

## Endowing matrix-free carbon dots with color-tunable ultralong phosphorescence by self-doping

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### I. Experimental Section.

#### Materials

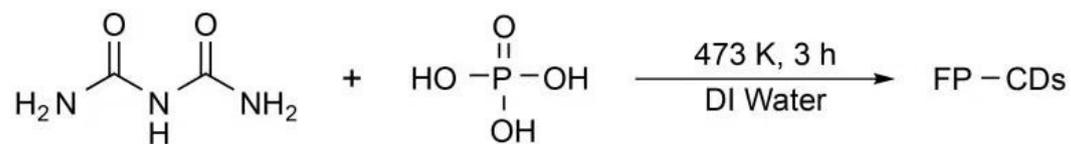
Unless other noted, following reagents used in the experiments including biuret, phosphoric acid and deionized (DI) water were purchased from commercial sources without further purification.

## Measurements

Transmission electron microscopy (TEM) was performed using a JEM 1011 instrument (JEOL, Japan) and JEM 2100F instrument (JEOL, Japan). Fourier transform infrared (FT-IR) spectra were obtained on a BRUKER TENSOR27 FT-IR spectrometer. XPS were carried out with PHI 5000 Versa Probe (UIVAC-PHI, Japan). UV-Visible absorption spectra were obtained using UV-3600 spectrophotometer (Shimadzu, Japan). Fluorescence/phosphorescence emission spectra and excitation spectra were measured using Hitachi F-4600. The lifetimes were obtained on Edinburgh FLSP1000 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe 900), a nanosecond hydrogen flash-lamp (nF 920), a microsecond flash-lamp ( $\mu$ F 900), respectively. The luminescent photos were taken by a Cannon EOS 700D camera.

## Synthesis

**Synthesis of FP-CDs:** Biuret (1.5 g) was added into a 100 mL beaker with 15 mL DI water. And then 2.0 mL of phosphoric acid was added into the beaker with stirring. After heated in 473 K for 3 hours, the mixture was cooled down to room temperature. The obtained solid was dissolved in DI water (200 mL). Subsequently, the aqueous solution of the crude product was successively filtered by the filter papers and 0.22  $\mu$ m membranes to remove impurities and agglomerated particles. After that, the solvent was removed by rotary evaporation. Finally, yellow powders were obtained after drying at 353 K. (Scheme S1)



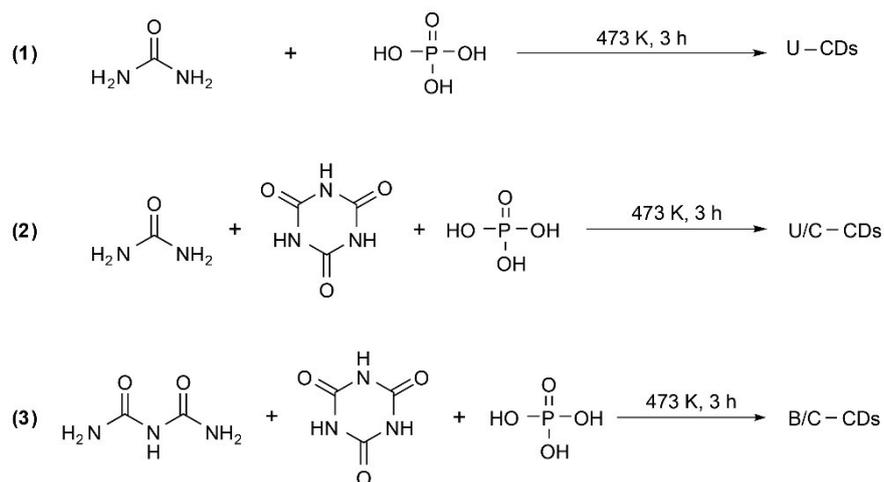
**Scheme S1.** Synthetic route for FP-CDs.

**Synthesis of U-CDs:** Urea (1.5 g) was added into a 100 mL beaker with 10 mL DI water. And then

0.2 mL of phosphoric acid was added into the beaker with stirring. After heated in 473 K for 3 hours, the mixture was cooled down to room temperature. Finally, the U-CDs were obtained by washing with deionized water three times. (Scheme S2-1)

**Synthesis of U/C-CDs-1 and U/C-CDs-2:** Urea (1.18 g) and 1,3,5-triazinane-2,4,6-trione (CYAD, 0.125 g for U/C-CDs-1 and 0.4 g for U/C-CDs-2) were added into a 100 mL beaker with 10 mL DI water. And then phosphoric acid (0.25 mL for U/C-CDs-1 and 0.4 mL for U/C-CDs-2) was added into the beaker with stirring. After heated in 473 K for 3 hours, the mixture was cooled down to room temperature. Finally, the U/C-CDs-1 and U/C-CDs-2 were obtained by washing with deionized water three times. (Scheme S2-2)

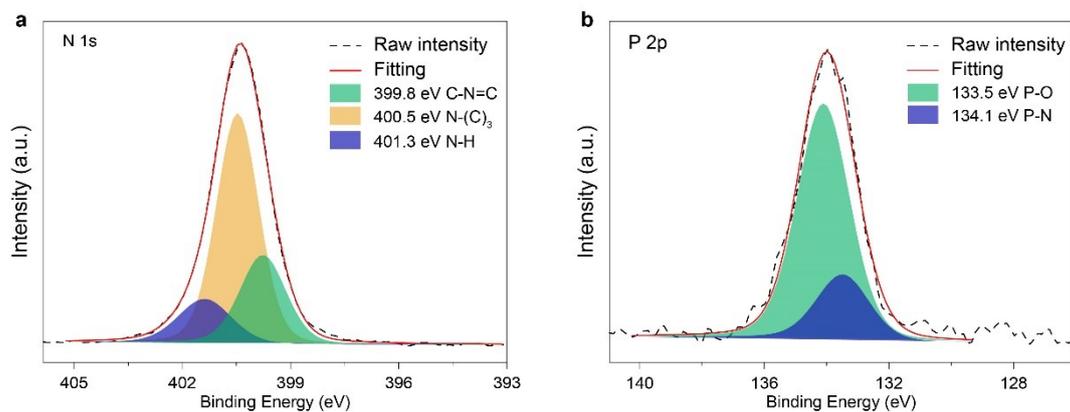
**Synthesis of B/C-CDs:** Biuret (1.5 g) and 1,3,5-triazinane-2,4,6-trione (0.1 g) were added into a 100 mL beaker with 15 mL DI water. And then 3.0 mL of phosphoric acid was added into the beaker with stirring. After heated in 473 K for 3 hours, the mixture was cooled down to room temperature. The obtained solid was dissolved in DI water (200 mL). Subsequently, the aqueous solution of the crude product was successively filtered by the filter papers and 0.22  $\mu\text{m}$  membranes to remove impurities and agglomerated particles. After that, the solvent was removed by rotary evaporation. Finally, yellow powders were obtained after drying at 353 K. (Scheme S2-3)



