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One-step hydrothermal synthesis of chiral carbon dots with high asymmetric catalytic activity for enantioselective direct aldol reaction

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S1 Experimental

S1.1 Materials

Citric acid monohydrate (CA), cyclohexanone and dimethyl sulfoxide were purchased from Sinopharm, P-nitrobenzaldehyde were from Macklin, and D-proline (D-Pro) were obtained from Sigma-Aldrich. All the reagents were used without any further purification. A cellulose dialysis bag with 500-1000 Da was purchased from Sangon Biotech (Shanghai) Co., Ltd.

S1.2 Preparation of chiral CQDs

Chiral CQDs were synthesized through hydrothermal reaction of CA and D-Pro illustrated in Scheme 1. Typically, CA (0.6600 g, 3 mmol) and D-Pro (0.6600 g, 6 mmol) were sufficiently dissolved into 10 mL ultrapure water by ultrasonic for 20 min. Then the mixed solution was transferred into a 30 mL Teflon-sealed autoclave and hydrothermally heated at 180 ^{o}C for a certain time. When the reaction was completed, the Teflon-sealed autoclave cooled naturally in the air and the yellow solution was acquired. The yellow solution was condensed by rotating evaporation. After the condensed solution were dialyzed against a 500–1000 Dalton (g/mol) cellulose dialysis membrane for 3 day and freeze-dried, light yellow chiral CQDs were obtained. The chiral CQDs were named CA-D_P-CQDs. Effect of hydrothermal time on the structure and property of CA-D_P-CQDs was studied. Without special statement, hydrothermal time was referred to 4 h.

For comparison, CQDs were also similarly prepared using single CA or D-Pro as raw materials. The time of hydrothermal synthesis were set as 4 h. The obtained

carbon dots were named CA-CQDs with single CA as raw materials and D_P-CQD with single D-Pro as raw materials, respectively.

S1.3 Characterization

High resolution transmission electron microscopy (HRTEM) images were obtained on a FEI/Philips Tecnai G2 F20 field transmission electron microscope. Fourier transform infrared (FT-IR) spectra were collected on a FT-IR spectrometer (Spectrum One, Perkin Elmer). The circular dichroism (CD) spectra were recorded on a JASCO J-815 spectropolarimeter. Absolute photoluminescence quantum yield were measured on Quantaurus-QY 97 established by Hamamatsu. Proton nuclear magnetic resonance (^{1}H NMR) were recorded on a Bruker Avance 400 (400 MHz) spectrometer. High-resolution mass spectrometry (HRMS) was performed on a Bruker LC-MS-MAXIS (Electrospray Ionization, ESI). Enantiomer ratios were determined by High Performance Liquid Chromatography (HPLC, Hanbon Sci.&Tech.) equipped with a chiralpak AD-H column.

S1.4 Direct aldol reaction

To a suspension of *p*-nitrobenzaldehyde (75.5 mg, 0.5 mmol) and cyclohexanone (500 uL, 4.8 mmol) in 1.5 ml DMSO, a solution of CA-D_P-CQDs (Total CQDs with 0.6600 g of D-Pro as raw materials) in water (500 uL) was added and stirred for certain time. Then the product was extracted with AcOEt and the CA-D_P-CQDs remained in water layer. The organic layer was dried over Na_2SO_4 and the crude was purified by column chromatography (AcOEt/n-Hexane, 1:3). The enantiomeric excess (ee) was determined by HPLC: Chiralpak AD-H, hexanes:2-propanol of 80:20, flow

rate of 1 mL/min. The reusability of CA-D_P-CQDs was tested by adding the reactants to the water layer extracted from the organic layer.

The products included anti (major) and syn (minor) isomer of 2-hydroxy (4-nitrophenyl) methyl cyclohexanone. HPLC as shown in Fig. S1: anti：t_S=13.5 min**,** t_R=17.3 min**;** syn**:** t_S =11.6 min**,** t_R=12.5 min. ^{1}H NMR (400 MHz, $CDCl_3$) as shown in Fig. S2: 8.17 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 5.42 (s, *J* = 8.5 Hz,1H), 4.88 (d, *J* = 8.3 Hz, 1H), 4.09 (s, 1H), 2.74–2.21 (m, 2H), 2.17–1.96 (m, 1H), 1.91–1.43 (m, 4H), 1.40–1.12 (m, 1H). HRMS (ESI) as shown in Fig. S3**.** : calculated for $C_{13}H_{15}O_4N\ Na^+$: 272.0894, found: 273.0930.

