Electronic Supplementary Information

Natural deep eutectic solvent assisted synthesis and applications of chiral carbon dots

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Experimental section

Materials

Choline chloride (ChCl) and urea were purchased from Adamas Reagent Co., Ltd. *Vine teas* were obtained from Zhangjiajie Nuokang Ecological Co., Ltd. The dialysis membrane tubing was obtained from Shanghai Qiaoxin Trading Co., Ltd. L-Arginine (L-Arg), L-Leucine (L-Leu), L-Tryptophan (L-Try), D-/L-Glutamate (D-/L-Glu), L-Valine (L-Val), L-Phenylalanine (L-Phe), D-/L-Methionine (D-/L-Met), L-Isoleucine (L-Iso), L-Proline (L-Pro) and glycerin were procured from Beijing Solarbio science□technology co., Ltd. D-Leucine (D-Leu), D-Tryptophan (D-Try), D-/L-Lysine (D-/L-Lys), D-Threonine (D-Thr), D-/L-Valine (D-/L-Val), D-Phenylalanine (D-Phe), D-(-)-fructose and tetrabutylammonium chloride (TBAC) were obtained from Shanghai Xianding Biological Technology Co., Ltd. L-Threonine (L-Thr) and L-Phenylalanine (L-Phe) were obtained from Chengdu Kelong Chemical Co., Ltd. D-Arginine (D-Arg) and D-/L- Histidine (D-/L-His) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. D_2O were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. All reagents were of analytical grade and deionized water was used for prepare all aqueous solutions.

Characterization

The surface morphologies and the sizes of the synthesized chiral carbon dots (CCDs) were characterized on a high-resolution transmission electron microscope (JEOL Ltd, JEM 2100F) and an atomic force microscope (AFM) (MFP-3D-BIO, Oxford-instruments, USA). The elemental analysis of the obtained materials was observed on an energy dispersive spectrometer (EDS) (Horiba, EX-250). Fourier transform infrared (FT-IR) spectra were measured on an IR Affinity-1S FT-IR spectrophotometer (Shimadzu, Japan). The X-ray diffraction (XRD) patterns were conducted on a Bruker D8 advance X-ray diffractometer (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) examined by the Thermo Fischer, ESCALAB Xi+ were used to analyze the surface electronic states. The Nuclear Magnetic Resonance (NMR) analysis of NADES was performed in D_2O on an Agilent DD2 400-MR spectrometer (Agilent Technologies, USA). The Raman spectra of CCDs were examined on LabRAM HR Evolution (Horiba Scientific). Circular dichroism (CD) spectral measurements were performed on an

automatic recording spectrophotometer (CHIRASCAN, Applied Photophysics, UK) in a 1mm cell at 298 K. The synchronous fluorescence and three dimensional (3D) fluorescence experiments and the fluorescence lifetimes were measured with an Edinburg Instruments FLS1000 spectrofluorometer (UK) and fluorescence spectrometer (RF-6000, Shimadzu, Japan), respectively. The optical fluorescence spectra were detected on a fluorescence spectrometer (RF-5301PC, Shimadzu) and the UV-visible spectra were obtained on the Shimadzu UV-2600 spectrometer.

Determination of quantum yield (QY) of CCDs

The QY of the CCDs was acquired with quinine sulfate in 0.1 M H_2SO_4 (QY = 54%) as the standard fluorophore. The calculation of QY follows the following formula:

$$Q = Q_S \times (F/F_S) \times (A_S/A) \times (n/n_S)$$

Where Q and Q_S are the QY of CCDs and standard solution, respectively. A and A_S show the absorbance of CCDs and quinine sulfate, respectively, while F and F_S are the fluorescence intensity of CCDs and quinine sulfate. The n is the refractive index.

