Electronic Supplementary Information

Tunable multimodal printable up-/down-conversion nanomaterials for gradient information encryption

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Experimental section

Materials

O-phenylenediamine (O-PD), H_3PO_4, polyvinyl alcohol (PVA, 1750 ± 50), ethyl acetate, silica powder (200-300 mesh), ethyl alcohol, NH_4F, and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., Ltd. Urea, $NaNO_3$, $Bi(NO_3)_3 \cdot 5H_2O$, $Er(NO_3)_3 \cdot 5H_2O$, $Tm(NO_3)_3 \cdot 6H_2O$, and $Yb(NO_3)_3 \cdot 5H_2O$ were purchased from Aladdin. All of the reagents and materials were used as received without further purification.

Preparation of liquid N, P-doped CDs

Liquid N, P-doped CDs were synthesized by a hydrothermal method. Different liquid N, P-doped CDs were obtained by fine-controlling the volume ratio of deionized water (DI) and H_3PO_4 (volume ratios of DI:H_3PO_4 were 30:0, 25:5, 20:10, 15:15, 10:20, and 5:25). In detail, 0.3 g of O-PD was dissolved in a mixed solution of DI/H_3PO_4 (30 mL). The obtained solution underwent an ultrasonic dispersion procedure for 10 min until completely dissolved. The mixture was transferred into a 50 mL poly(tetrafluoroethylene) (Teflon)-lined autoclave and reacted at 180°C for 12 h. After cooling to room temperature, the obtained CDs solution was transferred into a 50 mL centrifuge tube. The as-prepared N, P-doped CDs in liquid obtained by a hydrothermal process are nearly black and opaque. The column chromatography method is useful for obtaining single wavelength CDs from a mixture CDs solution.[1] Thereby, a further purification procedure of column chromatography is applied to obtain clear solutions.

Synthesis of powdered N, P-doped CDs

For fabricating the N, P-doped CDs with FL and afterglow emissions, the as-

prepared liquid CDs samples were handled with a post-treatment of urea. Typically, 10 mL of liquid CDs and 5 g of urea were added into a 50 mL round-bottom flask and reacted at 155°C for 6 h. The powdered N, P-doped CDs were fully dissolved in DI water with ultrasonic treatment for 20 min until completely dissolved. The precipitate was centrifuged once under 8000 rpm for 5 min and then was dried on a stove for 12 h at 80°C.

Synthesis of $NaBiF_4$ upconversion nanoparticles (UCNPs)

The Er^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+} doped $NaBiF_4$ UCNPs were synthesized by a coprecipitation process and a hydrothermal procedure, based on a modification of previous reports.[2,3] Taking the preparation of $NaBiF_4$:2%Er^{3+}/20%Yb^{3+} UCNPs as an example, 0.05 mol lanthanide nitrates (the molar ratio of $Bi(NO_3)_3 \cdot 5H_2O$, $Er(NO_3)_3 \cdot 5H_2O$, $Yb(NO_3)_3 \cdot 5H_2O$ is 0.78:0.02:0.20) and 0.1 mol $NaNO_3$ were added to a 200 mL beaker containing 50 mL ethylene glycol (solution 1). 0.2 mol NH_4F was added to a 150 mL beaker containing 100 ml ethylene glycol (solution 2). The two kinds of solutions were dissolved fully at 40°C. Solution 2 was poured into solution 1 to form a mixture under stirring vigorously at 40°C. The mixture was kept in a water bath at 40°C for 10 min. The as-synthesized white precipitate was stood for 30 min to gather 30 mL solution with highly concentrated precipitate after removing the supernatant. The mixture was transferred into a 50 mL Teflon-lined autoclave for a further reaction at 180°C for 6 h. New white production with a high degree of crystallinity was obtained by centrifugation and washing with ethanol/DI water for several times, and finally dried at 80°C for 12 h. The $NaBiF_4$:0.5%Tm^{3+}/20%Yb^{3+} UCNPs was prepared with the same

procedures except for the difference in raw material of activators of Er^{3+} and Tm^{3+}. The $NaBiF_4$:2%Er^{3+}/20%Yb^{3+} and $NaBiF_4$:0.5%Tm^{3+}/20%Yb^{3+} UCNPs are recorded as NBF-G and NBF-B for further discussion.

Formulation of security inks

Security inks (1): For liquid N, P-CDs samples, 10 mL of liquid CDs was dried, and then 3 mL of PVA aqueous solution (1 g of PVA in15 mL of DI water) was injected. Security inks were obtained by ultrasonic dispersion and vibration. Security inks (2): For powdered N, P-CDs and UCNPs samples, 2 mL of PVA aqueous solution was injected into a centrifuge tube containing 0.1 g of powdered CDs, and then the mixture was handled with an ultrasonic dispersion and vibration to form a homogeneous security ink.

Characterization

The XRD data were recorded on a Bruker D8 advance with Cu Kα radiation (λ = 0.15406 nm, 40 kV, 40 mA). The morphology of UCNPs was carried out on a SEM (Hitachi S-4800) and a TEM (JEM-2100). FT-IR spectra were carried out on a Nexus 670 FT-IR spectrophotometer. XPS results were obtained from a Thermo Scientific K-Alpha equipped with a monochromatic Al Ka X-ray source. The XPS results were tested on an X-ray photoelectron spectrometer (Thermo Fischer, ESCALAB Xi+). The UV-Vis diffuse reflection spectra were recorded on a PerkinElmer Lambda 950 spectrophotometer (PerkinElmer, America) equipped with an inner 150 mm integral sphere. UV-Vis spectra of CDs in liquid were tested on a UV-Vis spectrophotometer (UV-2550). FL (including excitation and emission spectra) and RTP spectra were

measured on a F-4600 spectrophotometer attached with a 500 W xenon lamp. Security patterns were printed using a screen plate with 300 mesh counts through the screen-printing method. Fluorescent images were captured with a Nikon D750 camera and the printed QD codes were analyzed by a mobile phone (HUAWEI Mate 40E, OCE-AN50). Note that UCL patterns were captured with a continuous image collection process by using a wireless timer remote controller (TW-283). Upconversion spectrum was tested on a SENS-9000 spectrophotometer equipped with an external 980 nm laser with the excitation power density changed from 0.31 W/cm^{-1} to 1.14 W/cm^{-1}. The settings of slit and accumulation time are 2 nm and 100 ms, respectively. The upconversion quantum yields were tested on FLS1000 with the PMT-1010 detector, a 208 times attenuation plate, and an excitation power density of 38 W/cm^{-1}. FL and PL quantum yields of power CDs were measured on FLS1000 after excitation at 365 nm excitation for 15 s.

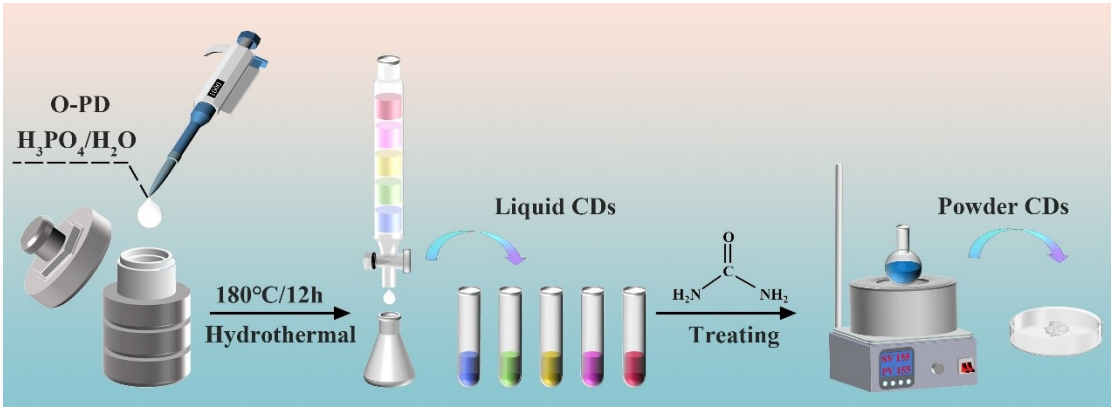

Fig. S1 The schematic diagram of the preparation of liquid CDs and powdered CDs.

