Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

NaCl nanocrystal-encapsulated carbon dots as a solution-based sensor for phosphorescent sensing of trace amounts of water in organic solvents

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Abstract

Supporting Information includes the details of the synthetic procedures (Experimental section) TEM images (Figure S1) and excitation-dependent emission spectra (Figure S2), FI-IR spectrum and TEM images of the PDDA-CDs@NaCl in water (Figures S3 and S4),fluorescence and phosphorescence spectra of the PDDA-CDs@NaCl in different organic solvent systems (Figure S5),phosphorescence photographs (Figure S6) and Comparison of the PDDA-CDs@NaCl with previously reported CD-based sensors for the determination of the water content in ethanol and methanol. (Table S1).

Experimental Section

Synthesis of the CDs from citric acid and polyethyleneimine. According to the previously reported procedure,[1] 0.5 g of polyethyleneimine and 1.0 g of citric acid were dissolved in 10.0 mL of hot water in a 25-mL glass bottle. Subsequently, the resultant solution was heated at 180 °C for a period of about 15-30 min until complete evaporation of deionized water. Subsequently, 1 mL of deionized water was injected into the gel-like solution, and the obtained solution was evaporated again. The above-discussed procedure associated with evaporation of the solvent and addition of deionized water was conducted several times until the gel-like solution turned to an orange color. After that, 10 mL of ethanol was injected into the gel-like solution, followed by centrifugation at 10000 rpm for 15 min. The collected precipitate corresponding to the CDs was re-dispersed in 10 mL of deionized water and then preserved in a refrigerator at 4 °C.

Synthesis of the CDs from citric acid and urea. 1.0 g of citric acid and 1.0 g of urea were prepared in 10.0 mL of deionized water. The resultant mixture was transferred to a 25-mL stainless steel autoclave, followed by heating in an oven at 180° C for 7 h. After cooling to ambient temperature, the obtained CDs were poured into a glass bottle. Afterward, the solution was left undisturbed for 20 min, allowing large-sized CDs to settle down by gravity. The clear upper solution was

filtrated with a 0.22-μm nylon membrane (Millipore, USA). The purified CDs were stored in a glass container at 4 °C.

Synthesis of the CDs from citric acid and cysteine. Based on an earlier published work,[2] the dissolution of L-cysteine (0.3 g) and citric acid (0.1 g) were performed in 0.5 mL of deionized water. The obtained solution was placed in a silica crucible and heated in a muffle furnace at 260 °C for 3 min. The produced ash (approximately 10 mg) was dispersed in deionized water (10 mL), sonicated at 150 W for 5 min, and then centrifuged at 12,000 rpm for 10 min. The resultant supernatant equivalent to the as-made CDs was kept at 4 °C.

Synthesis of the CDs from *o*-phenylenediamine and L-histidine. A solution (30 mL) containing 0.324 g of o-phenylenediamine and 0.162 g of L-histidine was incubated with 0.6 mL of HCl. The mixture was transferred to a poly(tetrafluoroethylene) (Teflon™)-lined autoclave (100 mL), followed by heating at 180 °C in an oven for 4 h. The product was centrifugated at 10000 rpm for 30 min and then treated with a 0.22-μm nylon membrane (Millipore, USA). The purified CDs were stored at 4 °C.

Synthesis of the CDs from citric acid and guanidine. A solution consisting of citric acid (0.5 g) and guanidine hydrochloride (0.25 g) was mixed with 0.5 mL of deionized water, followed by heating in a muffle furnace at 200 °C for 1 h. Thereafter, the formed ashes were dispersed in deionized water (7 mL), sonicated at 150 W for 5 min, and then centrifugated at 12000 rpm for 10 min. The resultant supernatant, the as-made CDs, was kept at 4 °C.