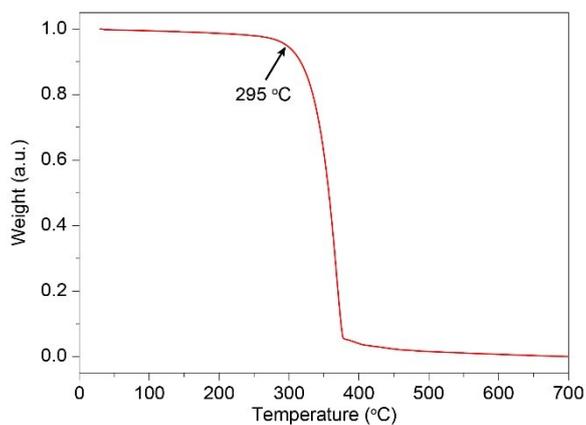
**Scheme S2.** Synthetic routes for U-CDs, U/C-CDs and B/C-CDs.

**The detailed information for applications:** The potential applications for UV-light detection, encryption and afterglow LED devices were demonstrated on the basis of FP-CDs powders. Firstly, the FP-CDs powders mixed with Aloe vera gel as an ink. Then the ink was painted on filter paper for color chart. Under different excitation, ultralong phosphorescence with different colors were observed. For information encryption, masks with different patterns were firstly prepared. Then the masks were covered on scotch tape. After that, the FP-CDs powders were sprinkled on it and the excess powder were shook off. The corresponding patterns were obtained for encryption. As to afterglow LED devices, the FP-CDs powders with glue was firstly mixed. Then the mixture was coated on LED beads with different emission wavelengths. After drying, we obtained integrated LEDs with afterglow emission.

## I. Structure characterizations.

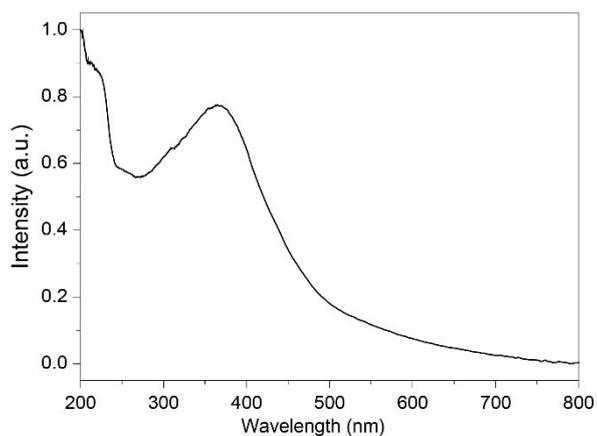


**Figure S1.** (a) HR XPS spectra for N 1s and (b) P 2p of the FP-CDs.

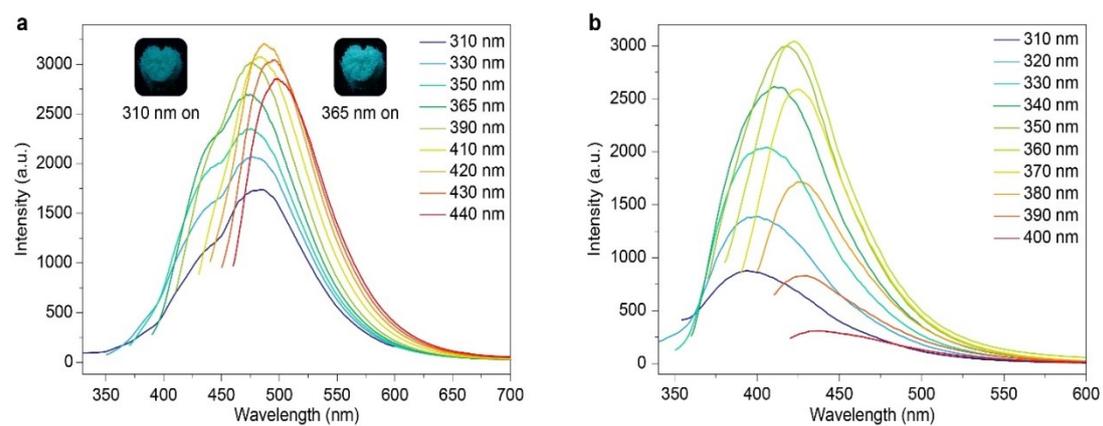


**Figure S2.** Thermogravimetric analysis curve of the FP-CDs.

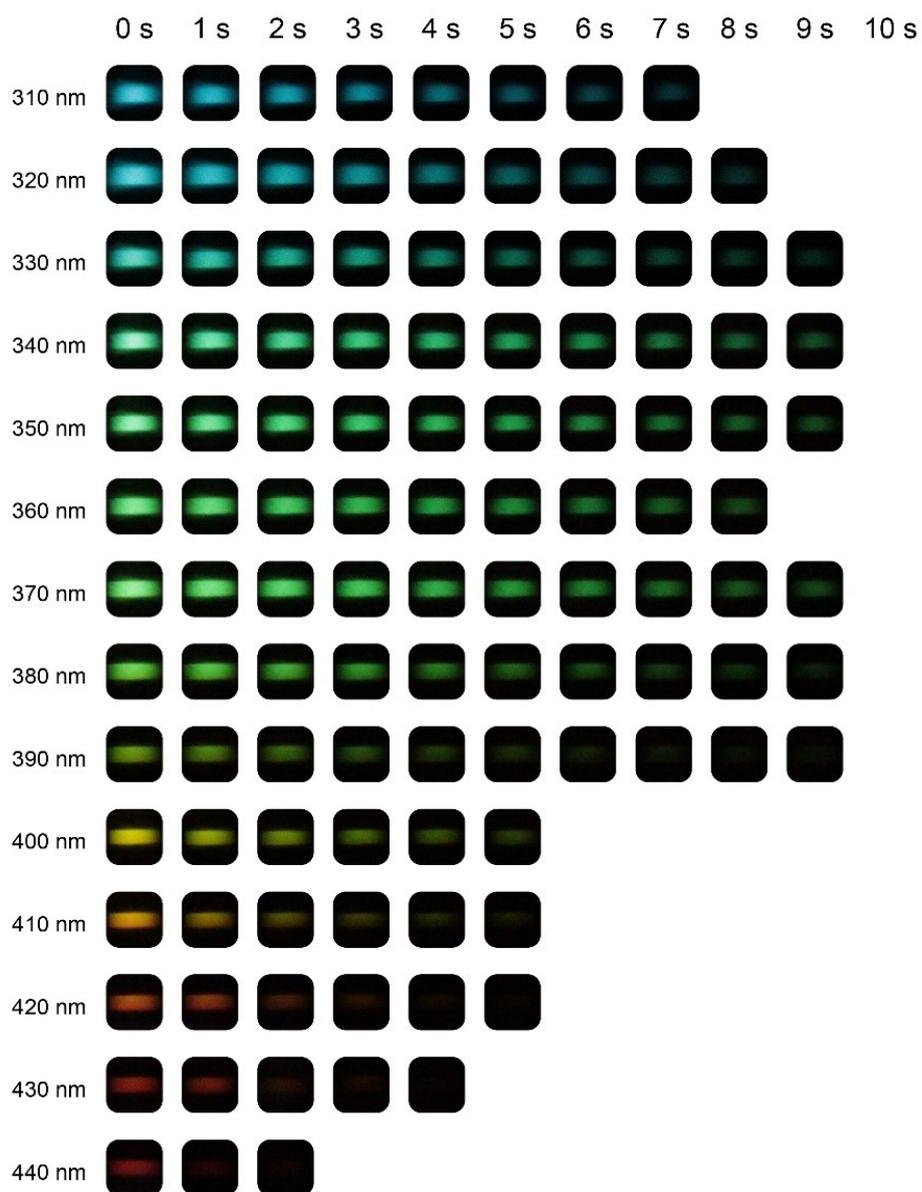
## III. Photophysical properties of CDs.