Pretreatment of actual samples

Urine and human serum samples were obtained from ourselves (healthy people) and were treated according to the literature[1, 2]. 1.0 mL urine samples or serum samples were mixed with an equal volume of acetonitrile and centrifuged at 12,000 rpm for 10 min. The clear supernatant was filtered through a 0.22 μm filter. Two different brands of energy drinks and milk samples were purchased from a local supermarket (Chongqing, China). Before use, the energy drinks were centrifuged at 8000 rpm for 5 min and then the supernatant was filtered through a 0. 22 μm filters [3]. 2 g of milk sample was weighted into 10 mL of trichloroacetic acid/methanol (2:8, v/v), and then stirred for 5 min. After centrifugation (10000 rpm for 10 min), the supernatant was filtered with a 0.22 μm filter to remove lipids. Sodium hydroxide was used to adjust the pH of the treated sample to 7.0 [4, 5]. And all the obtained filtrate were concentrated at 50 °C in the vacuum oven and diluted with deionized water before use.

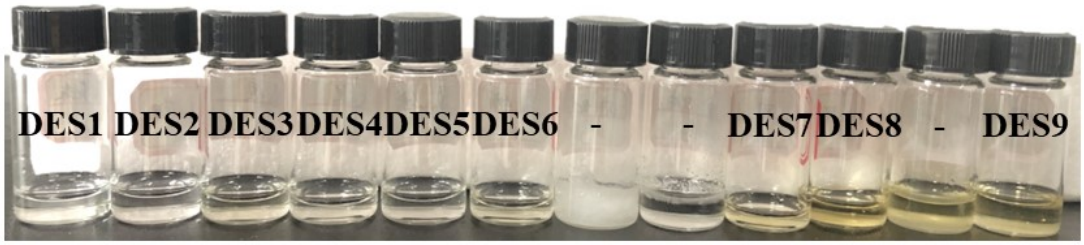

Fig. S1 Picture of different DESs

(DES1-9 represent different DESs, the composition of which is described in detail in **Table S1,** and - means that the mixture of HBA and HBD failed to synthesize liquid DES)

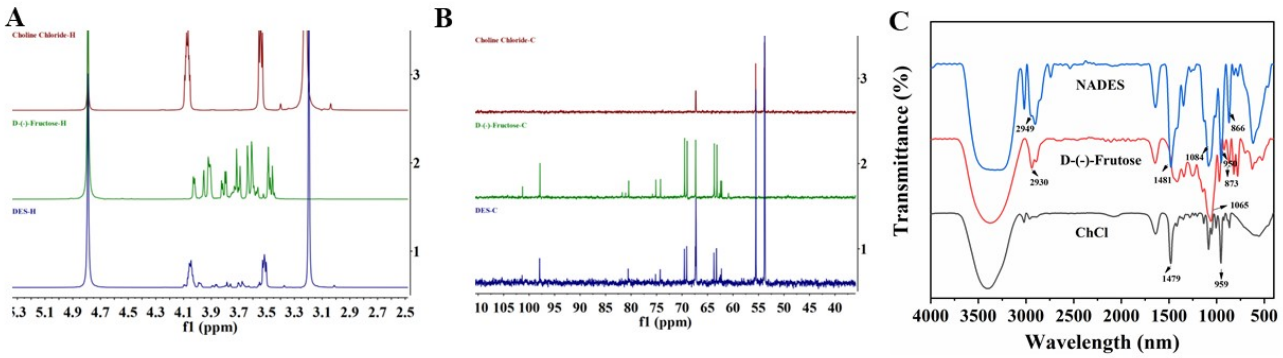

Fig. S2 NMR (A, B) and FT-IR (C) spectra of DESs raw materials, DESs, and CCDs.

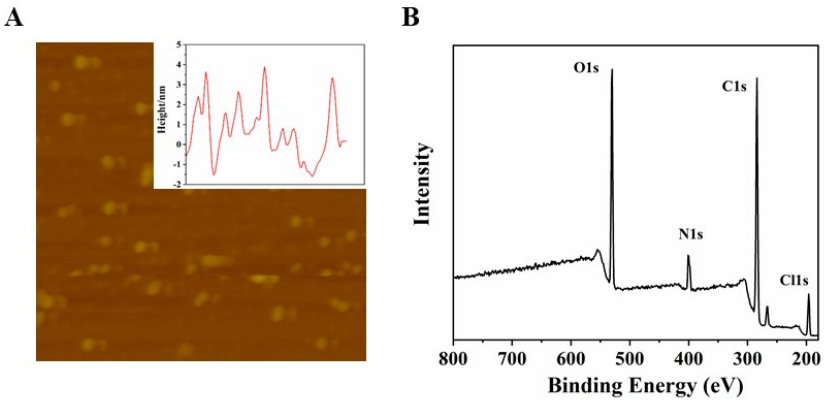

Fig. S3 A. AFM image of CCDs. The inset shows the particle size distribution of CCDs; B. XPS full spectrum of CCDs.

