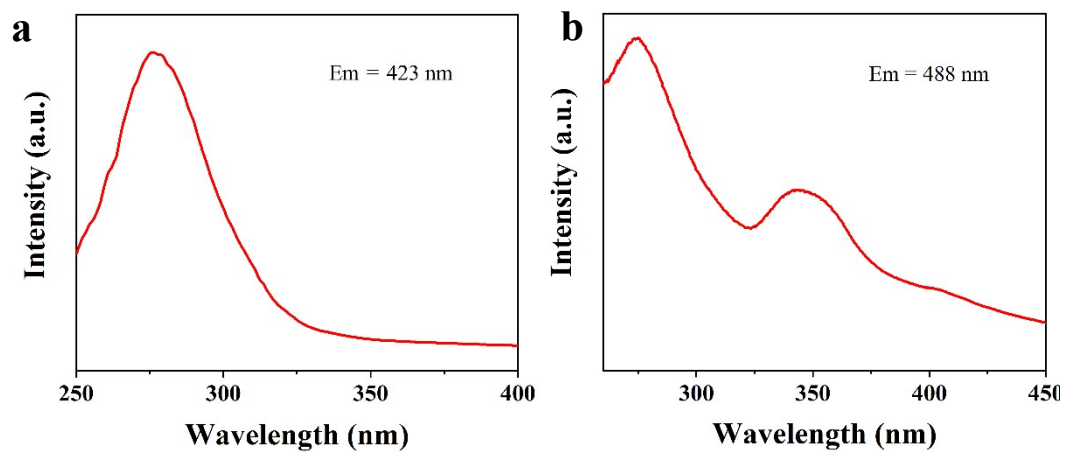


Figure S8. The delayed 10 ms PL excitation spectrum of BCDs-0.1N (a) Monitored at 423 nm. (b) Monitored at 488 nm.

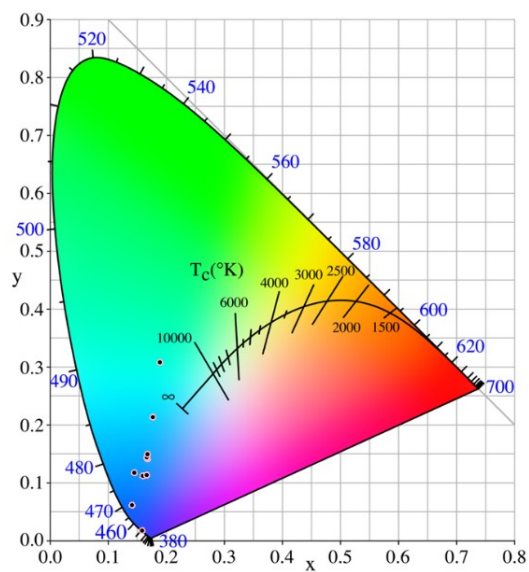


Figure S9. The PL emission CIE coordinate diagram of BCDs-0.1N under the excitation from 240 to 420 nm.

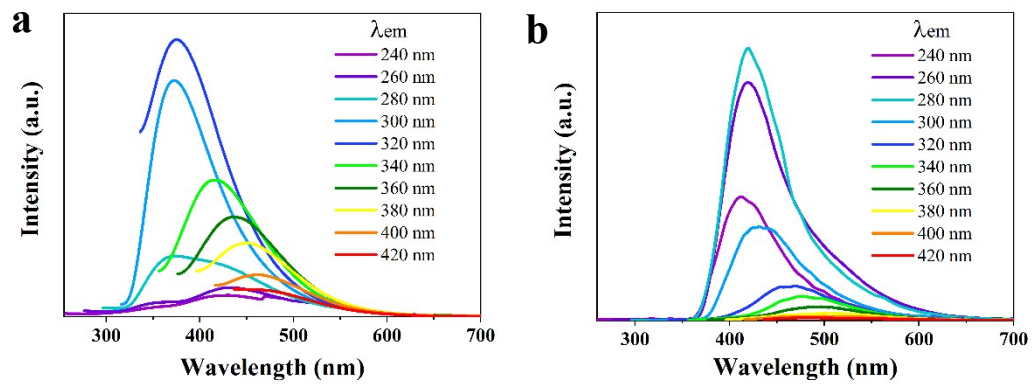


Figure S10. Optical properties of the BCDs-0.2N (a) The PL emission spectra under different excitation wavelengths of the BCDs-0.2N. (b) The afterglow emission spectra under different excitation wavelengths of the BCDs-0.2N.