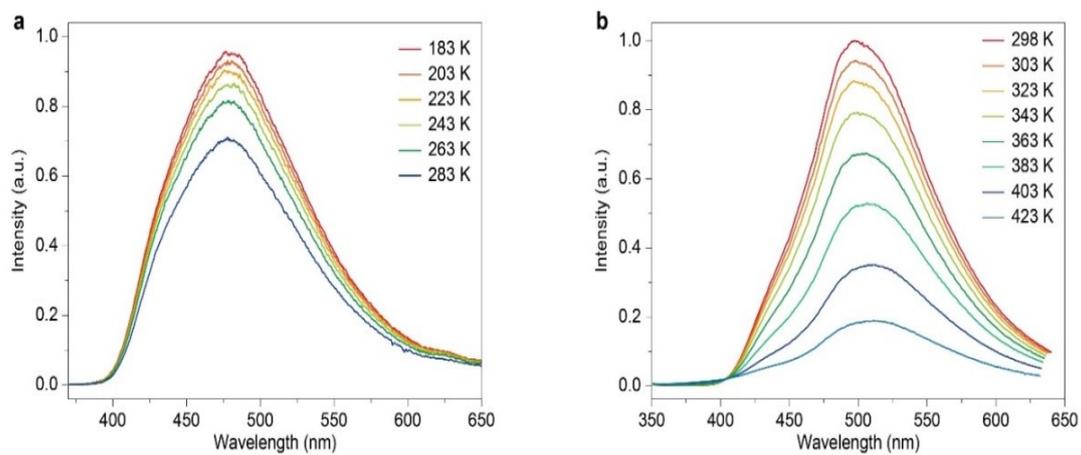
**Figure S3.** Absorption spectrum of FP-CDs powders.



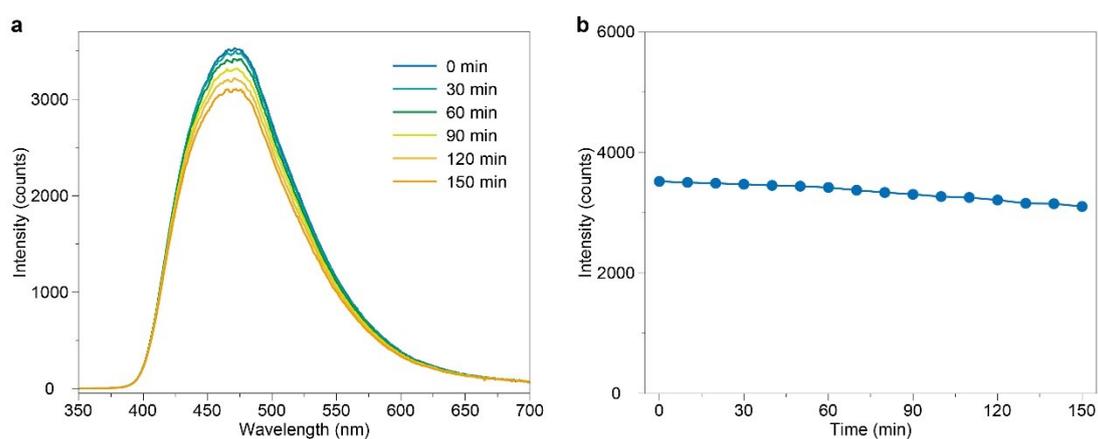
**Figure S4.** (a) PL spectra of the FP-CDs powders excited from 310 to 440 nm at room temperature. Inset: Photographs taken under 310 and 365 nm excitation, respectively. (b) PL spectra of FP-CDs in aqueous solution excited from 310 to 400 nm.



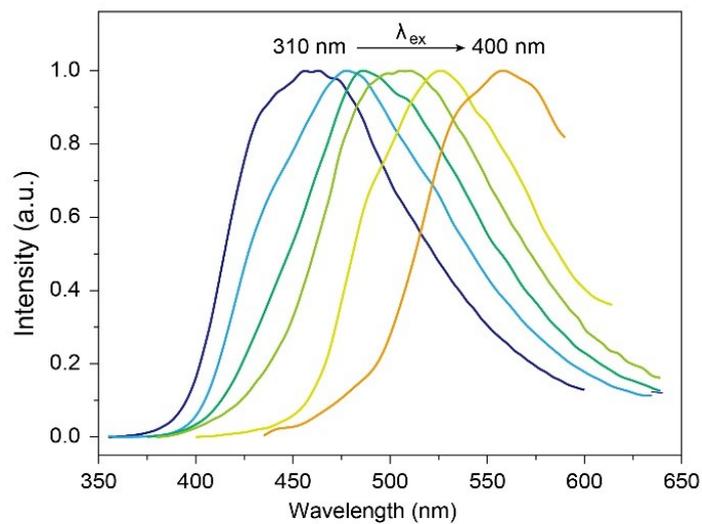
**Figure S5.** Photographs of phosphorescence with different delay time under different excitation wavelengths.