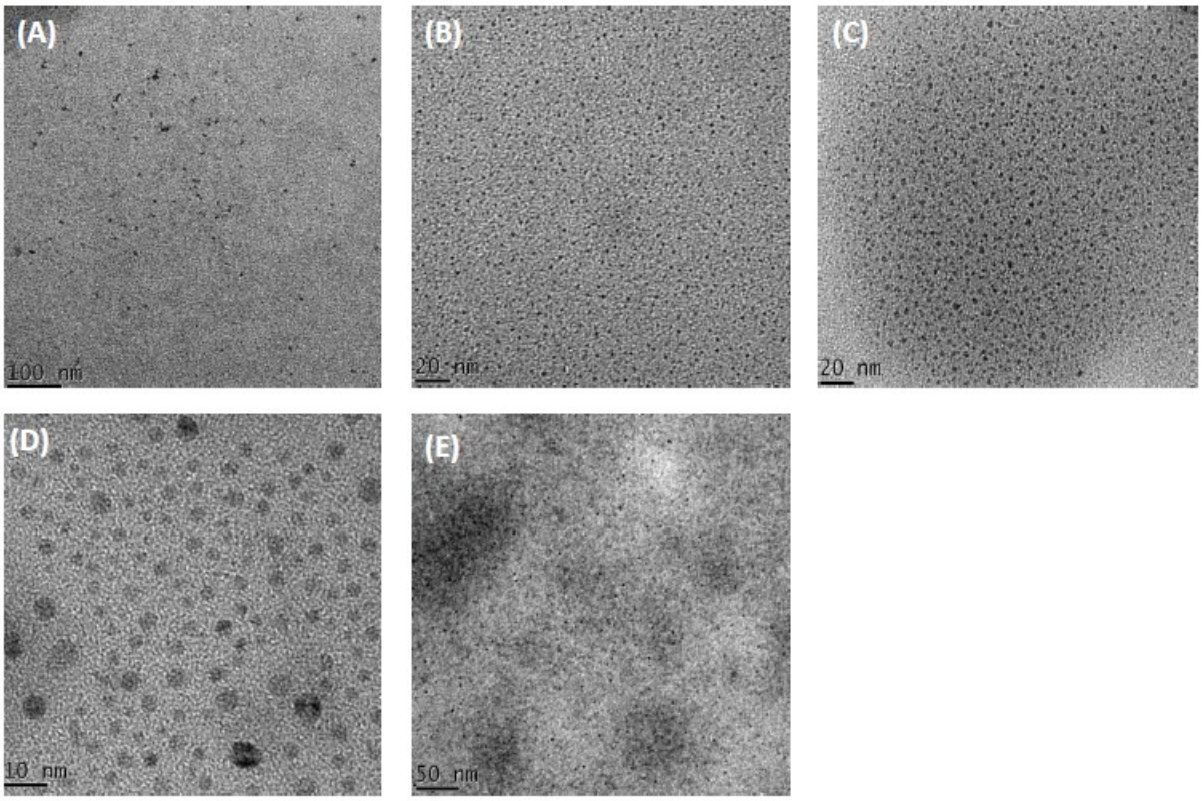

Fig. S1 TEM images of the CDs synthesized from (A) citric acid and polyethyleneimine, (B) citric acid and urea, (C) citric acid and cysteine, (D) histidine and o-phenylenediamine, and (E) citric acid and guanidine.