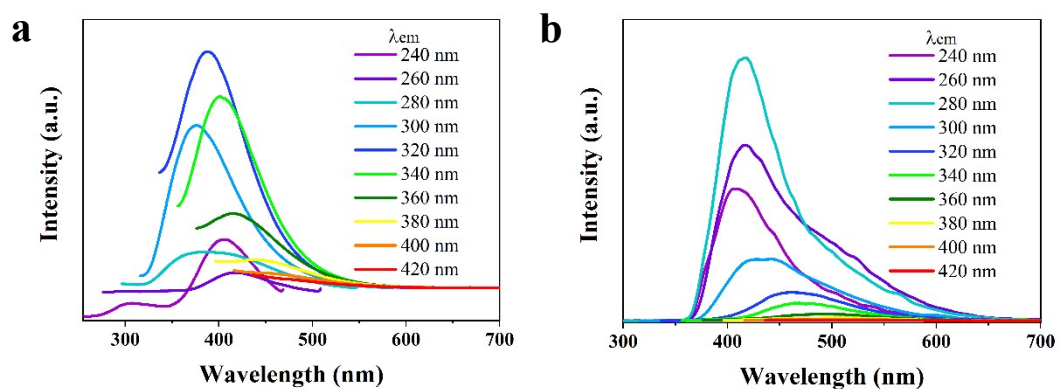


Figure S11. Optical properties of the BCDs-0.3N (a) The PL emission spectra under different excitation wavelengths of the BCDs-0.3N. (b) The afterglow emission spectra under different excitation wavelengths of the BCDs-0.3N.

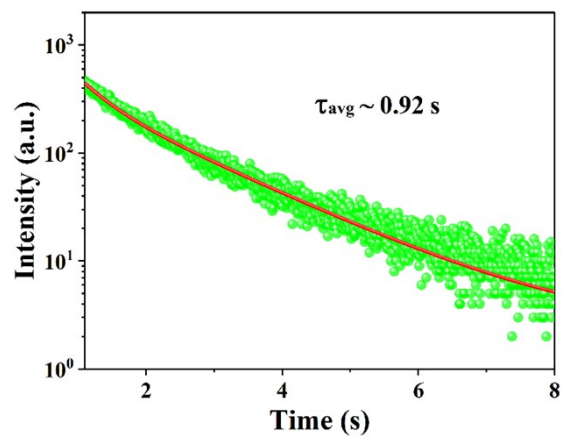


Figure S12. Afterglow decay curve and lifetimes of BCDs-0.1N monitored at 488 nm with 343 nm excitation.

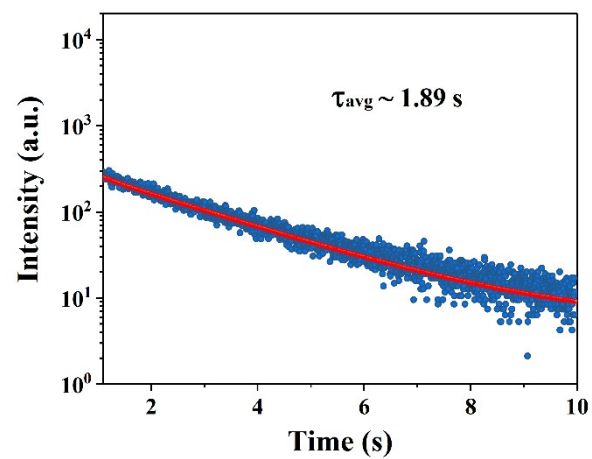


Figure S13. Afterglow decay curve and lifetimes of BCDs-0.2N monitored at 420 nm with 273 nm excitation.