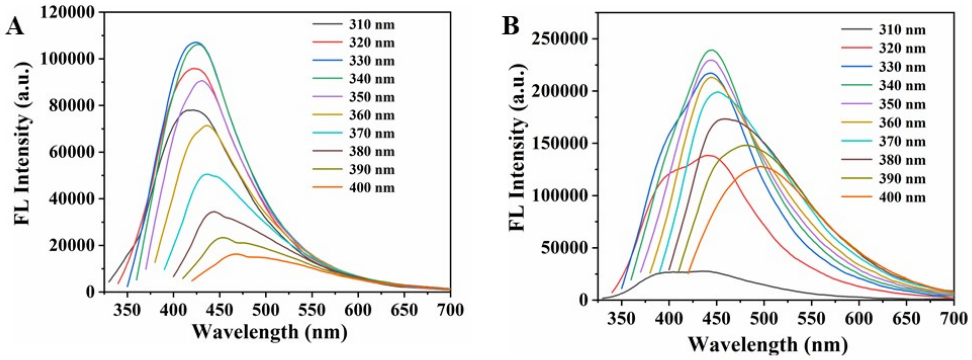

Fig. S4 Excitation-dependent emission spectra of CDs (A) and CCDs (B).

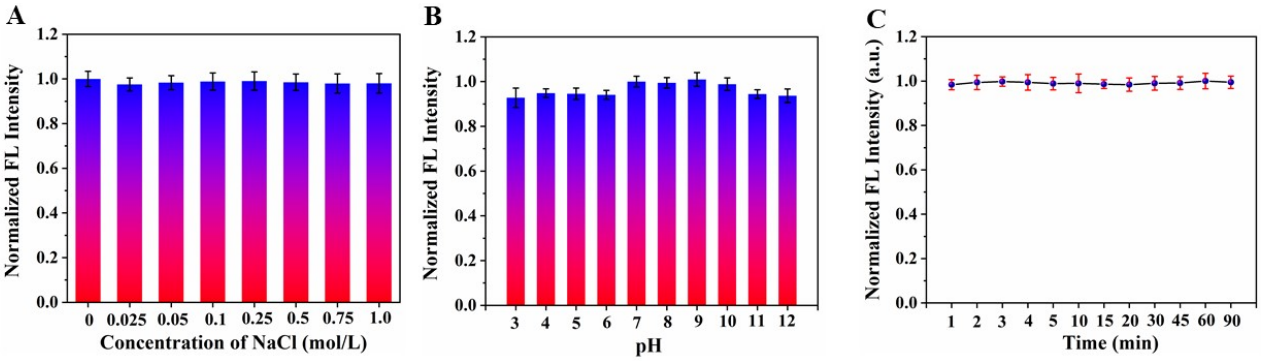

Fig. S5 Effect of concentration of NaCl and pH value on the fluorescence intensity of CCDs aqueous solution (A, B). C. The stability of CCDs.