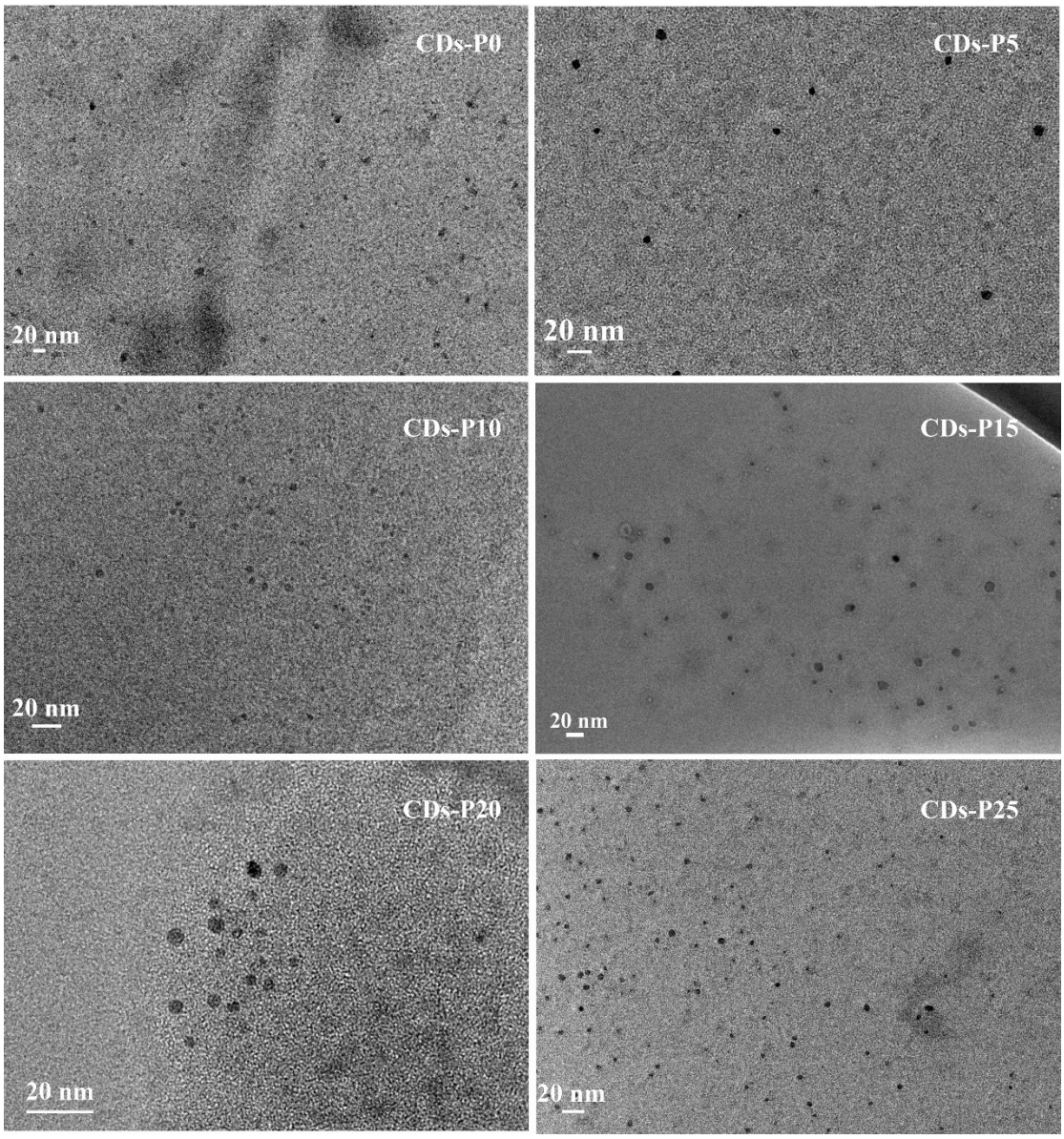

Fig. S2 TEM images of CDs-P0, CDs-P5, CDs-P10, CDs-P15, CDs-P20, and CDs-P25.

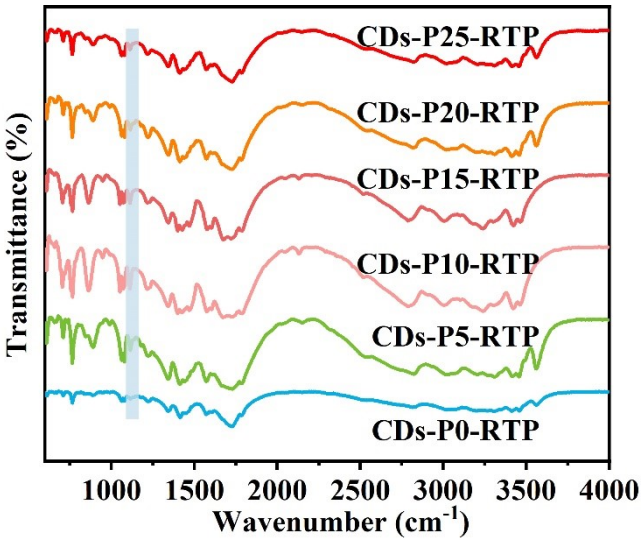

Fig. S3 FT-IR spectra of CDs-P0-RTP, CDs-P5-RTP, CDs-P10-RTP, CDs-P15-RTP, CDs-P20-RTP, and CDs-P25-RTP.