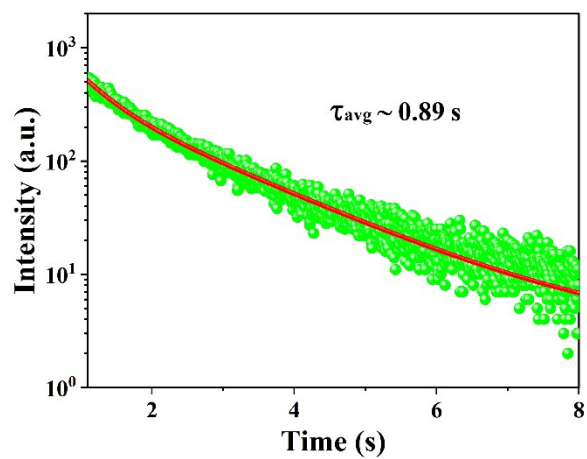


Figure S14. Afterglow decay curve and lifetimes of BCDs-0.2N monitored at 479 nm with 343 nm excitation.

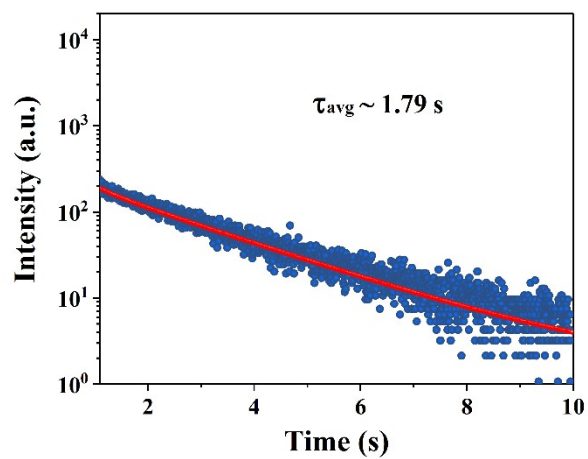


Figure S15. Afterglow decay curve and lifetimes of BCDs-0.3N monitored at 416 nm with 273 nm excitation.

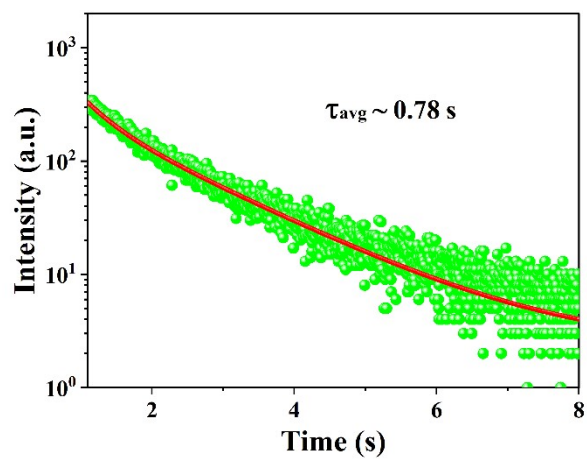


Figure S16. Afterglow decay curve and lifetimes of BCDs-0.3N monitored at 471 nm with 343 nm excitation.