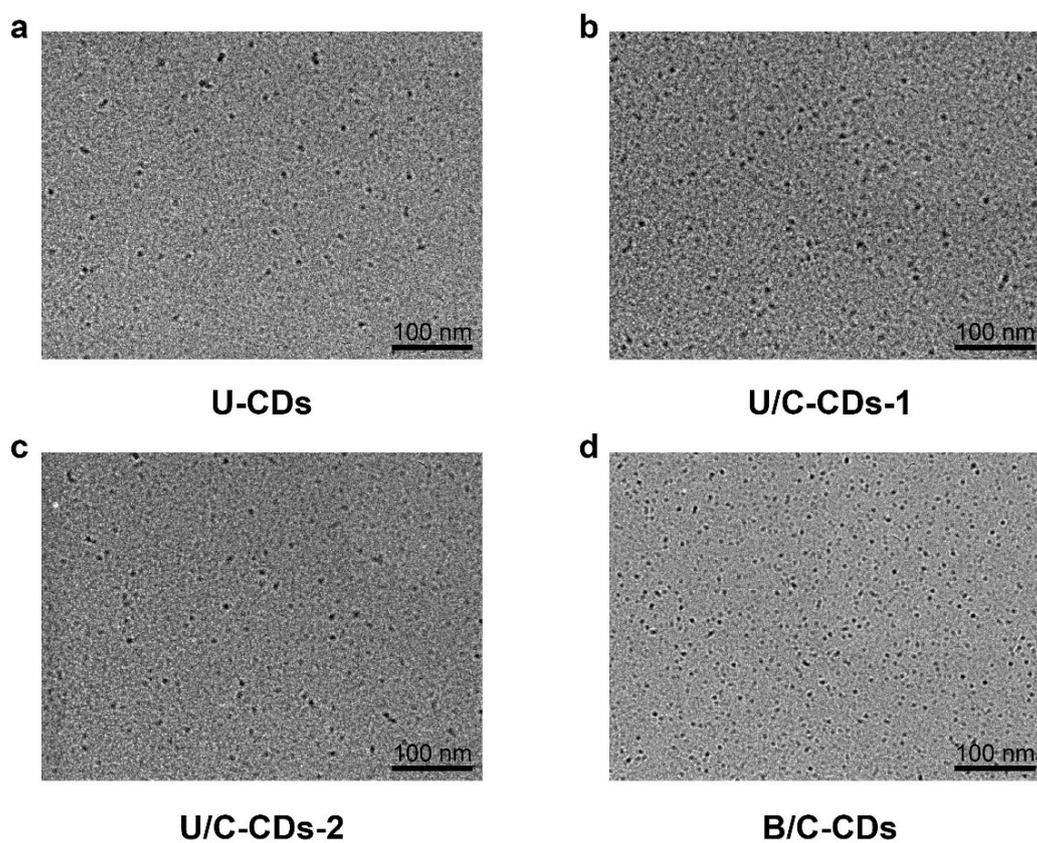
**Figure S6.** Phosphorescence spectra of the FP-CDs powders (a) under 310 nm excitation at different temperatures from 183 to 283 K and (b) under 330 nm excitation at different temperatures from 298 to 423 K.



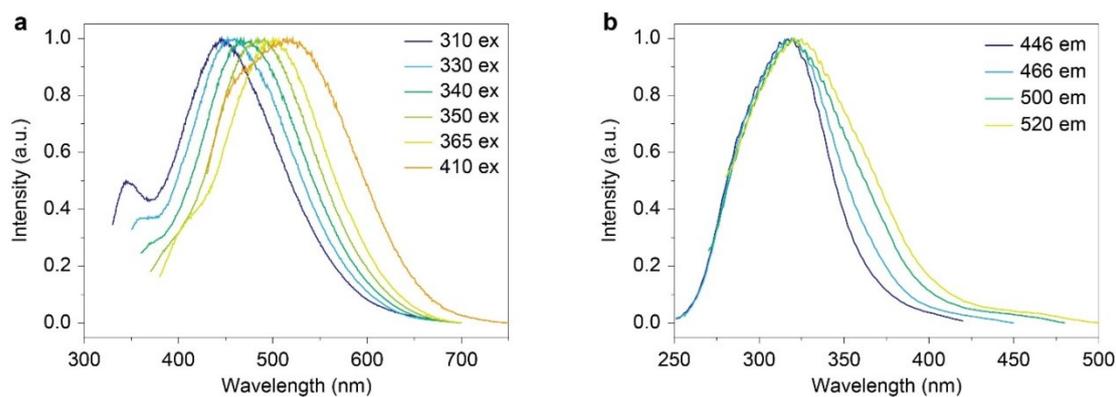
**Figure S7.** (a) Phosphorescence spectra of the CDs explored in moisture atmosphere for different time (HR: 80%). (b) Peak intensity of phosphorescence as a function of time.



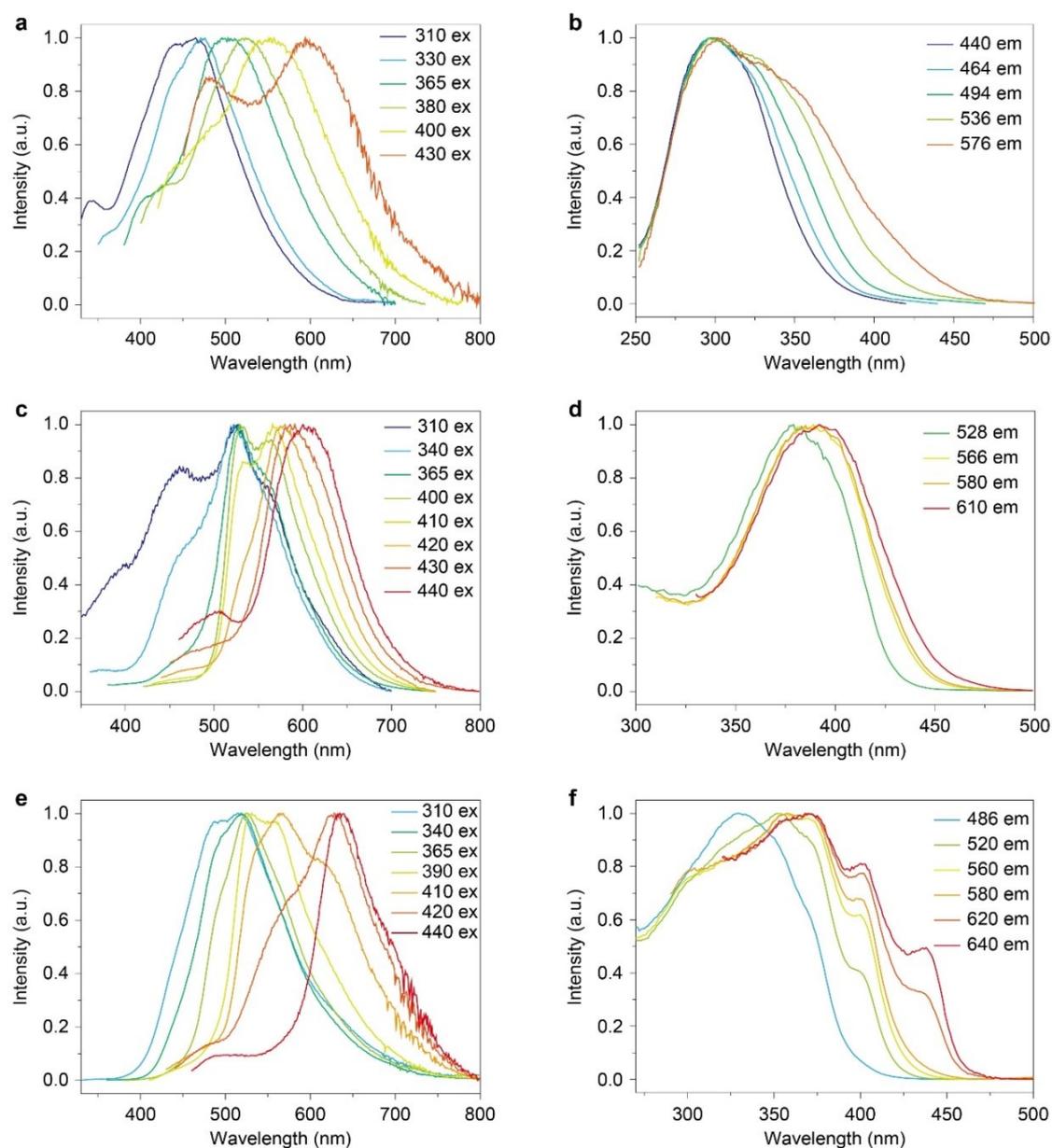
**Figure S8.** Excitation-dependent phosphorescence spectra of the FP-CDs in aqueous solution excited from 310 to 400 nm at 77 K.