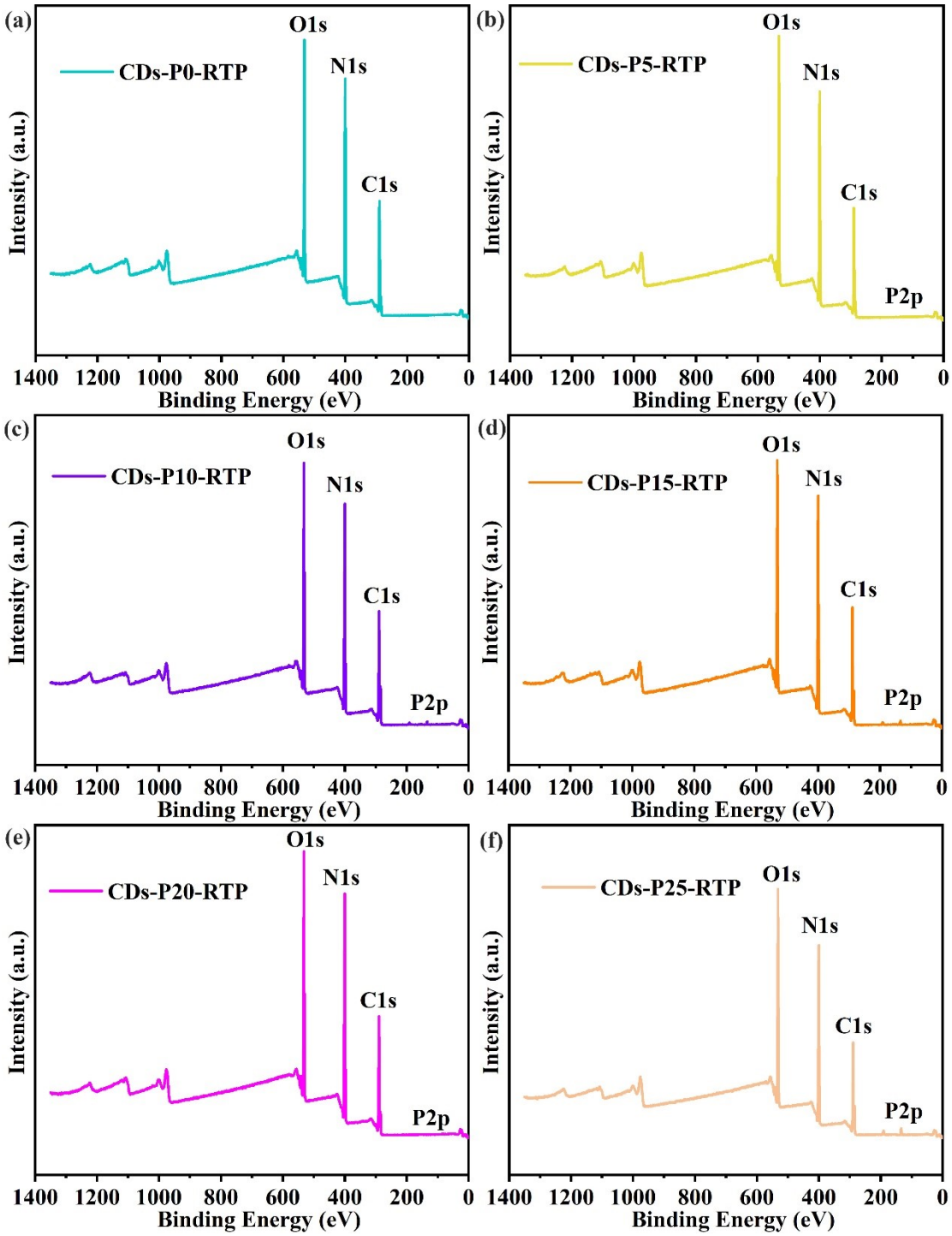

Fig. S4 Full XPS spectra of (a) CDs-P0-RTP. (b) CDs-P5-RTP. (c) CDs-P10-RTP. (d) CDs-P15-RTP. (e) CDs-P20-RTP, and (f) CDs-P25-RTP.

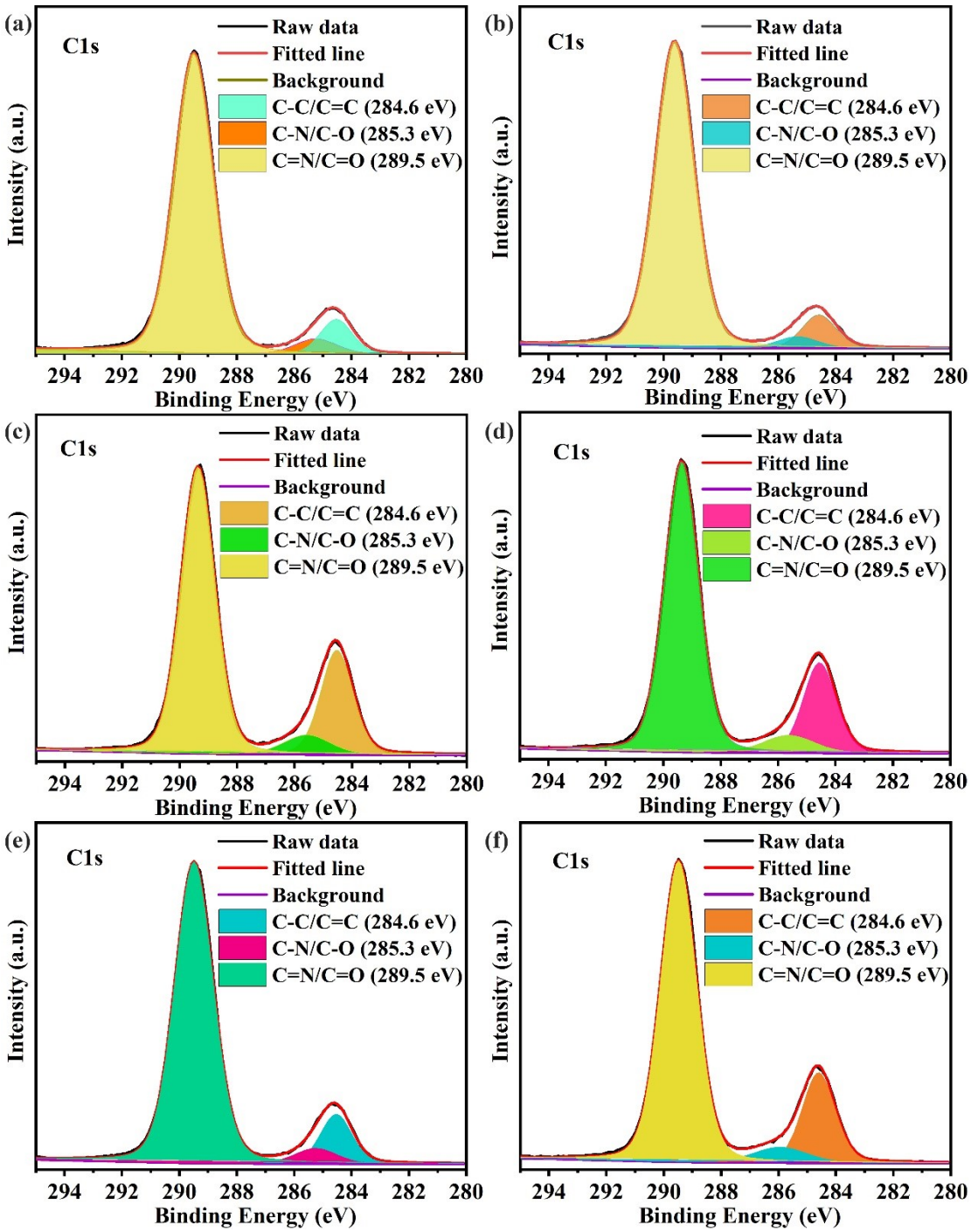

Fig. S5 High resolution XPS spectra of C1s of (a) CDs-P0-RTP. (b) CDs-P5-RTP. (c) CDs-P10-RTP. (d) CDs-P15-RTP. (e) CDs-P20-RTP, and (f) CDs-P25-RTP.