S2 Photoluminescence analysis

Photoluminescence (PL) study was carried out with Fluorescence Spectrophotometer (F-7100, France JY company). Fig. S4a shows that, with the increase of the excitation wavelength from 310 nm to 400 nm, the emission peak of CA-D_P-CQDs undergoes a red shift. The luminescent intensity reaches a maximum at emission wavelength of 420 nm when excitation wavelength is adjusted to 340 nm (Fig. S4b). The PL spectra indicate that CA-D_P-CQDs has the property of fluorescence.

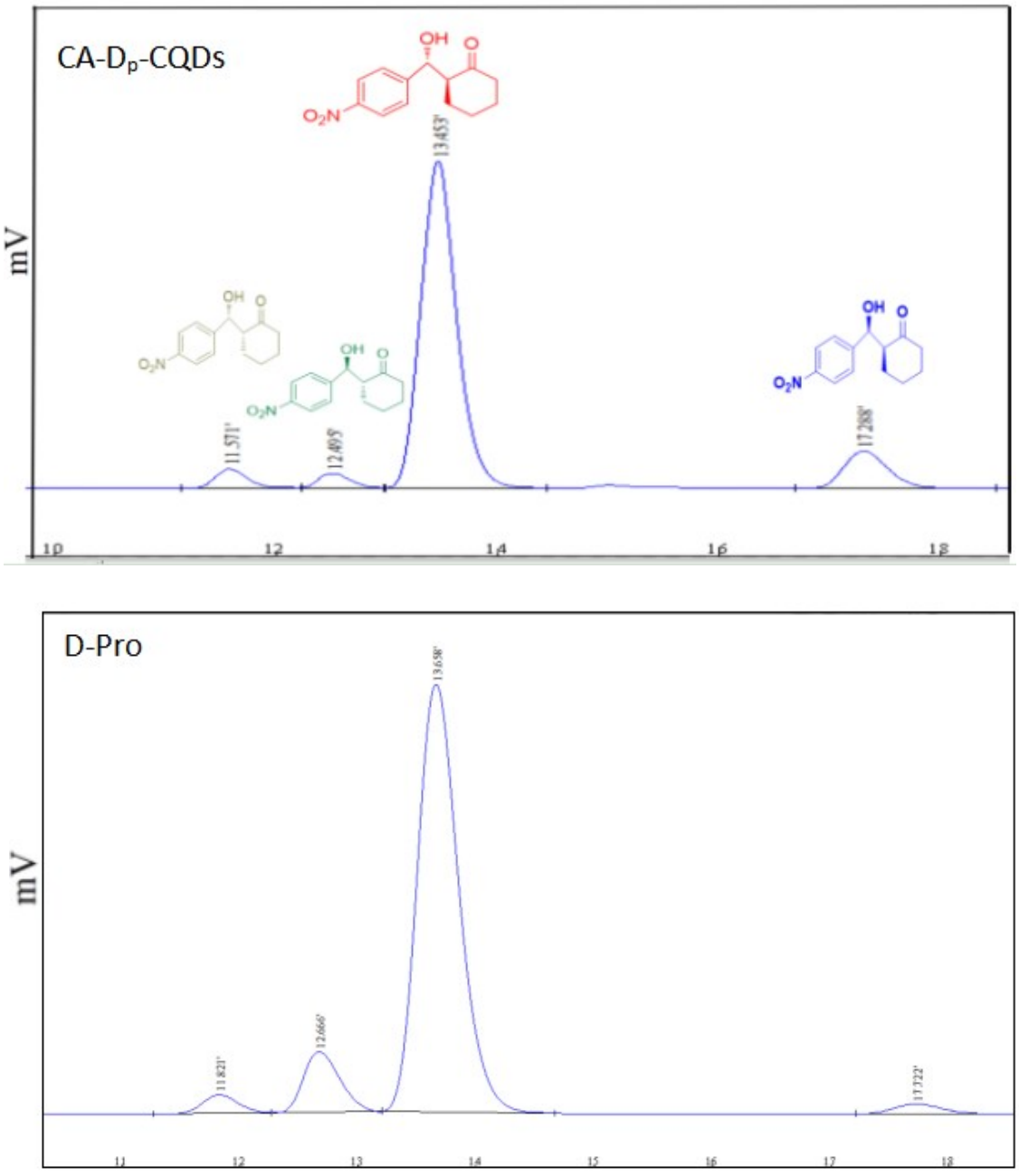

Fig. S1 HPLC of products versus retention time by CA-D_P-CQDs and D-Pro.