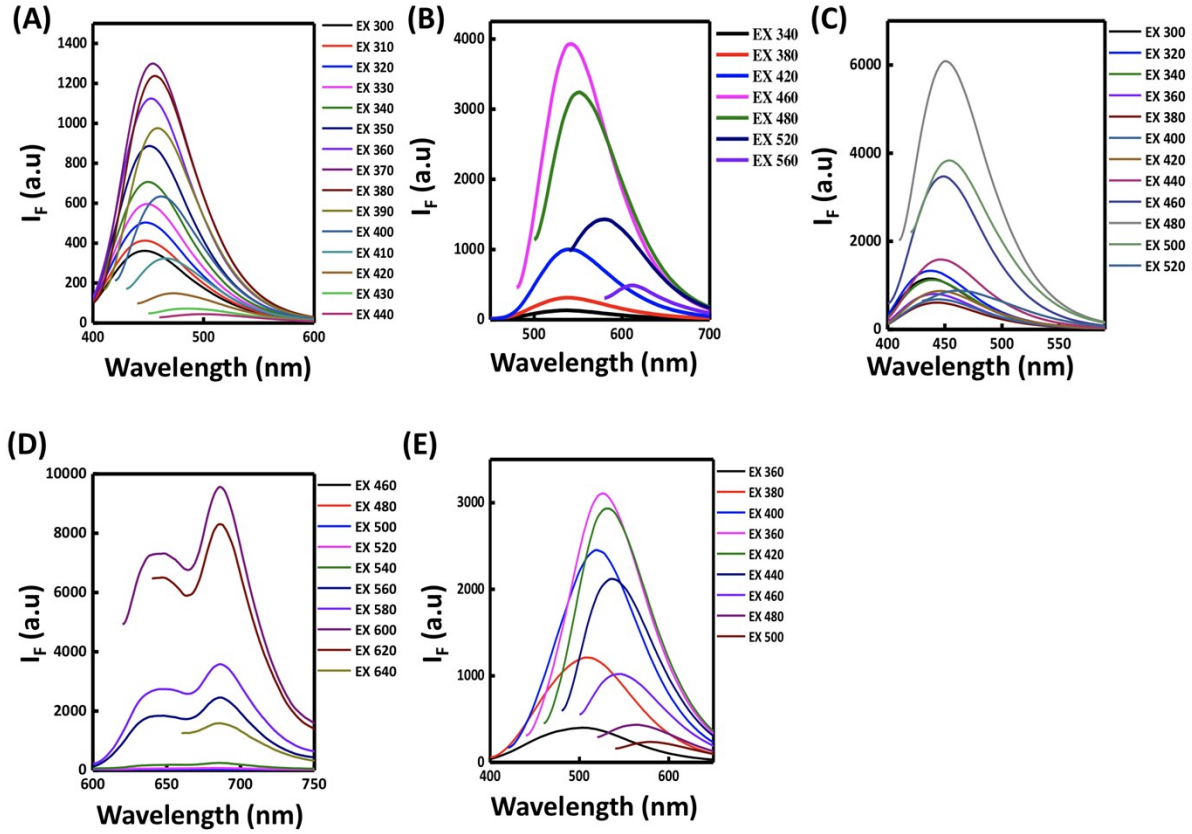

Fig. S2 Effect of the excitation wavelength on the fluorescence spectra of the CDs synthesized from (A) citric acid and polyethyleneimine, (B) citric acid and urea, (C) citric acid and cysteine, (D) histidine and o-phenylenediamine, and (E) citric acid and guanidine.

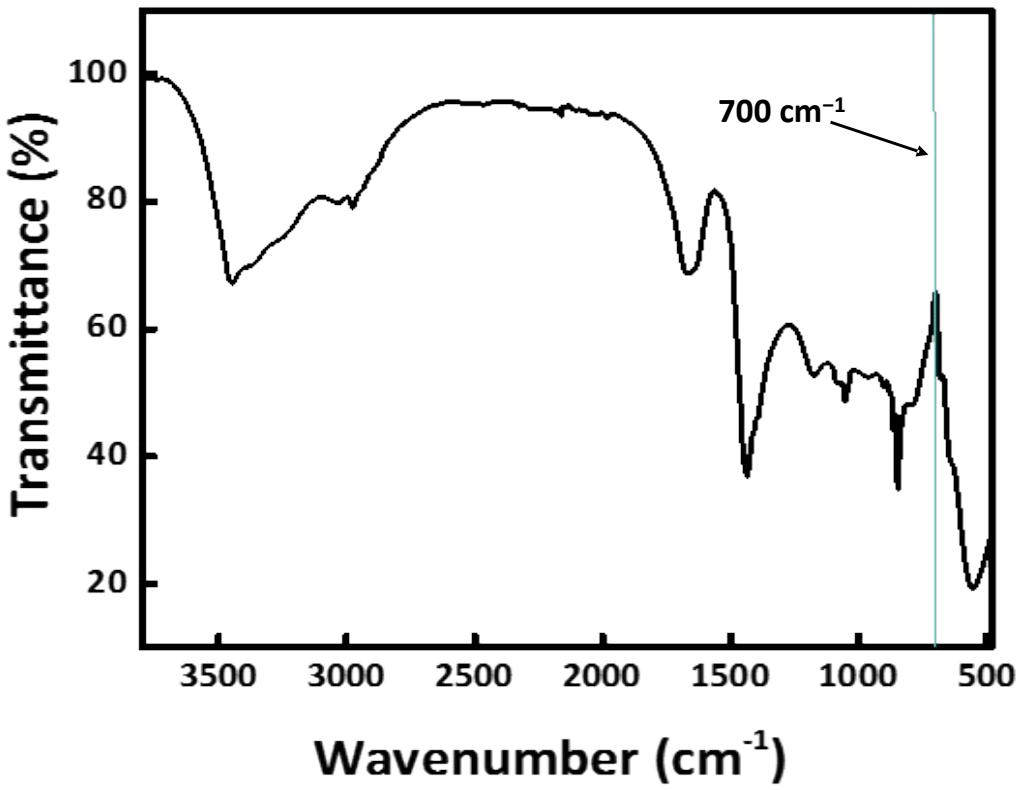

Fig. S3 FT-IR spectrum of the PDDA-CDs@NaCl in water. The arrow indicates the disappeared peak corresponding to the C–Cl stretching vibration.