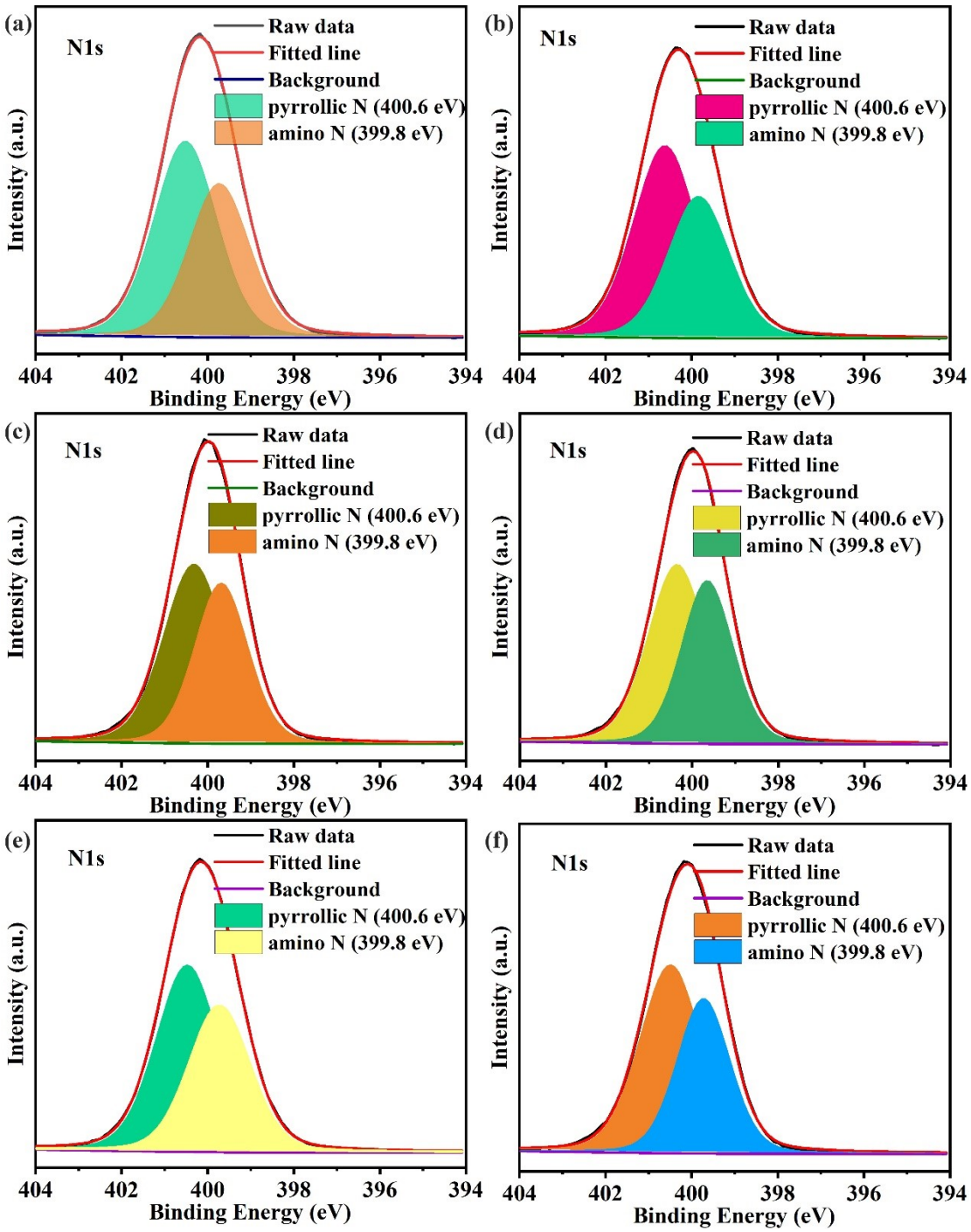

Fig. S6 High resolution XPS spectra of N1s of (a) CDs-P0-RTP. (b) CDs-P5-RTP. (c) CDs-P10-RTP. (d) CDs-P15-RTP. (e) CDs-P20-RTP, and (f) CDs-P25-RTP.

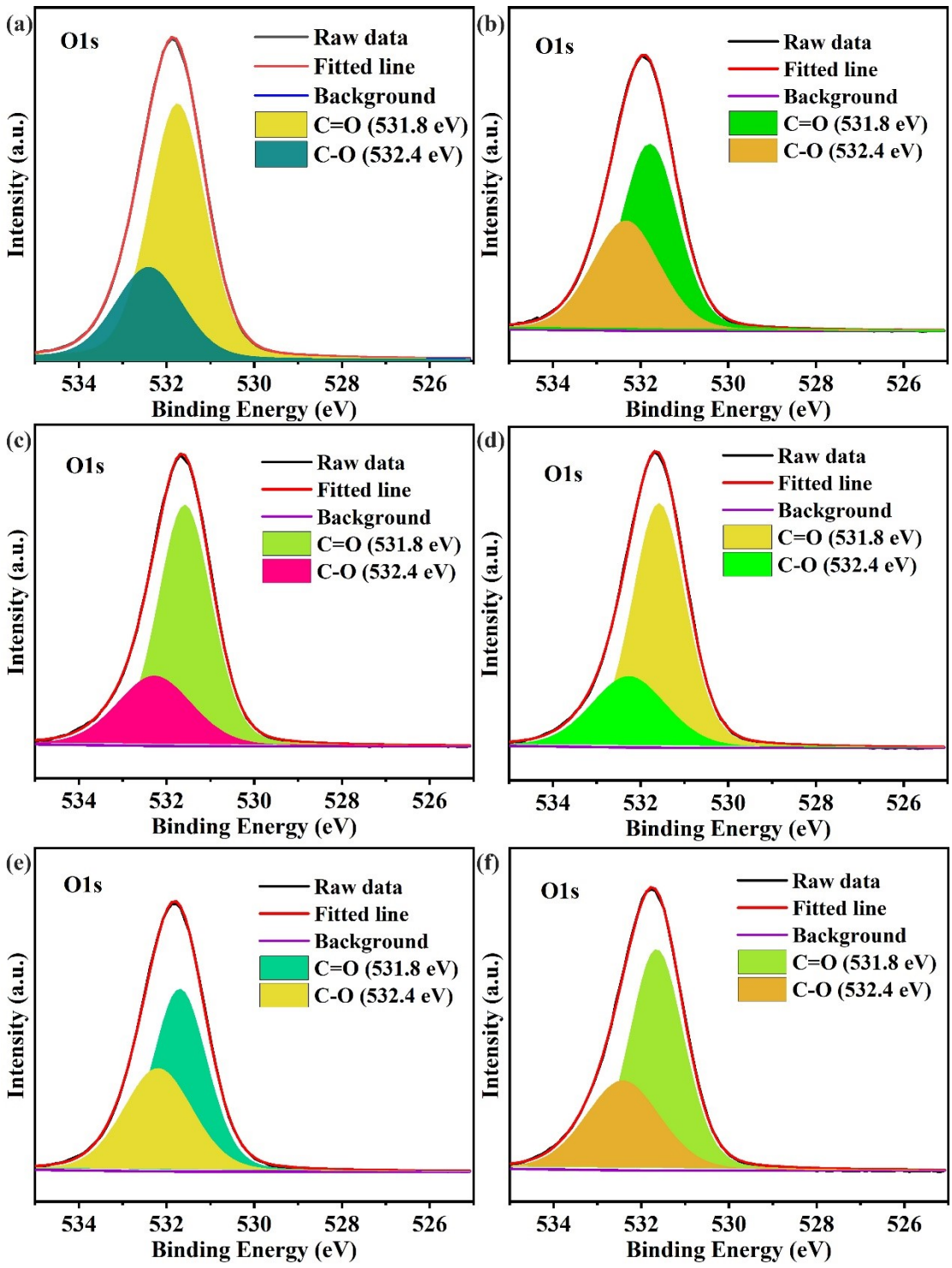

Fig. S7 High resolution XPS spectra of O1s of (a) CDs-P0-RTP. (b) CDs-P5-RTP. (c) CDs-P10-RTP. (d) CDs-P15-RTP. (e) CDs-P20-RTP, and (f) CDs-P25-RTP.