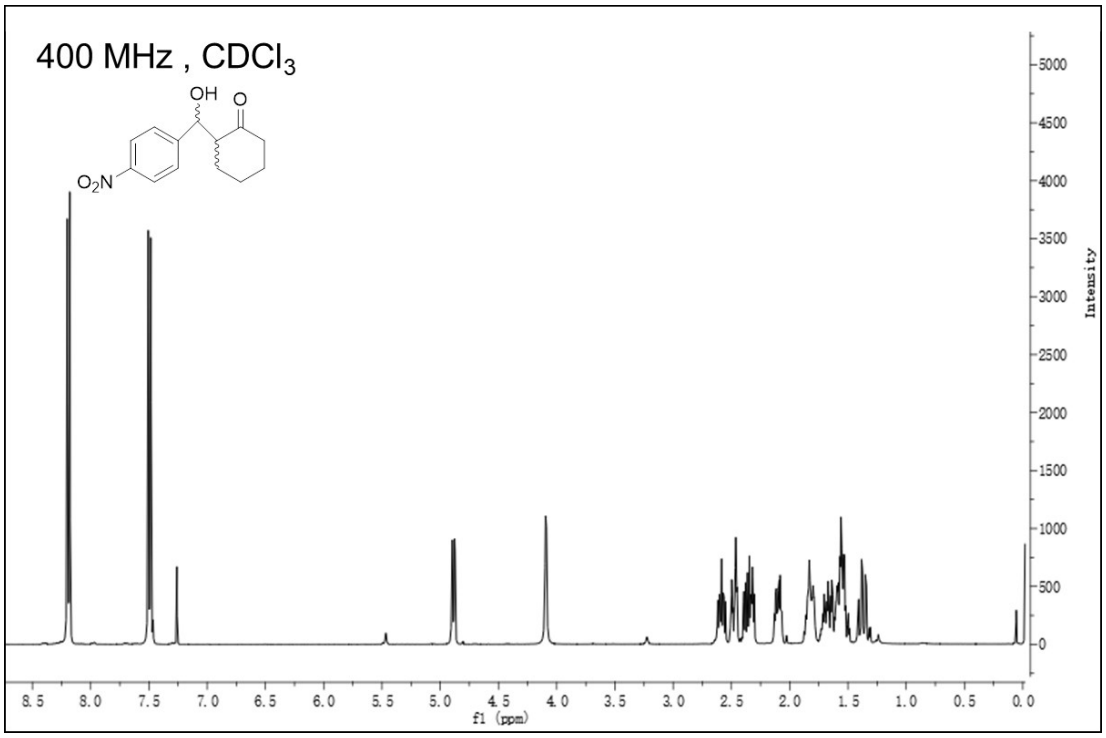

Fig. S2 ^{1}H NMR (400Hz) of 2-hydroxy (4-nitrophenyl) methyl cyclohexanone.