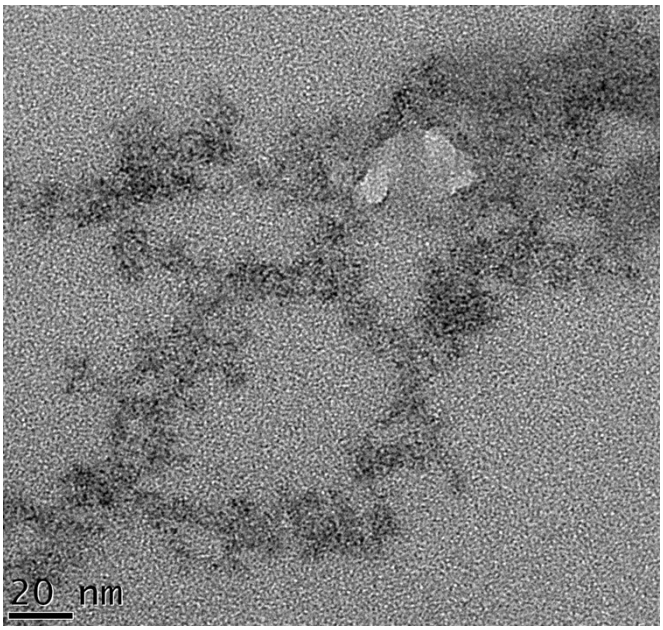

Fig. S4 TEM images of the PDDA-CDs@NaCl in water.