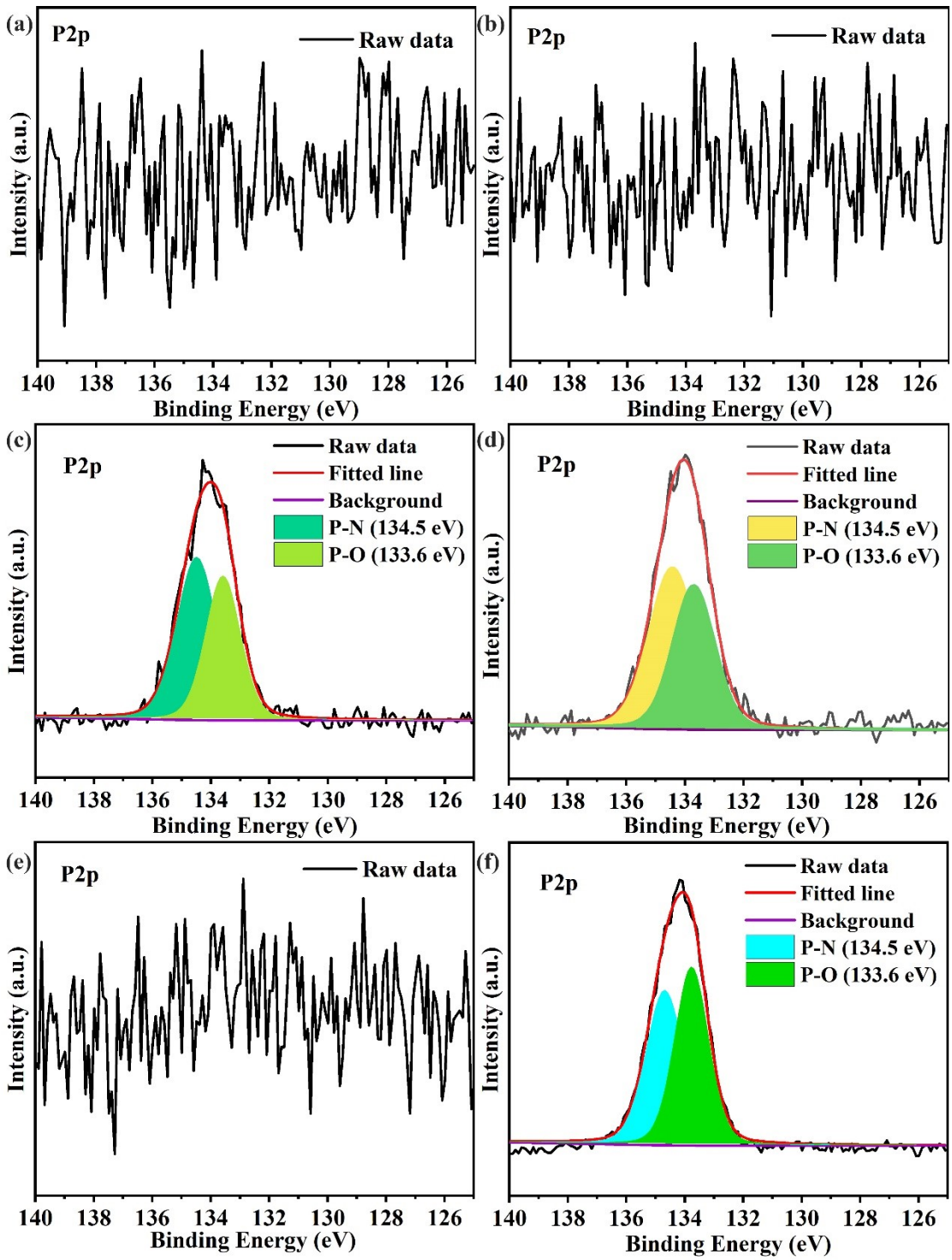

Fig. S8 High resolution XPS spectra of P2p of (a) CDs-P0-RTP. (b) CDs-P5-RTP. (c) CDs-P10-RTP. (d) CDs-P15-RTP. (e) CDs-P20-RTP, and (f) CDs-P25-RTP.

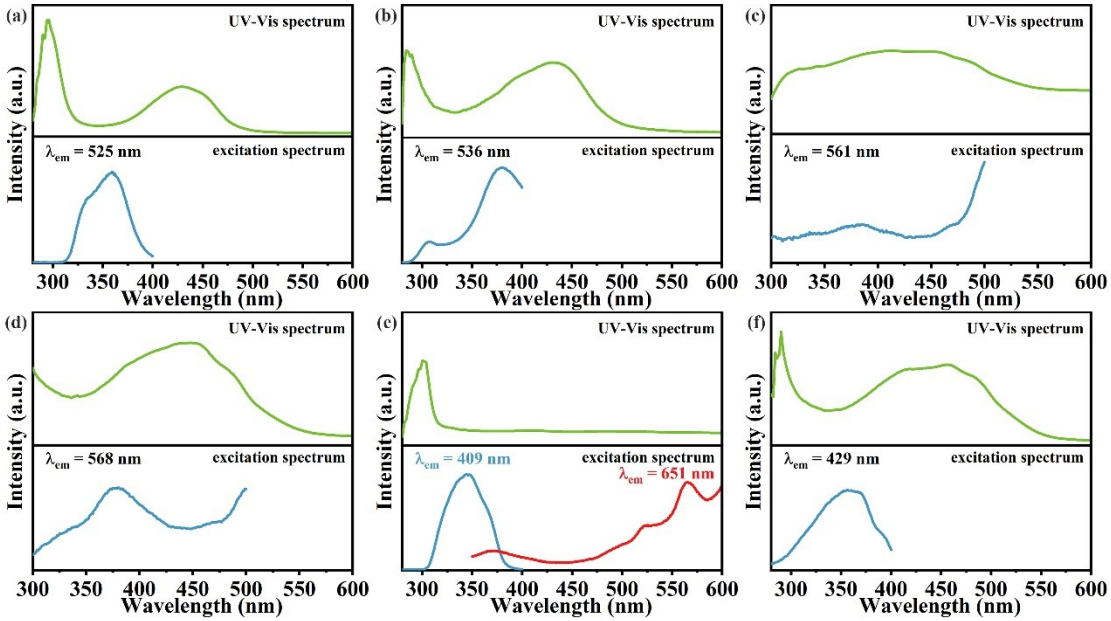

Fig. S9 The UV-Vis spectra and excitation spectra of liquid CDs (a) CDs-P0, (b) CDs-P5, (c) CDs-P10, (d) CDs-P15, (e) CDs-P20, and (f) CDs-P25.

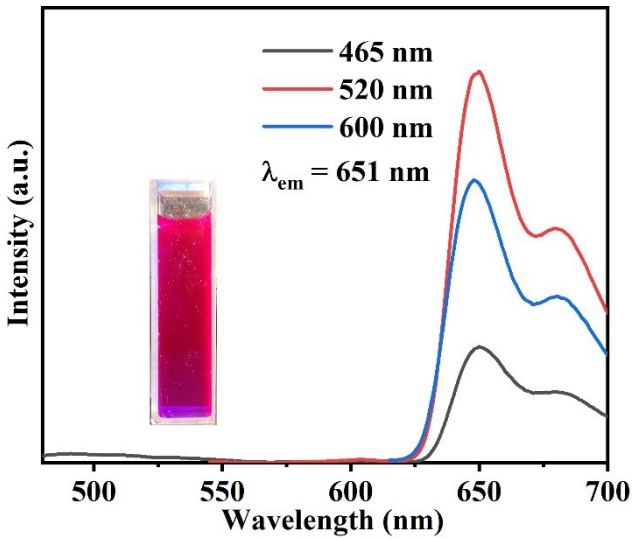

Fig. S10 Fluorescent spectra and actual photographs of the CDs-P20.

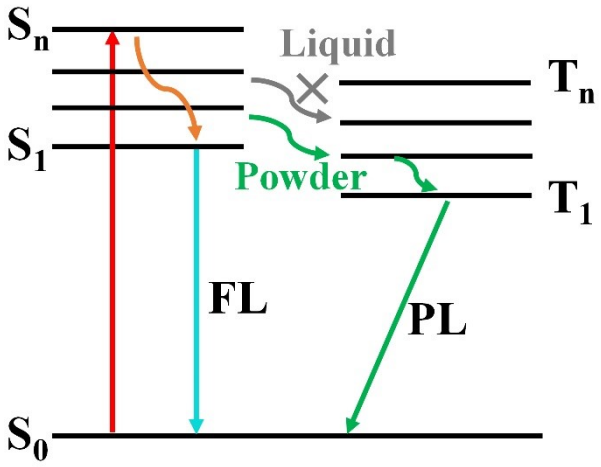

Fig. S11 The schematic illustration of liquid and powdered CDs systems.