**Figure S9.** TEM images of (a) U-CDs, (b) U/C-CDs-1, (c) U/C-CDs-2 and (d) B/C-CDs.

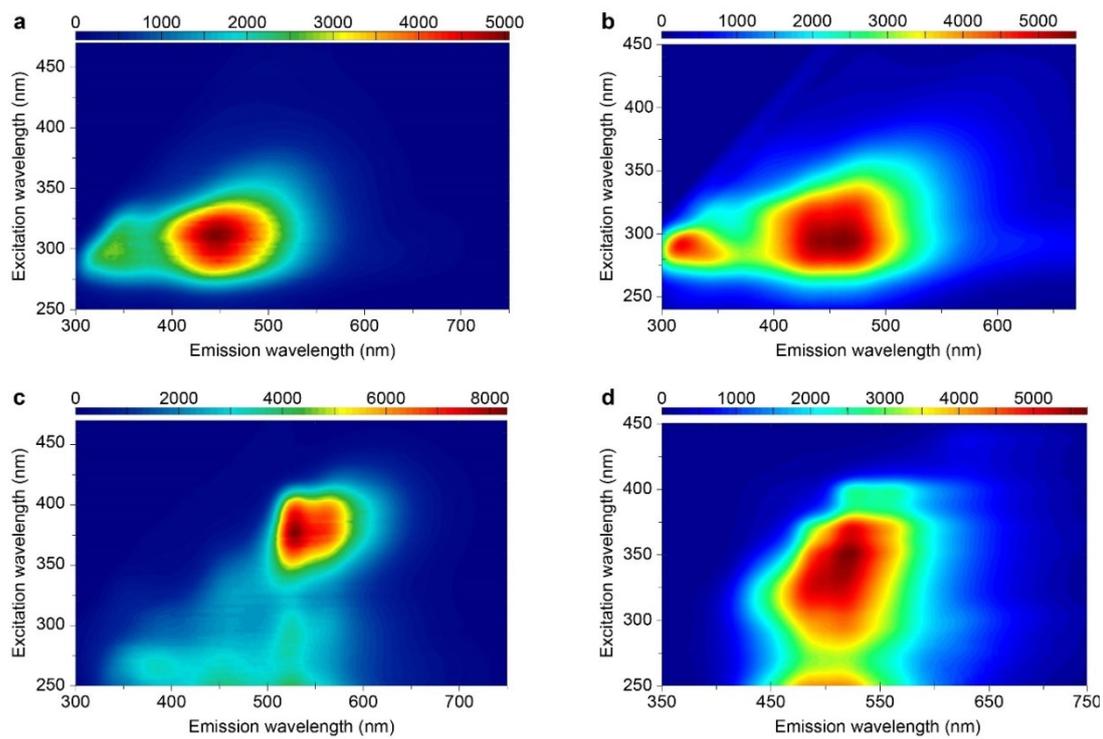


**Figure S10.** Excitation-dependent phosphorescence spectra (a) and phosphorescence excitation spectra (b) of U-CDs.

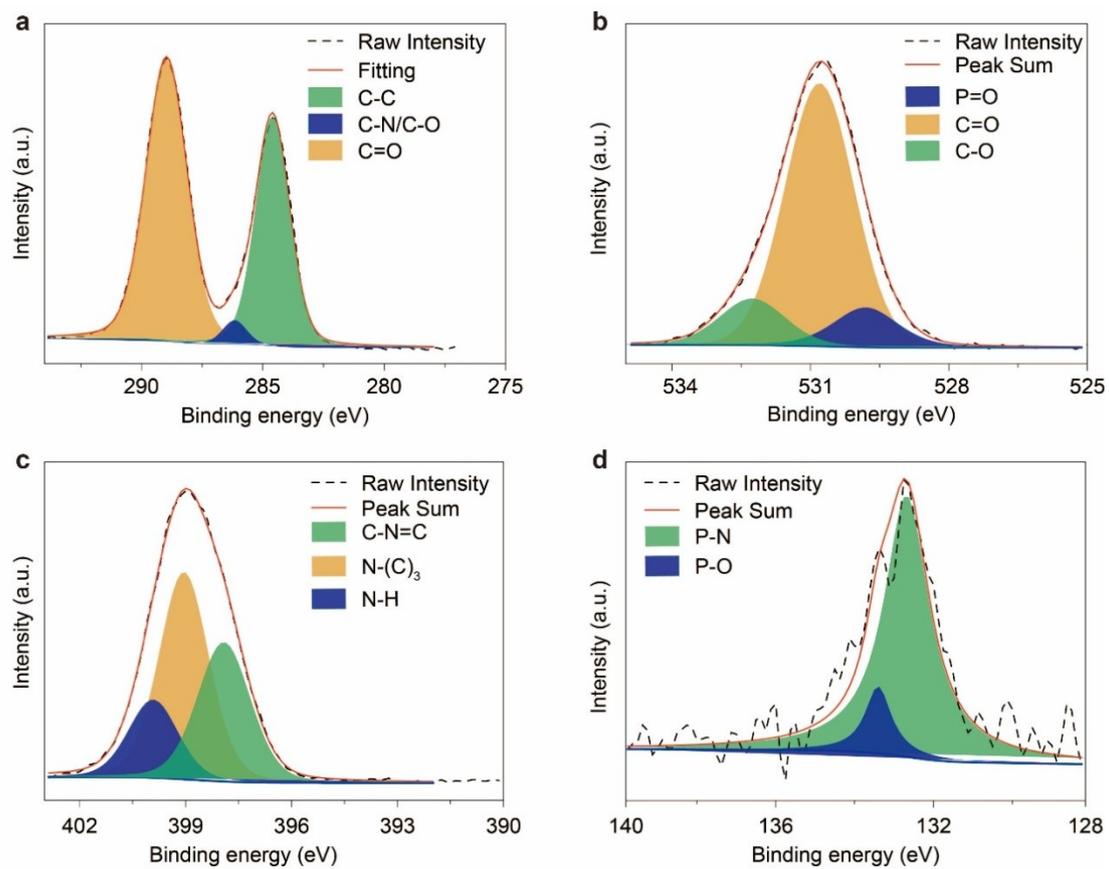


**Figure S11.** Excitation-dependent phosphorescence spectra (a, c and e) and