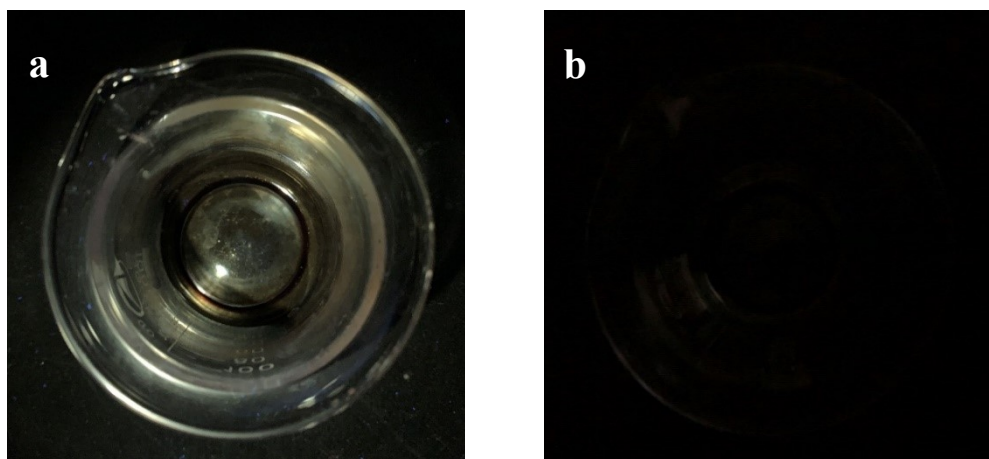


Figure S17. Digital photographs of CDs-1 before and after ceasing the UV lamp 365 nm (a) UV on (b) UV off.

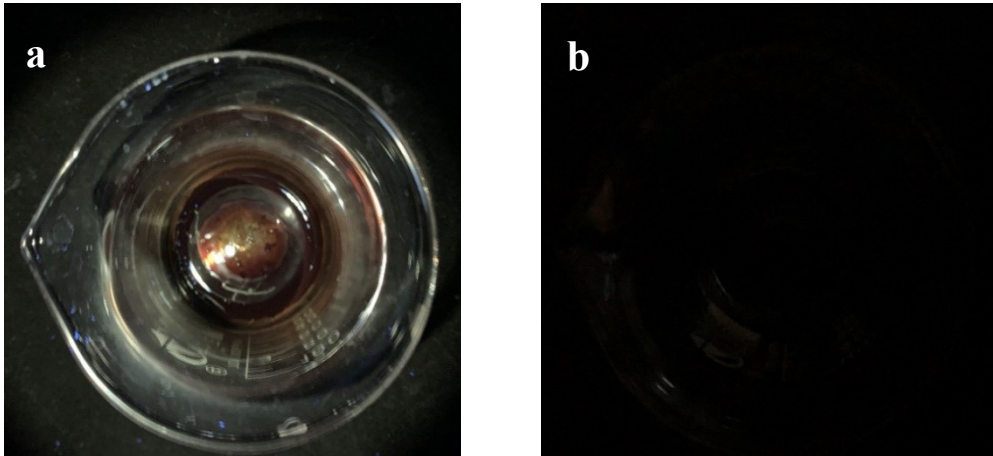


Figure S18. Digital photographs of CDs-2 before and after ceasing the UV lamp 365 nm (a) UV on (b) UV off.

UV on UV off

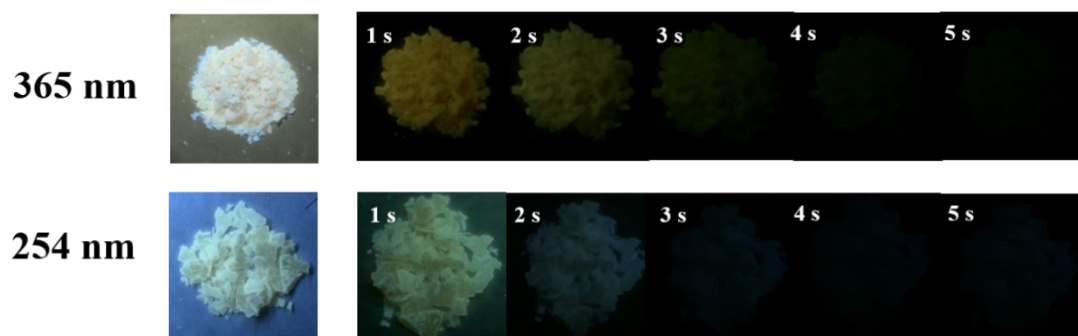


Figure S19. Digital photographs of BCDs before and after ceasing the UV lamp 365 nm and 254 nm, respectively.