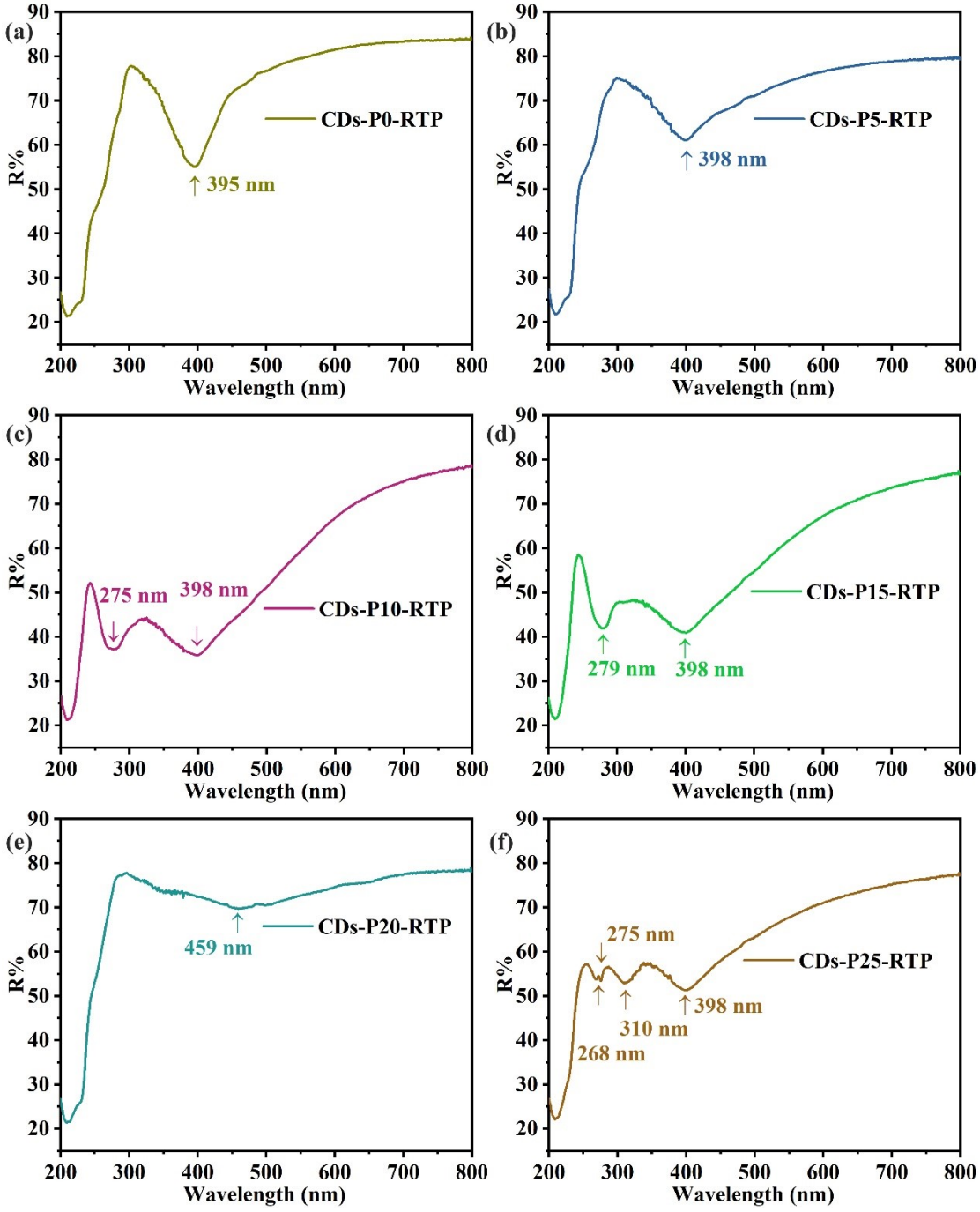

Fig. S12 Diffuse reflectance spectra of (a) CDs-P0. (b) CDs-P5. (c) CDs-P10. (d) CDs-P15. (e) CDs-P20, and (f) CDs-P25.

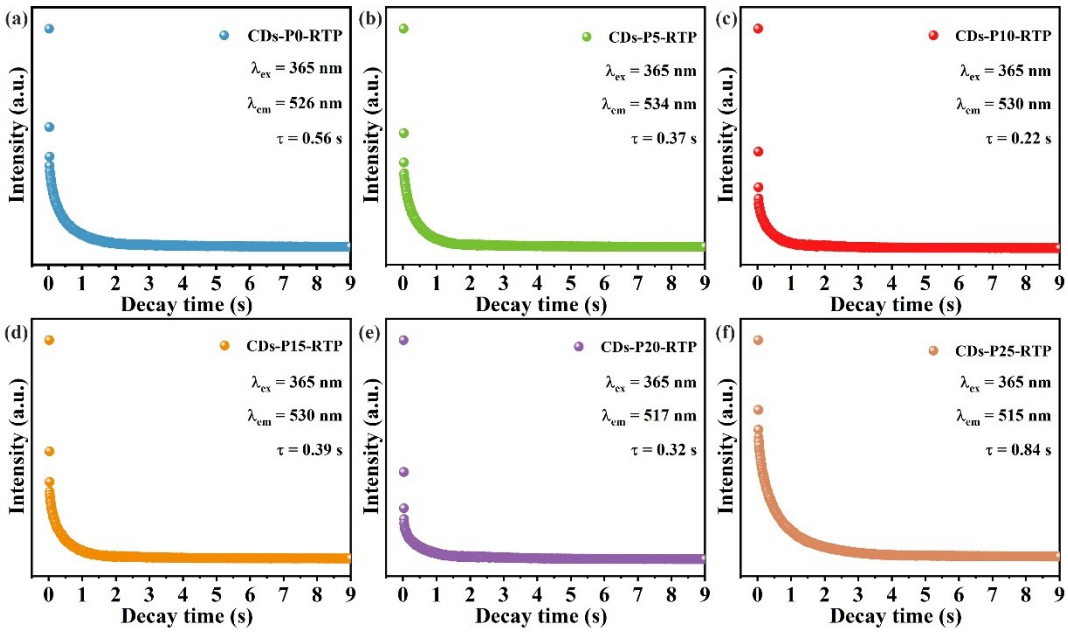

Fig. S13 RTP decay spectra of CDs-P0-RTP, CDs-P5-RTP, CDs-P10-RTP, CDs-P15-RTP, CDs-P20-RTP, and CDs-P25-RTP under 365 nm excitation.

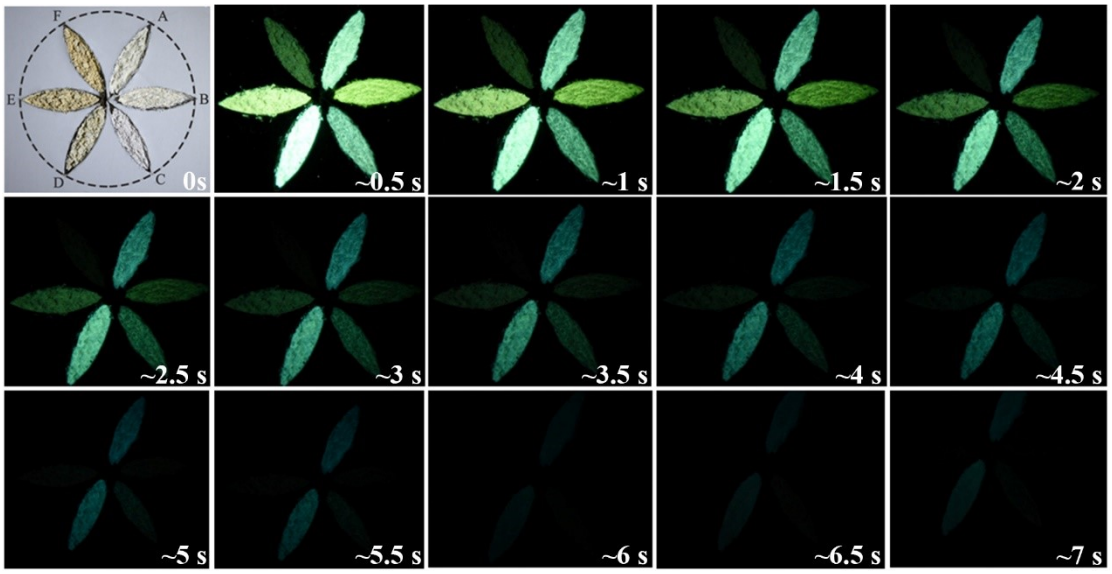

Fig. S14 RTP images of powdered CDs (a) CDs-P0-RTP. (b) CDs-P5-RTP. (c) CDs-P20-RTP. (d) CDs-P25-RTP. (e) CDs-P15-RTP, and (f) CDs-P10-RTP after removal of UV excitation. The diameter of the circle is 7.2 cm.

