Electronic Supplementary Information (ESI)

Room-temperature preparation of chiral covalent organic framework for selective adsorption of amino acid enantiomers

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Supporting Methods

Chemicals and Materials. All the used chemicals were at least analytical grade. Ultrapure water was obtained from Wahaha group co. Ltd (Hangzhou, China). 4,4',4''-(1,3,5-Triazine-2,4,6-triyl)trianiline (Tz) and 1,4-dihydroxyterephthalaldehyde (Da) were bought from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. (Jilin, China). N,N-dimethylacetamide (DMAC), o-dichlorobenzene (o-DCB), n-butul alcohol (n-BuOH), D-tryptophan (D-Trp), L-tryptophan (L-Trp), D-histidine (D-His), L-histidine (L-His), D-aspartic acid (D-Asp), L-aspartic acid (L-Asp), D-serine (D-Ser), L-serine (L-Ser) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). N, N-dimethylformamide (DMF), ethanol, tetrahydrofuran (THF), dichloromethane (DCM), dichloroethane (EDC), acetic acid, toluidine blue O (TBO), were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). D-camphanic acid (D-cam) was purchased from Shanghai Yuanye Biotechnology Co. Ltd.

Instruments and Characterization. The powder X-ray diffraction spectrometry (PXRD) data were measured on a D2 PHASER diffractometer (Bruker, German) using Cu Kα radiation. The Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Nicolet IR IS10 spectrometer (Nicolet, USA) with pure KBr pellets. N₂ adsorption experiments were performed on Autosorb-IQ (Quantachrome, USA). Zeta potential determination was carried out on a Malvern Nano-ZSE (Worcester shire, UK). SEM images were recorded on a SU1510 (Hitachi, Japan) scanning electron microscope. TEM images were obtained on a JEM-2100 transmission electron microscope (JEOL,
Japan) with an accelerating voltage of 200 kV. A QTRAP 4500 LC-MS (AB SCIEX, USA) with ACQUITY UPLC HSS C18 (2.1 x 150 mm, 1.8 µm) was used for determination of amino acids.

**Preparation of D-camphor acid chloride.** D-cam (260.3 mg, 1.3 mmol) was dissolved in thionyl chloride (20 ml) with 4 drops of DMF. The mixture was stirred under reflux for 4 h. After most of the thionyl chloride solvent was removed by atmospheric distillation, 5 ml of dichloroethane was added. The rotary evaporation was then applied to further distillation of the excess solvent to obtain a pale-yellow solid D-camphor acid chloride (D-cam-COCl).

![Chemical structure of D-camphor acid chloride](image)

**Room temperature synthesis of TzDa.** Tz (31.9 mg, 0.09 mmol), Da (21.6 mg, 0.13 mmol), o-dichlorobenzene (o-DCB, 1 mL), ethanol (1 mL), and 6 M aqueous acetic acid (0.2 mL) were mixed in a centrifuge tube (15 ml). After 10 min of sonication, the centrifuge tube was sealed and left undisturbed at room temperature for 3 days. The resulting dark red product was collected via centrifugation and washed with tetrahydrofuran (THF) and dichloromethane (DCM), and dried in a vacuum oven at 50 °C.

**Synthesis of CTzDa.** CTzDa was prepared through an esterification reaction between D-cam-COCl and TzDa. Briefly, 0.13 mmol of TzDa and 1.3 mmol D-cam-COCl, 400 µL of triethylamine were mixed and dispersed in 40 mL anhydrous tetrahydrofuran. The reaction was carried out for 12 h at room temperature. The obtained product was
washed with water, THF, and dichlorobenzene, dried in a vacuum oven at 50 °C.

The grafting content of D-camphoric acid. According to the typical previous works1, 2, CTzDa was dispersed in TBO solution (0.5 mM) at pH 10 and shaken for 2 h at 37 °C. After rinsed several times with deionized water to remove non-complexed dye, the CTzDa was rinsed in a 50 wt% acetic acid solution for four times. The concentration of TBO in desorbed acetic acid solutions were measured at 633 nm by UV-vis.

Adsorption and desorption experiments. In adsorption experiment, 5 mg of CTzDa was mixed with 10 mL D-amino acid or L-amino acid aqueous solution with certain initial concentration. After adsorption equilibrium, the CTzDa was isolated via filtration on 0.22 μm membrane while the supernatant was measured by LC-MS.