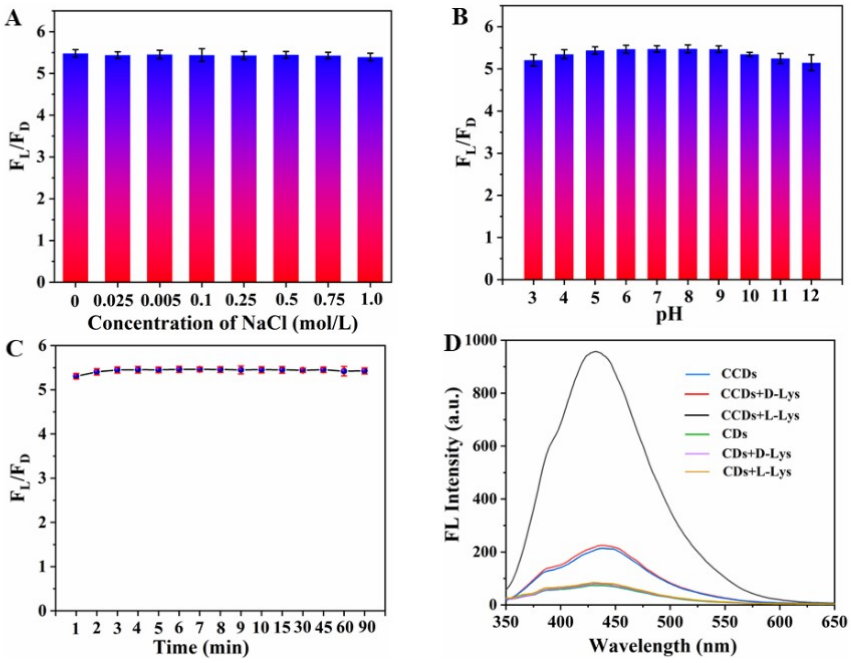

Fig. S6 Effect of concentration of NaCl (A), pH value (B), and incubation time (C) on CCDs to Lys enantiomers. D. The fluorescence spectra change of CDs and CCDs with Lys enantiomers.

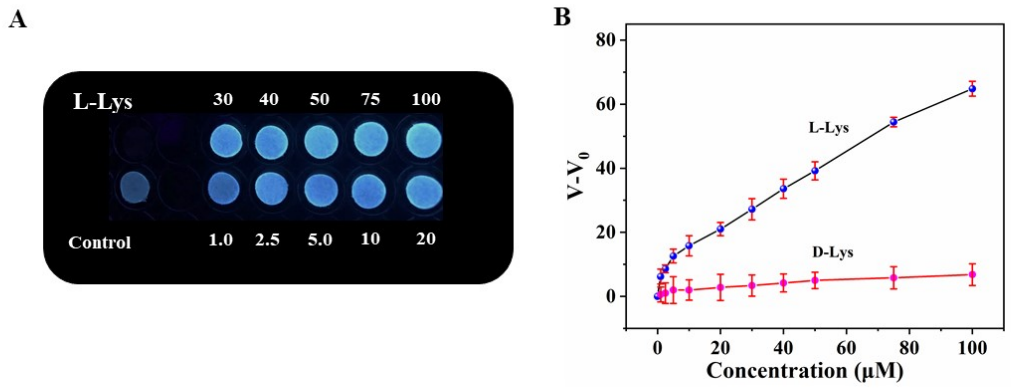

Fig. S7 A. The color change of CCDs embedded nano-papers as a function of L-Lys concentration. B. Plot of value change $V-V_0$ vs Lys concentration.