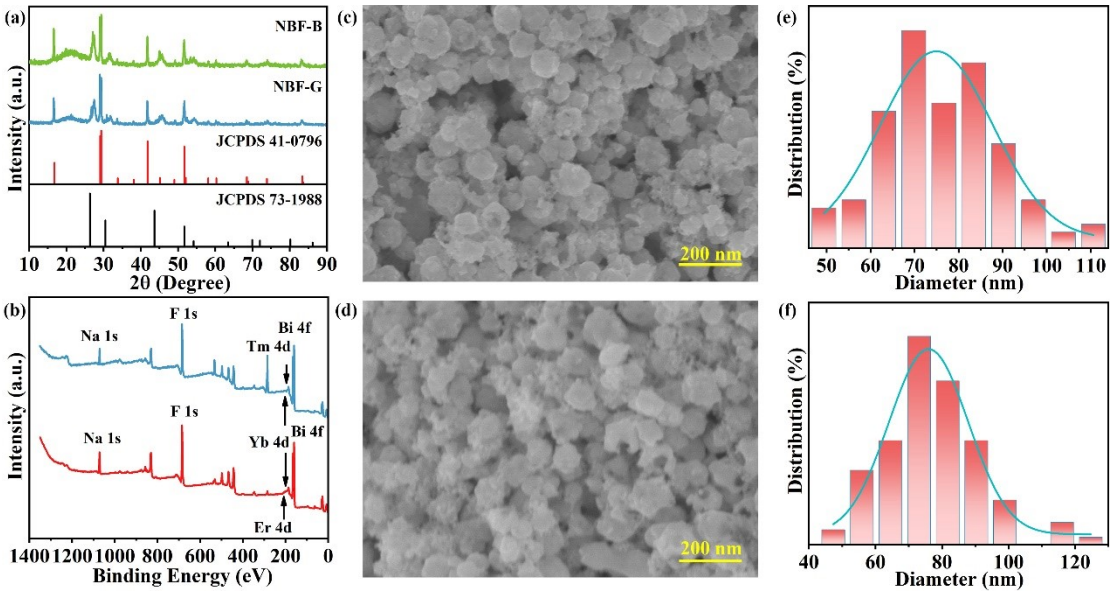

Fig. S15 (a) The XRD patterns and (b) full XPS spectra of NBF-G and NBF-B. SEM images of (c) NBF-G and (d) NBF-B. Diameter distribution patterns of (e) NBF-G and (f) NBF-B.

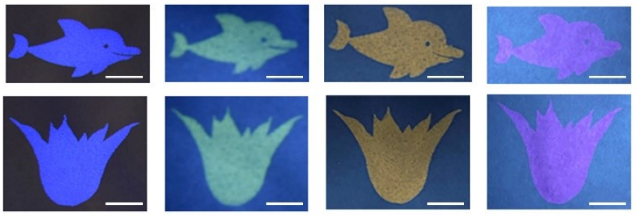

Fig. S16 Photographs of printing patterns based on liquid CDs upon UV excitation. The scale bar is 1 cm.

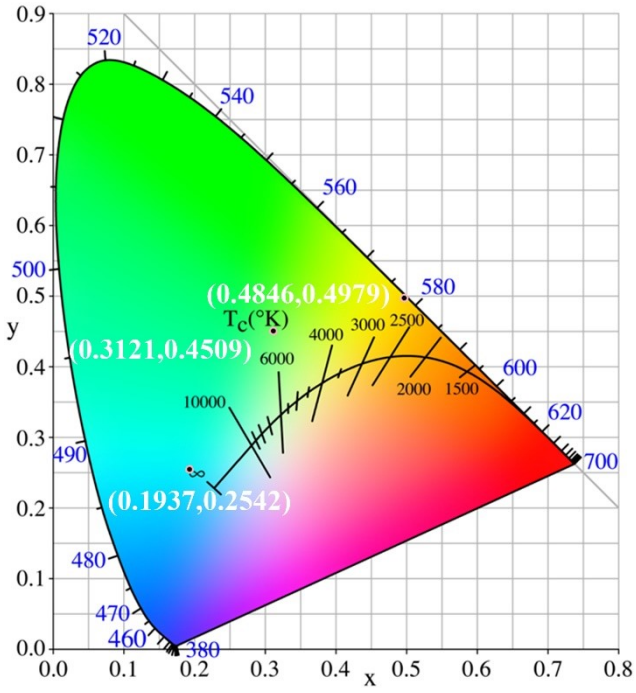

Fig. S17 The chromaticity coordinate of CDs-P15 and CDs-P15-RTP samples under UV excitation and removal of UV excitation.

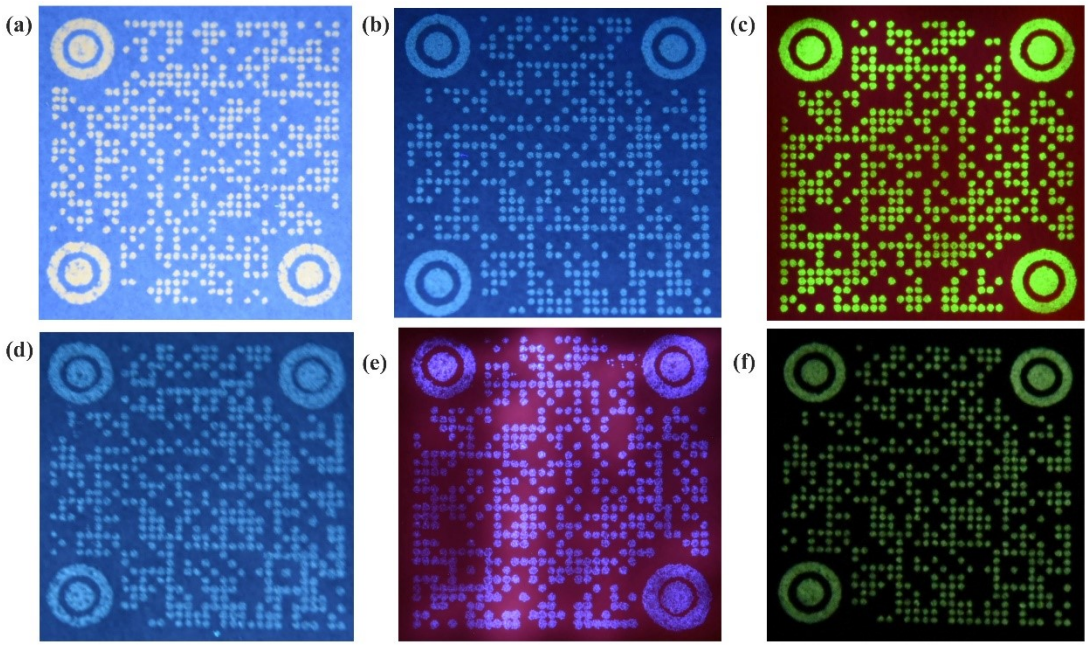

Fig. S18 Photographs of printing QD code based on different security inks (a) FL emission of CDs-P15 upon UV excitation. (b) and (c) FL emission and UCL of security ink including CDs-P15-RTP and NBF-G upon UV and 980 nm excitation (~1.14 W/cm^{-1}). (d) and (e) FL emission and UCL of security ink including CDs-P15-RTP and NBF-B upon UV and 980 nm excitation (~1.14 W/cm^{-1}). (f) RTP emission of CDs-P15-RTP after removal of UV excitation. The length and width sizes of QD code patterns are 3.2 × 3.2 cm.