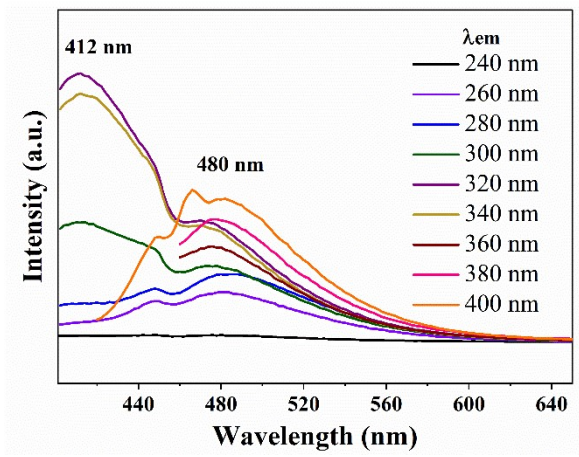


Figure S20. The PL emission spectra under different excitation wavelengths (240-400 nm) of CDs solution.

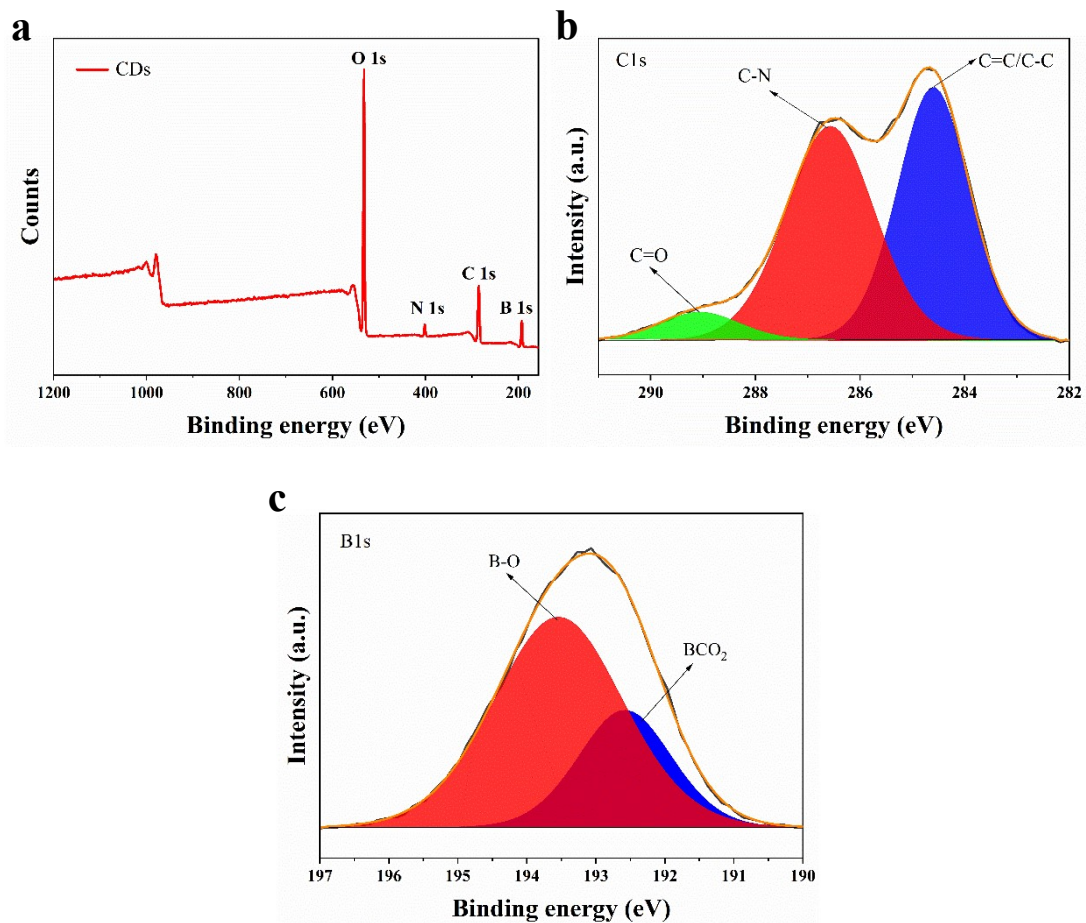


Figure S21. XPS of the CDs (a) XPS full-survey spectra of the CDs. (b) High-resolution of the C1s. (c) High-resolution of the B1s.

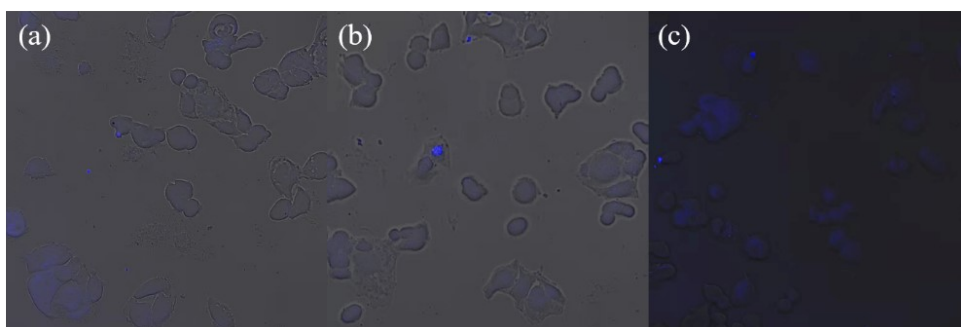


Figure S22. The CDs combine with HuH-7 cells dark-field image of fluorescence confocal