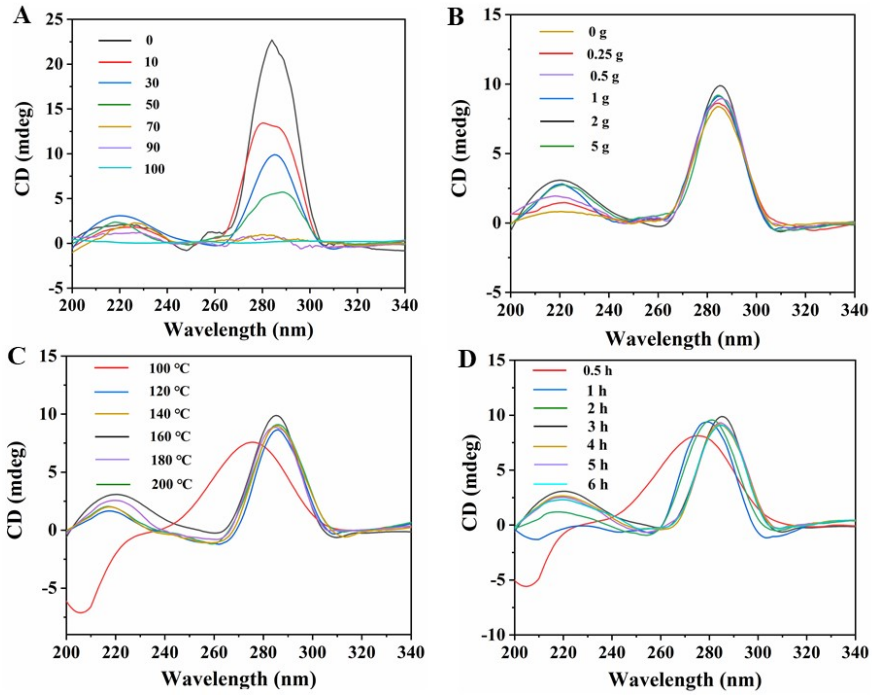

Fig. S8 CD spectra of CCDs under different synthesis conditions. A. The water content of the solvent. B. Dosage of *vine tea*. C. Reaction temperature. D. Reaction time.

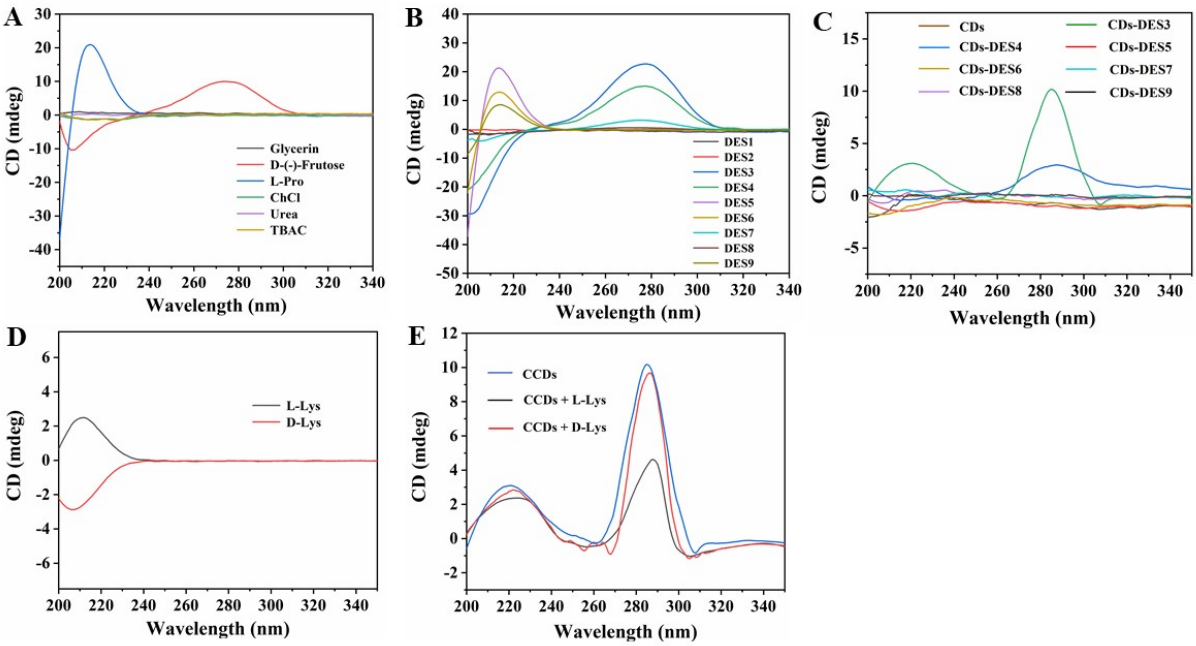

Fig. S9 CD spectra of raw materials of DESs (A), DESs (B), CCDs (C), Lys enantiomers (D). E. CD spectra of CCDs in the presence of Lys enantiomers.