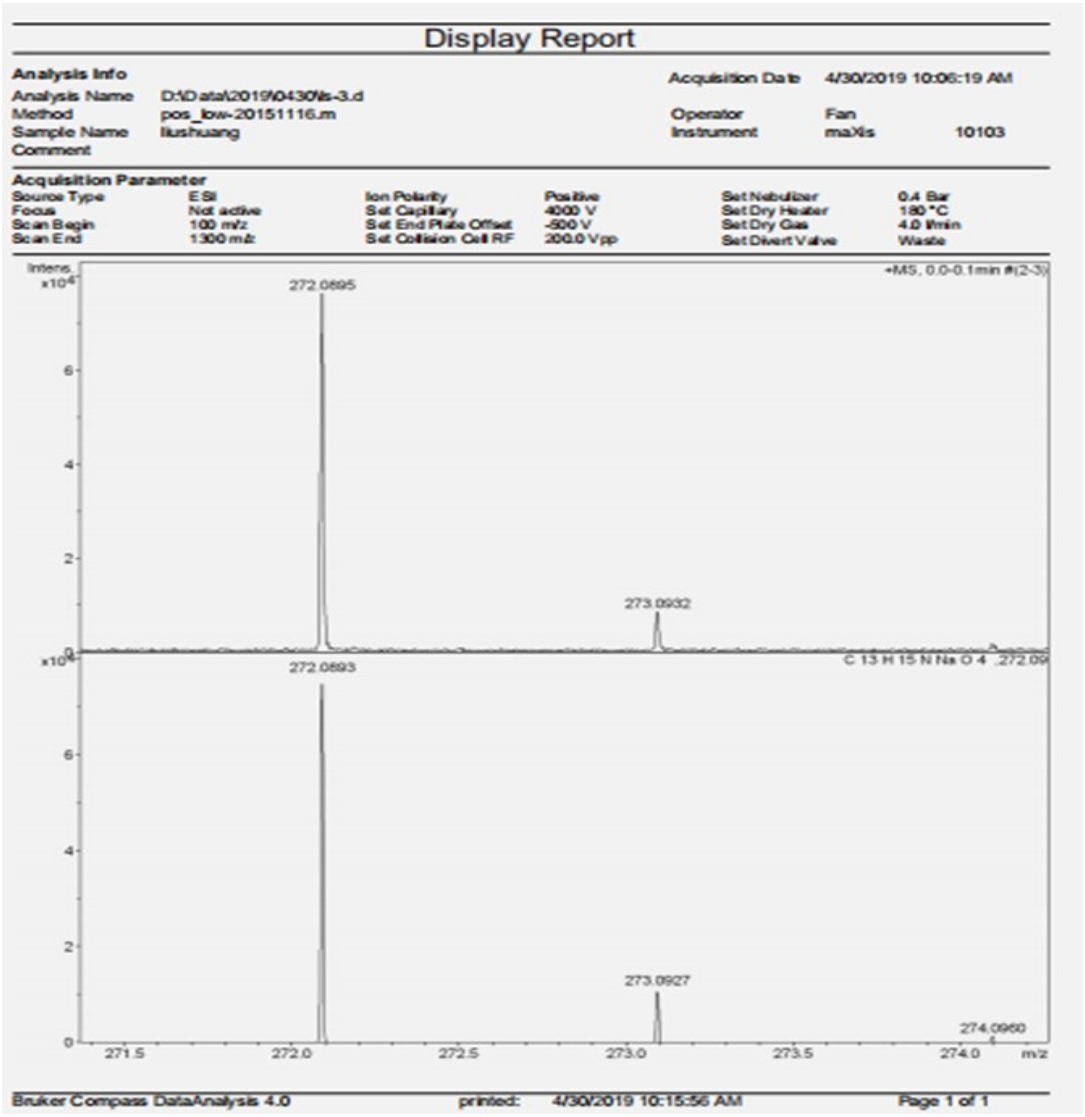

Fig. S3 HRMS (ESI) data of 2-hydroxy (4-nitrophenyl) methyl cyclohexanone.

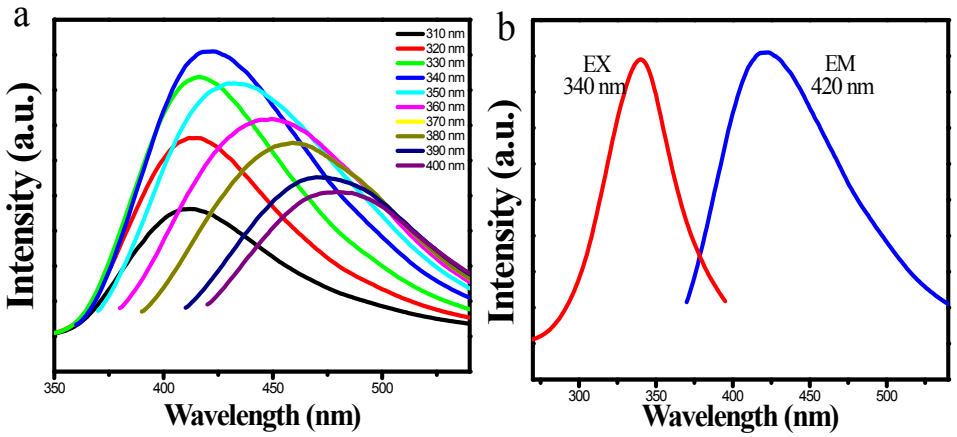

Fig. S4 PL spectra of CA-D$_P$-CQDs. (a) PL emission spectra with excitation wavelength from 310 nm to 400 nm in 10 nm increment and (b) PL excitation /emission spectra at 340 nm and 420 nm, respectively.