image under excitation of 405 nm at different concentration (a)1 mg/ml (b)2 mg/ml (c)5 mg/ml.

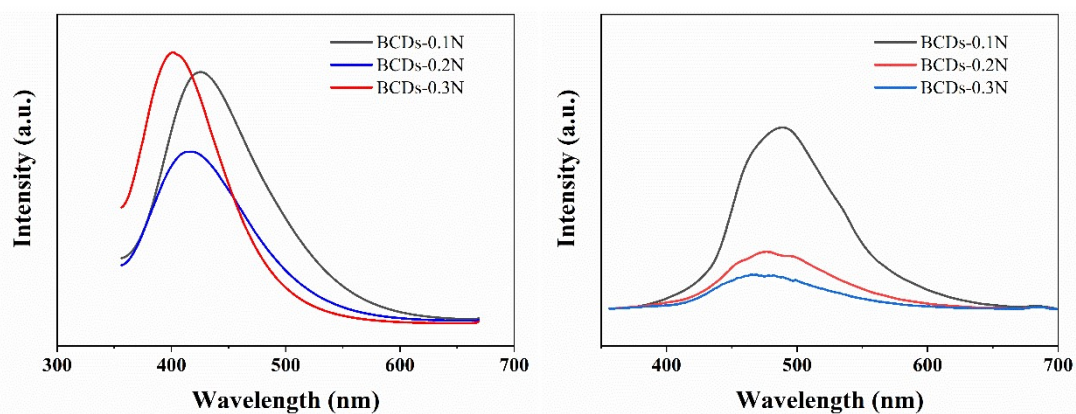


Figure S23. The spectra of the three BNCs (a) The steady-state photoluminescence spectrum of the BCDs-0.1N, BCDs-0.2N and BCDs-0.3N with 340 nm excitation. (b) The RTP spectra of the BCDs-0.1N, BCDs-0.2N and BCDs-0.3N with 340 nm excitation.

Table S1. Comparison of the blue RTP /TADF properties of CDs under UV light.