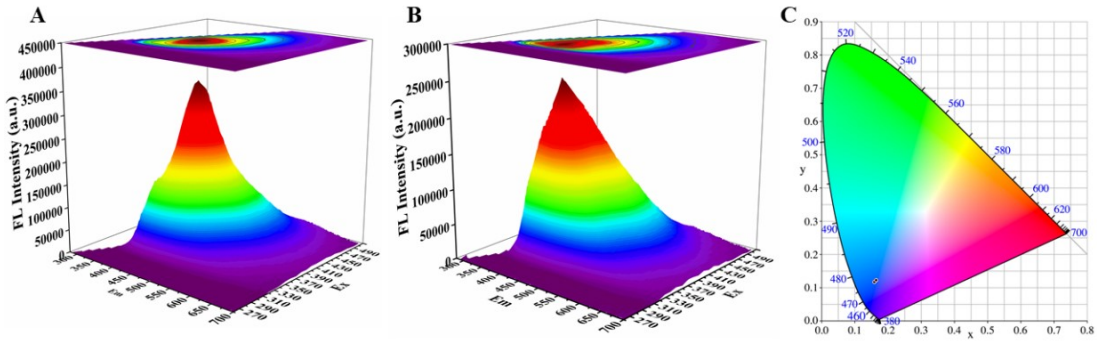

Fig. S10 3D fluorescent emission spectra of CCDs+L-Lys (A) and CCDs+D-Lys (B). C. Image of CIE of CCDs, CCDs+L-Lys, and CCDs+D-Lys.

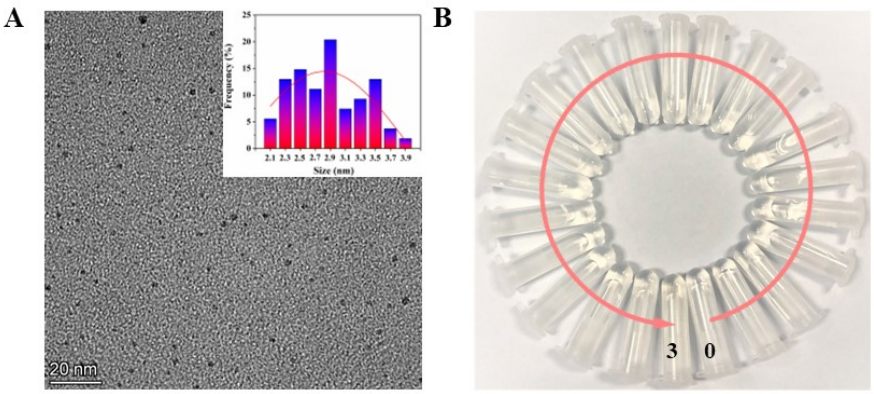

Fig. S11 A. HRTEM image of CCDs-L-Lys. The inset shows the particle size distribution of CCDs-L-Lys. B. The picture of the CCDs solution with the different concentration of L-Lys (0-3 mM).