phosphorescence excitation spectra (b, d and f) of U-CDs.

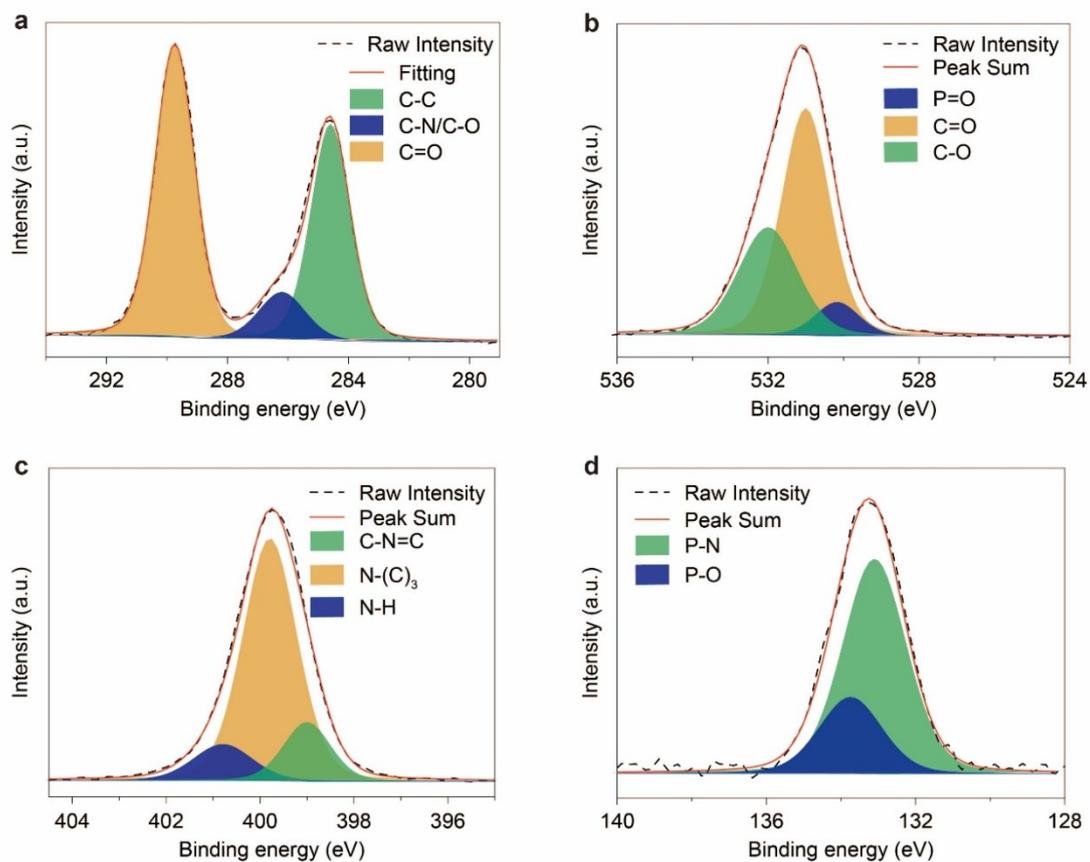
excitation spectra (b, d and f) of U/C-CDs-1, U/C-CDs-2 and B/C-CDs, respectively.



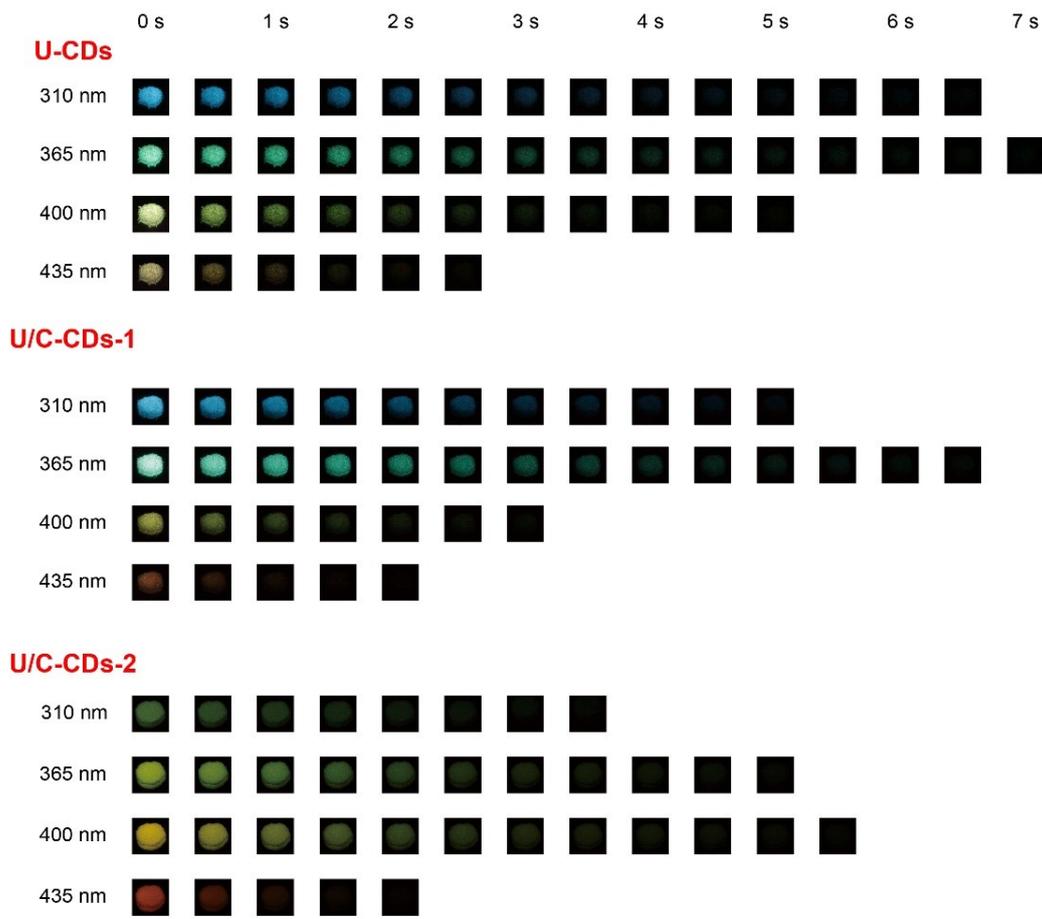
**Figure S12.** Phosphorescence-excitation mapping of (a) U-CDs, (b) U/C-CDs-1, (c) U/C-CDs-2 and (d) B/C-CDs under ambient conditions.