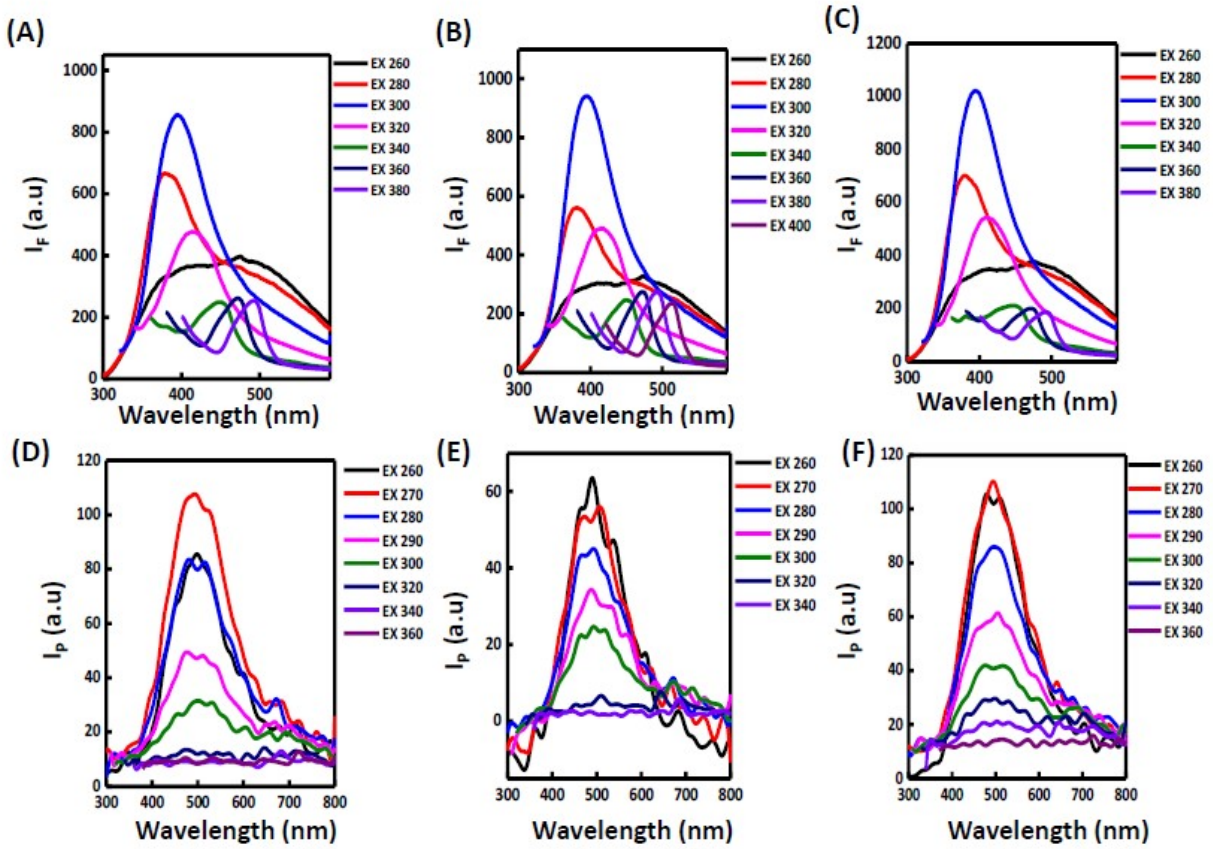

Fig. S5 (A, B, C) Fluorescence and (D, E, F) phosphorescence spectra of the PDDA-CDs@NaCl in (A, D) methanol, (B, E) DMSO, and (C, F) DMF.

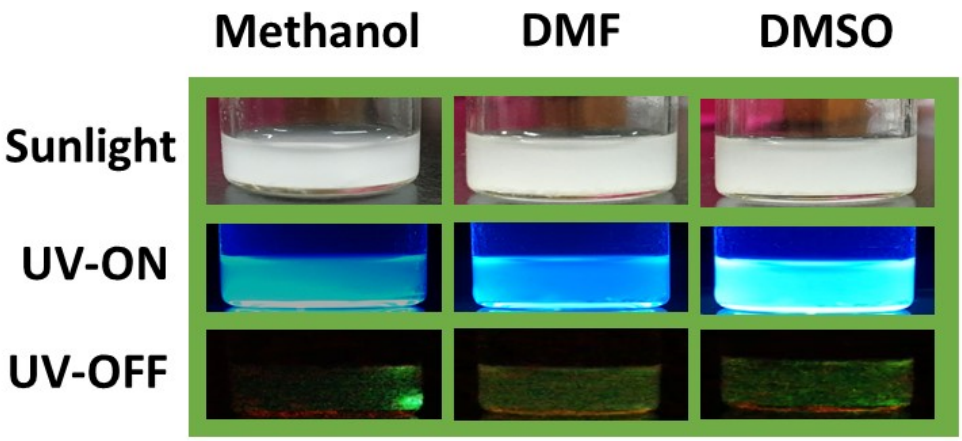

Fig. S6 Photographs representing PDDA-CDs@NaCl in Methanol, DMSO, and in DMF under sunlight, UV-ON and UV-OFF conditions.

Table S1. Comparison of the PDDA-CDs@NaCl with previously reported CD-based sensors for the determination of the water content in ethanol and methanol.

Probe[a]	Sensing methods	Solvents	Linear range (% v/v)	LOD (% v/v)	Reference
Tb^{3+}-MOF-encapsulated CDs	Fluorescence	Ethanol	2 to 30	0.28	3
1,3,6-trinitropyrene-related CDs	Fluorescence	Ethanol	0.3 to 4	0.399	4
Imidazole-related CDs	Fluorescence	Ethanol	5 to 20	0.1	5
o-phenylenediamine-based CDs	Fluorescence	Ethanol	5 to 20	0.1	6
Eu^{3+}-MOF-encapsulated CDs	Fluorescence	Ethanol	0.05 to 4	0.03	7
Lignin-derived CDs	Fluorescence	Ethanol	10 to 60	0.36	8
Bipyridine derivative–functionalized CDs	Fluorescence	Ethanol	~15 to 45	0.092	9
Dual-emission CDs	Fluorescence	Ethanol	0.3 to 5	0.13	10
Dual-emission CDs	Fluorescence	Methanol	0.3 to 2.4	0.07	10
Citrate- and carbamide-related CDs	Fluorescence	Ethanol	0.01 to 10	0.01	11
PDDA-CDs@NaCl	Phosphorescence	Methanol	0.125 to 12	0.04	This work
PDDA-CDs@NaCl	Phosphorescence	Ethanol	0.25 to1.25	0.08	This work

[a]MOF, metal organic frameworks; COF, covalent organic frameworks

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