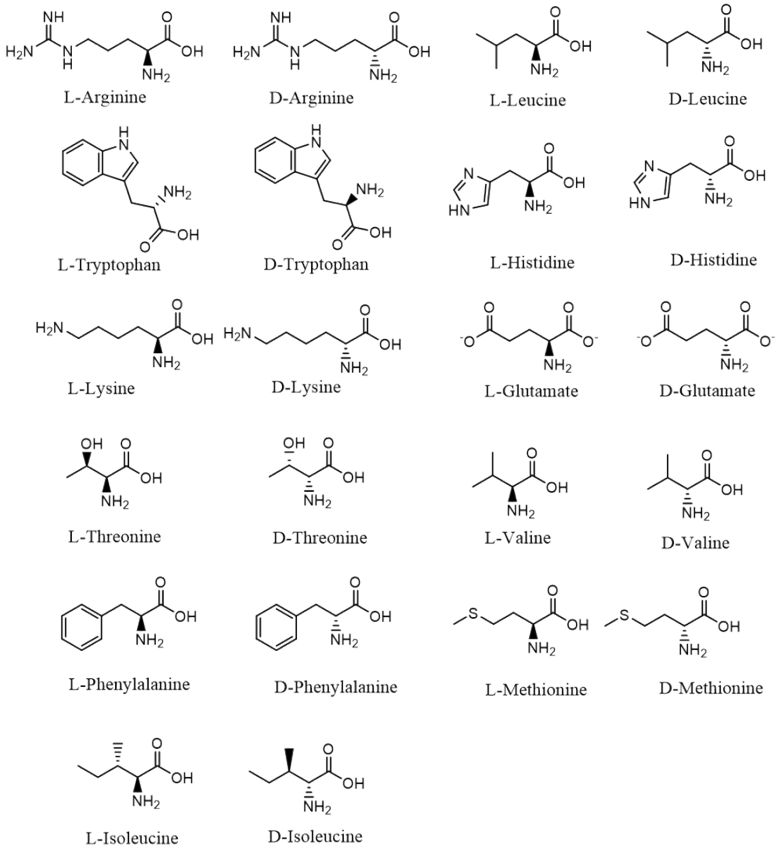

Fig. S12 The structures of amino acids.

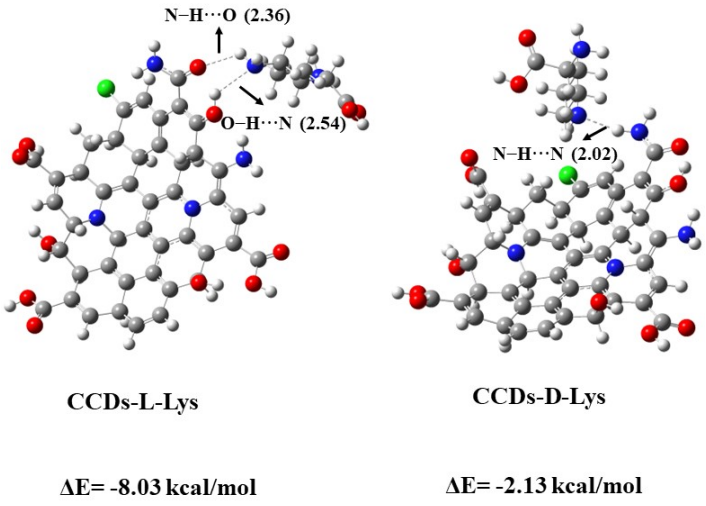

Fig. S13 Computational analysis for the interaction between CCDs and Lys enantiomers through DFT analysis at B3LYP/6-311+g (d, p) level. The geometrical structures of the CCDs-L-Lys and CCDs-D-Lys (the black dotted lines represent hydrogen bonds, and the numbers indicate the distance of the hydrogen bonds (Å)).

Table S1 The chirality of CCDs with different DESs.

HBA	HBD	Mole ratio	Abbreviation	CD (mdeg)	CD of CDs (mdeg)
Choline chloride (ChCl)	Urea	1:2	DES1	-	-
	Glycerin	1:3	DES2	-	-
	D-(-)-fructose	2:1	DES3	-29.41, 23.11	3.08, 9.92
	D-(-)-fructose	3:1	DES4	-19.28, 15.30	-0.51, 2.98
	L-proline	4:1	DES5	21.42	-1.54
	L-proline	6:1	DES6	12.72	-1.89
Tetrabutylammonium chloride (TBAC)	Urea	1:2	-	-	-
	Glycerin	1:3	-	-	-
	D-(-)-fructose	2:1	DES7	-4.41, 3.27	0.62
	D-(-)-fructose	3:1	DES8	-2.21, 1.01	0.64
	L-proline	4:1	-	-	-
	L-proline	6:1	DES9	8.77	-2.02

- means that the mixture of HBA and HBD failed to synthesize liquid DES or DES has no chirality.

Table S2 The chirality of CCDs under different preparation conditions.

Number	Water content (%)	Amount of *vine tea* (g)	Reaction temperature (°C)	Reaction time (h)	CD of CDs (mdeg)
1	0	2	160	3	1.89, 22.74

2	10	2	160	3	2.07, 13.41
3	30	2	160	3	3.08, 9.92
4	50	2	160	3	2.42, 5.76
5	70	2	160	3	2.23, 0.93
6	90	2	160	3	1.09, 0.54
7	100	2	160	3	-
8	30	0.25	160	3	1.54, 8.67
9	30	0.5	160	3	1.98, 8.99
10	30	1	160	3	2.84, 9.21
11	30	5	160	3	2.76, 9.18
12	30	2	100	3	-7.22, 7.69
13	30	2	120	3	1.70, 8.71
14	30	2	140	3	2.02, 8.99
15	30	2	180	3	2.58, 8.90
16	30	2	200	3	2.63, 8.92
17	30	2	160	0.5	-5.66, 8.12
18	30	2	160	1	-1.44, 9.29
19	30	2	160	2	1.23, 9.60
20	30	2	160	4	2.71, 9.30
21	30	2	160	5	2.42, 9.28
22	30	2	160	6	2.33, 9.13
23	30	0	160	3	0.74, 8.37
24	0	0	160	3	0.56, 20.55

- means that CDs has no chirality.