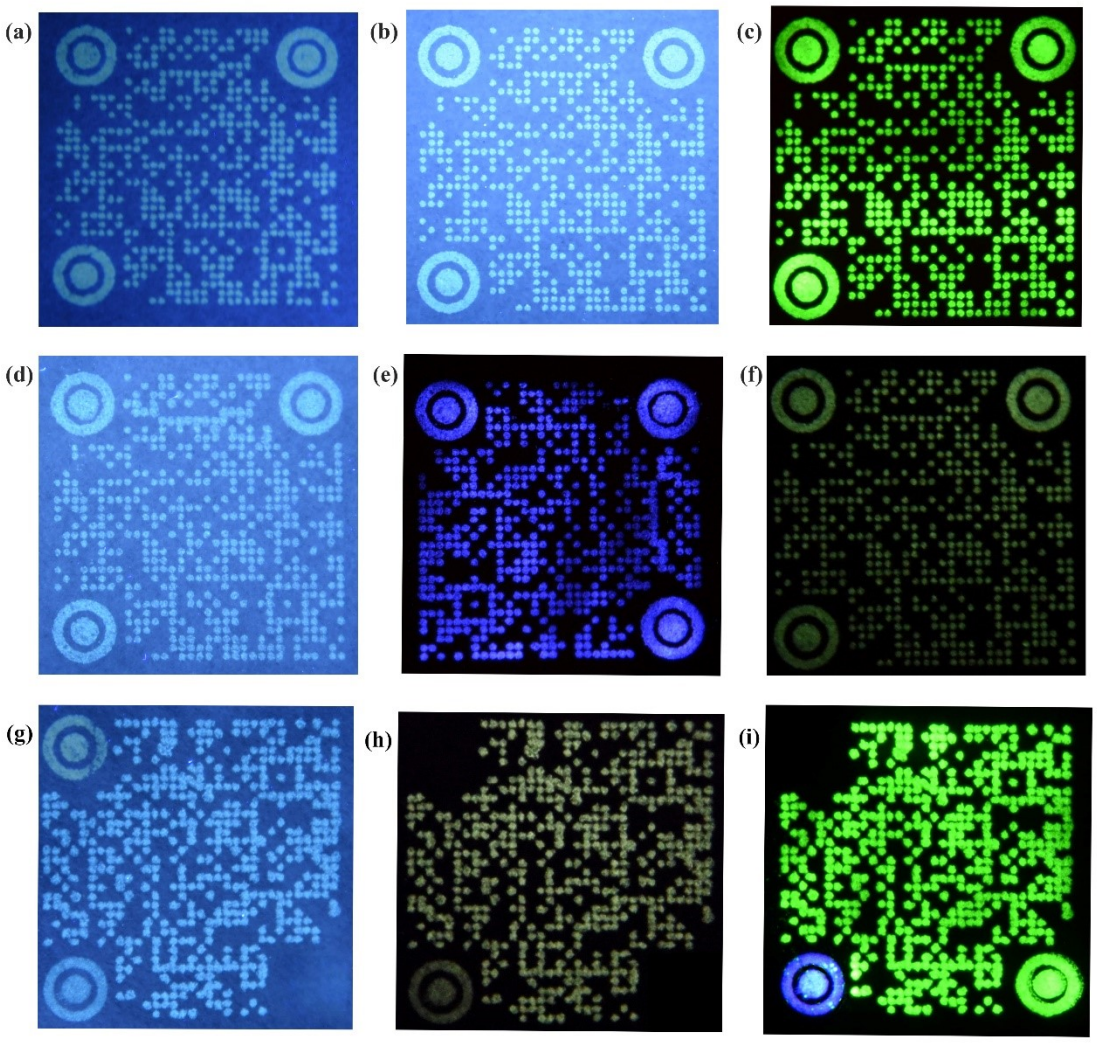

Fig. S19 Photographs of printing QD code based on different security inks (a) FL emission of CDs-P15 upon UV excitation. (b) and (c) FL emission and UCL of security ink including CDs-P15-RTP and NBF-G upon UV and 980 nm excitation (~1.14 W/cm^{-1}). (d) and (e) FL emission and UCL of security ink including CDs-P15-RTP and NBF-G upon UV and 980 nm excitation (~1.14 W/cm^{-1}). (f) RTP emission of CDs-P15-RTP after removal of UV excitation. (g) FL emission of CDs-P15 and CDs-P15-RTP upon UV excitation. (h) RTP emission of CDs-P15-RTP after removal of UV excitation. (i) UCL emission of NBF-G and NBF-B under the stimulation of 980 nm excitation (~1.14 W/cm^{-1}). The length and width sizes of QD code patterns are 3.2 × 3.2 cm.

Table S1 The content of C, N, O and P elements in as-prepared CDs samples.

Sample	C	N	O	P
CDs-P0-RTP	33.83	38.86	27.31	0
CDs-P5-RTP	33.67	38.36	27.84	0.13
CDs-P10-RTP	37.55	34.44	27.34	0.68
CDs-P15-RTP	36.44	35.05	27.70	0.8
CDs-P20-RTP	34.46	38.28	27.11	0.15
CDs-P25-RTP	34.83	34.45	29.33	1.39

Table S2 The high-resolution XPS analysis of C 1s.

Sample	C 1s		
	C-C/C=C (284.6 eV)	C-N/C-O (285.3 eV)	C=N/C=O (289.5 eV)
CDs-P0-RTP	87.03%	3.88%	9.09%
CDs-P5-RTP	88.28%	3.45%	8.27%
CDs-P10-RTP	69.64%	6.40%	23.96%
CDs-P15-RTP	72.32%	6.43%	21.25%
CDs-P20-RTP	84.08%	4.63%	11.29%
CDs-P25-RTP	74.11%	5.64%	20.25%

Table S3 The high-resolution XPS analysis of N 1s.

Sample	N 1s	
	Pyrrolic N (400.6 eV)	Amino N (399.8 eV)
CDs-P0-RTP	56.96%	43.04%
CDs-P5-RTP	58.28%	41.72%
CDs-P10-RTP	55.83%	44.17%
CDs-P15-RTP	55.27%	44.73%
CDs-P20-RTP	56.86%	43.14%
CDs-P25-RTP	58.50%	41.50%

Table S4 The high-resolution XPS analysis of O 1s.

Sample	O 1s	
	C=O (531.8 eV)	C-O (532.4 eV)
CDs-P0-RTP	58.61%	41.39%
CDs-P5-RTP	57.59%	42.41%
CDs-P10-RTP	71.24%	28.76%
CDs-P15-RTP	71.19%	28.81%
CDs-P20-RTP	58.35%	41.65%
CDs-P25-RTP	64.55%	35.45%

Table S5 The high-resolution XPS analysis of P 2p.

Sample	P 2p	
	P-N (134.5 eV)	P-O (133.6 eV)
CDs-P0-RTP	\	\
CDs-P5-RTP	\	\
CDs-P10-RTP	56.22%	43.78%
CDs-P15-RTP	55.46%	44.54%
CDs-P20-RTP	\	\
CDs-P25-RTP	49.11%	50.89%

Table S6 The chromaticity coordinate of liquid CDs samples.

Sample	CIE x	CIE y	Excitation	Color
CDs-P0	0.2904	0.5693	365 nm	Green
CDs-P5	0.3323	0.5772	365 nm	Green
CDs-P10	0.3672	0.4167	365 nm	Yellow
CDs-P15	0.4846	0.4979	365 nm	Yellow
CDs-P20	0.1583	0.0606	365 nm	Blue
	0.2399	0.1261	395 nm	Magenta
	0.7196	0.2804	520 nm	Red
CDs-P25	0.1590	0.0839	365 nm	Blue

Table S7 The chromaticity coordinate of CDs-P15 and CDs-P15-RTP samples under UV excitation.

Samples	CIE x	CIE y	Fluorescent category	Color
CDs-P15	0.4846	0.4979	FL	Yellow
CDs-P15-RTP	0.1937	0.2542	FL	Blue
CDs-P15-RTP	0.3121	0.4509	PL	Green

References

1. H. Ding, S. B. Yu, J. S. Wei and H. M. Xiong, ACS Nano 2016, **10**, 484-491.
2. P. Lei, R. An, S. Yao, Q. Wang, L. Dong, X. Xu, K. Du, J. Feng and H. Zhang, *Adv. Mater.*, 2017, **29**, 1700505.
3. P. Du, L. Luo, X. Huang and J. S. Yu, *J. Colloid. Interface Sci.*, 2018, **514**, 172-181.