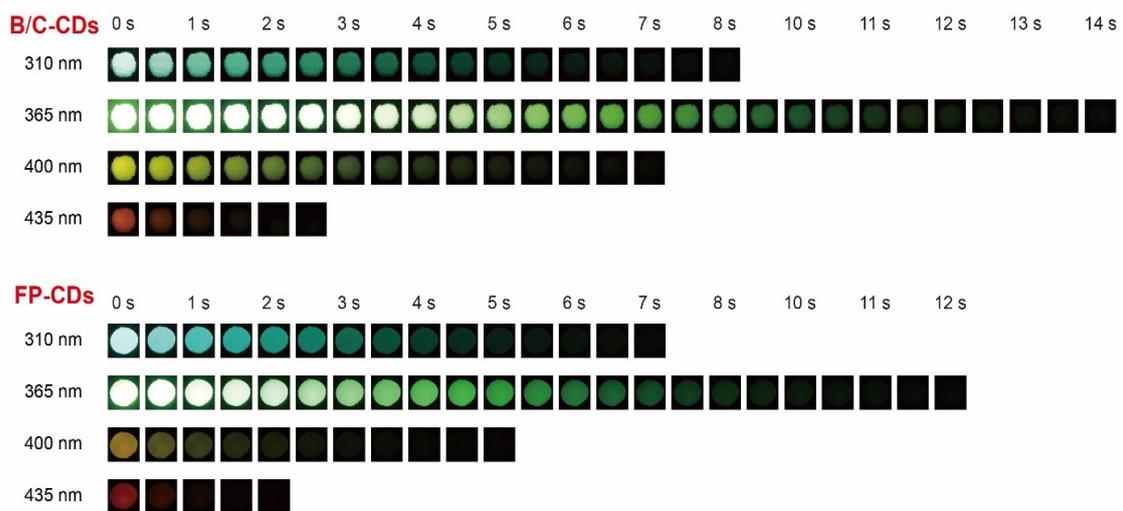
**Figure S13.** High-resolution XPS fitting results for the (a) C 1s ,(b) O 1s, (c) N 1s and (d) P 2p spectra of the U-CDs.



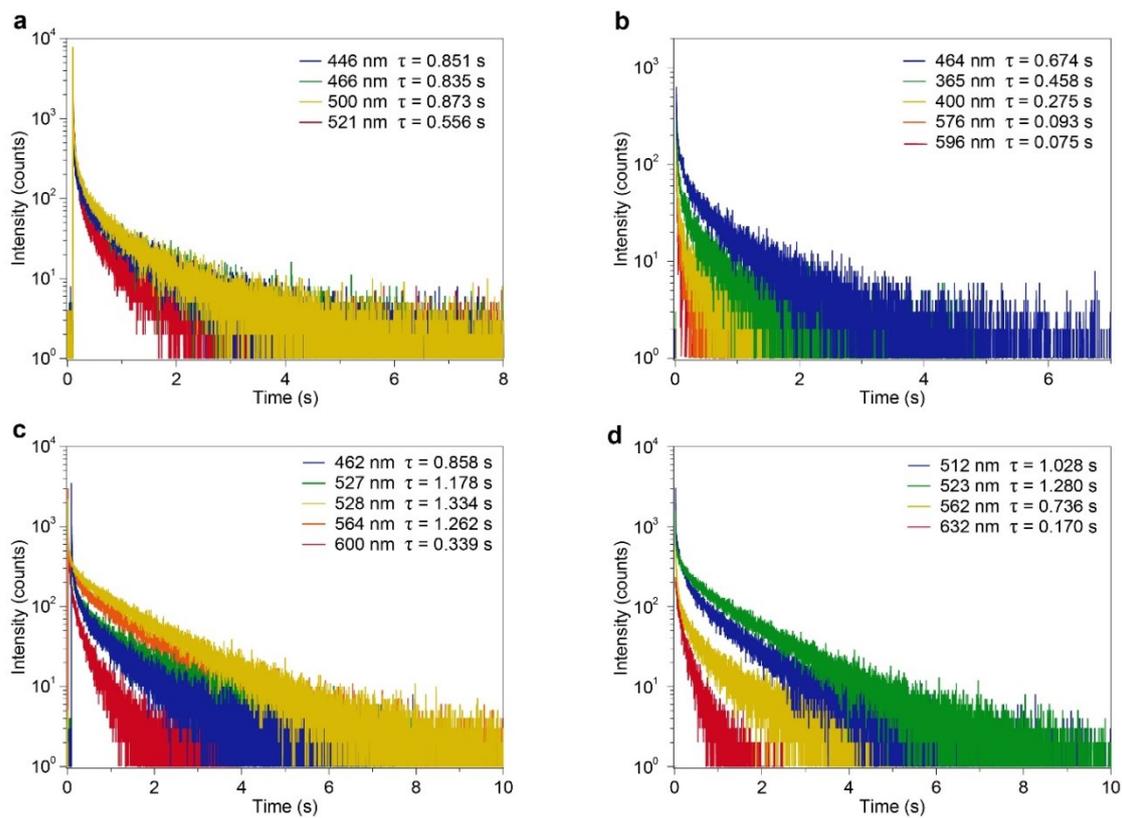
**Figure S14.** High-resolution XPS fitting results for the (a) C 1s, (b) O 1s, (c) N 1s and (d) P 2p spectra of the U/C-CDs-2.