Name	Emission Wavelength (nm)	Lifetime (s)	Ref.
CDs@AIPO-5 (blue TADF)	430	0.35	S1
NCD1-C (blue TADF)	430	1.11	S2
CDs@SBT-1 (blue TADF)	440	0.153	S3
CDs/PVA (blue TADF)	456	1.61	S4
Pht-CD (TADF)	497	0.32	S5
GOOD-60 (TADF)	499	0.125	S6
F, NCDs@SiO ₂ (TADF)	500	0.48	S7
CD@zeolite (TADF)	425-512	0.27-0.86	S8
m-CDs@CA(TADF)	425	1.22	S9
m-CDs#CA(TADF)	480	1.67	S9
m-CDs@CA	425	1 h (duration)	S9
CPDs	430	0.18	S10
CDs/silica	430	0.81	S11
CDs@clay	450	1.05	S12
c-CDs/BA	490	0.6	S13
BCDs-0.1N (TADF)	423	2.02	This work

Table S2. Production yield of the BCDs-xN (x=0.1,0.2,0.3)

BCDs-xN	Raw materials (g)	Resultant (g)	Production yield (%)	Average (%)
x=0.1	3.160	1.775	56.2	
x=0.2	3.270	1.817	55.6	53.5
x=0.3	3.379	1.647	48.7	

Table S3. The contents of C, O , B and N in BCDs-xN (x=0.1,0.2,0.3) determined by

XPS.

BCDs-xN	C Content (%)	O Content (%)	B Content (%)	N Content (%)
x=0.1	23.61	44.32	28.96	3.11
x=0.1	23.57	42.61	30.74	3.08
x=0.3	29.76	40.89	25.05	4.30

Table S4. Photophysical characteristics of BCDs-xN(x=0.1,0.2,0.3) under 273 nm.

BCDs-xN	λ_{em}	A_1	τ_1	A_2	τ_2	A_3	τ_3	τ_{ave}
	(nm)	(%)	(ms)	(%)	(ms)	(%)	(ms)	(s)
BCDs-0.1N	424	8.44	307.4	91.56	2175.7	-	-	2.02
BCDs-0.2N	420	1.17	27.63	11.79	436.47	87.04	2116.91	1.89
BCDs-0.3N	416	1.36	43.99	19.38	649.81	79.26	2095.10	1.79

Table S5. Photophysical characteristics of BCDs-xN(x=0.1,0.2,0.3) under 343 nm.

BCDs-xN	λ_{em} (nm)	A_1 (%)	τ_1 (ms)	A_2 (%)	τ_2 (ms)	A_3 (%)	τ_3 (ms)	τ_{ave} (s)
BCDs-0.1N	488	12.59	59.47	37.48	424.64	49.93	1504.06	0.92
BCDs-0.2N	479	16.15	61.69	38.76	431.83	45.10	1587.53	0.89
BCDs-0.3N	471	18.97	50.82	36.88	381.86	44.15	1421.23	0.78

The average lifetime was calculated via the Equation as followed:

$$\tau_{avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

wherein, "A " and "τ" represent the percentage and lifetime, respectively.

Table S6. The FL emission peaks, RTP emission peaks, and calculated ΔE_{ST} of three kinds of BCDs-xN(x=0.1, 0.2, 0.3) composites excited at 273 nm.

	FL peak (nm)	afterglow peak (nm)	ΔE_{ST} (eV)
BCDs-0.1N	422.2	423.4	0.008
BCDs-0.2N	422.5	425.1	0.018
BCDs-0.3N	418.1	422.8	0.033

Table S7. The FL emission peaks, RTP emission peaks, and calculated ΔE_{ST} of three kinds of

BCDs-xN(x=0.1,0.2, 0.3) composites excited at 343 nm.

	FL peak (nm)	RTP peak (nm)	ΔE_{ST} (eV)
BCDs-0.1N	426	488	0.37
BCDs-0.2N	417	480	0.39
BCDs-0.3N	403	471	0.44

Reference

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