Table S3 The element contents of CCDs and CDs.

Element	CDs	CCDs
C	92.74	64.88
N	2.66	8.21
O	4.60	23.05
Cl	-	3.86

Table S4 $V\text{-}V_0$ values in the eight different circular areas of a piece of CCDs micro-sensing paper after being immersed in the L-Lys aqueous solution (50 μM).

Circular	2 min		5 min		7 min		10 min		15 min		20 min		30 min	
areas	$V\text{-}V_0$	SD	$V\text{-}V_0$	SD	$V\text{-}V_0$	SD	$V\text{-}V_0$	SD	$V\text{-}V_0$	SD	$V\text{-}V_0$	SD	$V\text{-}V_0$	SD
1	5		14		21		41		40		42		42	
2	10		15		23		42		43		42		40	
3	9		14		24		43		43		40		37	
4	8	2.03	11	2.05	23	1.89	41	1.41	41	1.58	39	1.85	39	1.96
5	6		12		19		40		39		37		37	
6	11		16		24		39		40		38		38	
7	9		10		23		39		39		39		37	
8	7		14		20		40		41		38		41	

Table S5 Comparison of different materials for L-Lys detection.

Materials	Method	Raw materials	Preparation time	LOD	Sample	Reference
Titanium oxide nanoparticles/multi-wall carbon nanotube composite electrodes	Electrochemical method	Multi-wall carbon nanotube, titanium oxide nanoparticles	20 min	4 μM	Commercial syrup, urine	[6]
Molecular-driven gold nanorods assembly	Colorimetric	$HAuCl_4 \cdot 4H_2O$, $NaBH_4$, Cetyltrimethylammonium bromide, $AgNO_3$, L-ascorbic acid, Au seed solution	60 h	1.6 μM	Cookies, milk, bread	[7]

Copper nanoclusters (CuNCs)	Fluorescent sensing	$CuSO_4$, Chicken ovalbumin, NaOH	4 h	5.5 μM	Urine	[1]
Gold nanoclusters (AuNCs)	Fluorescent sensing	$HAuCl_4$, Papaya juice, NaOH	3 min	6 μM	Urine	[8]
Coordination complex	Fluorescent sensing	4′-(1H-1,2,4-triazole-1-yl)-[1,1′-biphenyl]-4-carboxylic acid, $Zn(NO_3)_2 \cdot 2H_2O$, DMF	24 h	5.6 μM	-	[9]
A polydiacetylenes-based colorimetric and fluorescent probe	Fluorescent sensing	10,12-pentacosadiynoic acid,1-aminopyrene, DMSO	36.5 h	10.26 μM	-	[10]
Chiral carbon quantum dots (modified by L-Cysteine)	Fluorescence enantiomer recognition	Citric acid, ethylenediamine, L-cysteine	12.5 h	0.3 μM	-	[11]
Chiral carbon dots (synthesized from citric acid and L-aspartic acid)	Fluorescence enantiomer recognition	Citric acid, L-Asp, NaOH	4 h	3.34 μM	-	[12]
Chiral carbon dots (synthesized from nature deep eutectic solvent and *vine tea*)	Fluorescence enantiomer recognition	Nature deep eutectic solvent, *Vine tea*	5 h	10 nM	Urine, plasma, energy drinks, and milk	This work

Table S6 The absolute fluorescence lifetime of CCDs in different systems (ns).

□	**CCDs**	**CCD_S-L-Lys**	**CCD_S-D-Lys**
Fluorescence lifetime	2.26	3.73	2.41

Reference:

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