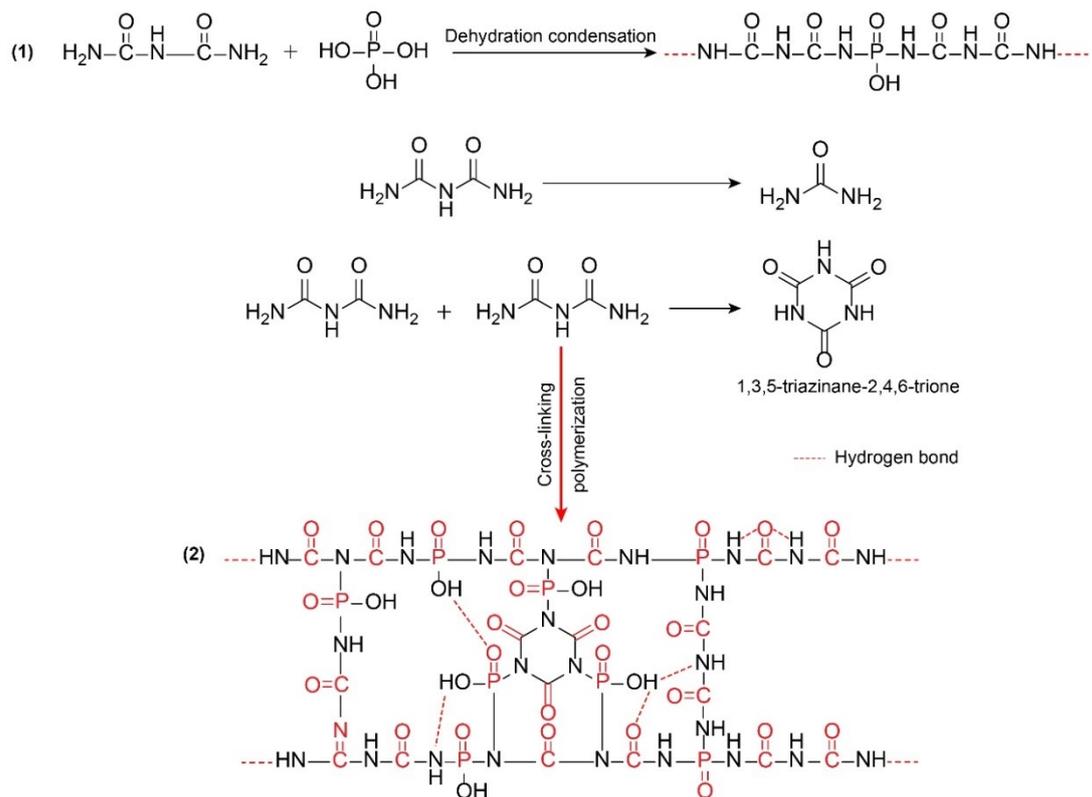
**Figure S15.** Photographs of phosphorescence with different delay time under different excitation wavelengths.



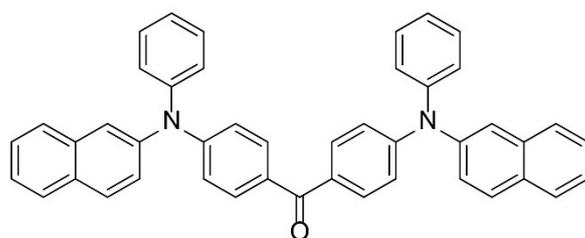
**Figure S16.** Photographs of phosphorescence with different delay time under different excitation wavelengths.



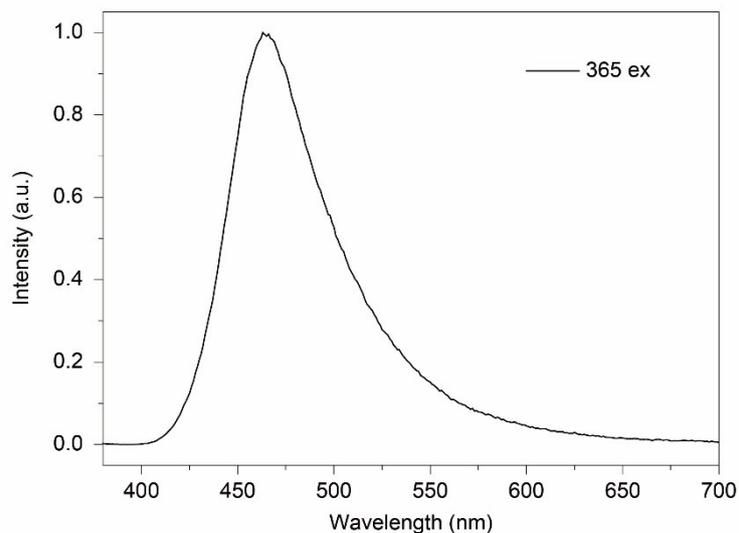
**Figure S17.** Time-resolved decay curves excited at different emission wavelengths for (a) U-CDs, (b) U/C-CDs-1, (c) U/C-CDs-2 and (d) B/C-CDs under ambient conditions, respectively.



**Figure S18.** Schematic diagram showing the formation of carbonyl-assisted clusters on the surface of carbon dots and the restriction of chromophores by covalent crosslinking and hydrogen bonding.



**Scheme S3.** Chemical structure of the bis(4-(naphthalen-2-yl(phenyl)amino)phenyl)methanone molecule.



**Figure S19.** Fluorescence spectrum of the bis(4-(naphthalen-2-yl(phenyl)amino)-phenyl)methanone molecule in solid state.

**Table S1.** Phosphorescence lifetimes of FP-CDs powder under ambient conditions. <sup>[a]</sup>

Compounds	Wavelength (nm)	Phosphorescence						
		$\tau_1$ (ms)	$A_1$ (%)	$\tau_2$ (ms)	$A_2$ (%)	$\tau_3$ (ms)	$A_3$ (%)	$\langle\tau\rangle$ (ms)
FP-CDs	484	26.32	4.70	240.59	18.77	1052.23	76.53	851.67
	522	89.65	7.25	1222.39	92.75	-	-	1140.27
	560	41.16	26.25	815.44	73.75	-	-	612.19
	617	34.21	26.09	392.01	73.91	-	-	298.66
	633	0.79	5.61	26.69	19.23	256.24	75.16	197.77

[a] Determined from the fitting function of  $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$ ;  $\lambda_{\text{ex}} = 365$  nm according to the phosphorescence decay curves.

**Table S2.** The quantum yields of FP-CDs

<b>Excitation wavelength</b>	<b><math>\Phi_{\text{Total}}</math> (%)</b>	<b><math>\Phi_{\text{Phos.}}</math> (%)</b>
310	13.8	4.08
320	13.1	1.91
330	12.6	0.60
340	12.3	0.55
350	11.8	0.52
360	11.7	0.52
370	11.8	0.54
380	11.8	0.59
390	12.1	0.70
400	13.3	0.16
410	13.0	0.18
420	14.1	0.21
430	14.4	0.17
440	14.6	0.16