In desorption experiment, the amino acids was desorbed from CTzDa with elution solvent by ultrasonication for 5 min. The regenerated CTzDa was then collected and dried under vacuum at 50 °C.

Molecular docking studies. The structures of CTzDa and AAs were energetically minimized and recorded in PDB format using Discovery Studio 4.5. The AutoDockTools version 1.5.6 (ADT) was used to further optimize structure of COF and amino acids with adding Gasteiger charges, assigning polar hydrogen atoms and setting up rotatable bonds. Simultaneously, the pdbqt format files were generated using ADT. The molecular docking was carried out in suitable grid box size along the x, y, and z axes with a grid spacing of 1.000 Å. Finally, the nine binding models obtained were further analyzed to find the most suitable binding model in each case. The model with minimum energy and maximum number of poses clustered was selected.
The ADVina output results were used for the calculation of binding free energy change \( (\Delta G_{\text{bind}}) \). The binding constants \( (K_{\text{bind}}) \) was further obtained using \( K_{\text{bind}} = \exp(\Delta G_{\text{bind}}/RT) \) at 25 °C. The ADVina output PDBQT files transform PDB files with pymol, Finally this PDB files analysis interaction force with Maestro.

**Adsorption studies**

**Adsorption isotherms fitting.** The main feature of the the Langmuir model is monolayer sorption onto the homogenous surface with a finite number of adsorption sites. The equation can be expressed as follows:

\[
q_e = \frac{C_e q_m b}{C_e b + 1}
\]  

(1)

Where \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of amino acids in solution, \( q_e \) (mg g\(^{-1}\)) is the equilibrium adsorption capacity, \( q_m \) (mg g\(^{-1}\)) is the maximum adsorption capacity, \( b \) (L mg\(^{-1}\)) is the Langmuir adsorption constant.

The main feature of the Freundlich isotherm is the non-uniform adsorption heat dissemination on uneven surface. The equation can be expressed as follows:

\[
\log q_e = \log K + \frac{1}{n} \log C_e
\]  

(2)

Where \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of amino acids in solution, \( q_e \) (mg g\(^{-1}\)) is the equilibrium adsorption capacity, \( K \) and \( n \) are the Freundlich adsorption constants, indicating the adsorption capacity and the adsorption intensity.

**Thermodynamic parameters.** That is free energy change \( (\Delta G, \text{kJ mol}^{-1}) \), enthalpy change \( (\Delta H, \text{kJ mol}^{-1}) \), and entropy change \( (\Delta S, \text{J mol}^{-1} \text{K}^{-1}) \). They were calculated by the following equations:
\[ K_0 = \frac{q_e}{C_e} \]  

(3)

\[ \Delta G = -RT \ln K_0 \]  

(4)

\[ \ln K_0 = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \]  

(5)

\( q_e \) (mg g\(^{-1}\)) is the equilibrium adsorption capacity, \( C_e \) (mg L\(^{-1}\)) is the equalized concentration, \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( K_0 \) is distribution coefficient (L g\(^{-1}\)), \( T \) is the absolute temperature in Kelvin. In the equations above, \( K_0 \) was obtained from intercept by plotting \( \ln \left( \frac{q_e}{C_e} \right) \) versus \( q_e \). \( \Delta H \) and \( \Delta S \) were then obtained from the slope and intercept by plotting \( \ln K_0 \) versus \( 1/T \).

**Adsorption kinetics fitting.** Pseudo-first-order kinetics equation is given as follows:

\[ \ln \left( q_e - q_t \right) = \ln q_e - k_1 t \]  

(6)

The pseudo-second-order kinetics equation is shown as follows:

\[ \frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \]  

(7)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

(8)

where \( q_t \) is the adsorption capacity (mg g\(^{-1}\)) at a predetermined time \( t \) (min) and \( q_e \) is the equilibrium adsorption capacity (mg g\(^{-1}\)). \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant of pseudo-first-order and pseudo-second-order adsorption, respectively.
Supporting Figures

**Fig. S1** (a) PXRD patterns and (b) FT-IR spectra of TzDa synthesized under different conditions at room temperature.

**Fig. S2** FTIR spectra of D-cam-chloride and D-cam.

**Fig. S3** $^1$H NMR of D-cam-chloride.
Fig. S4 FTIR spectra of Tz, Da and TzDa.

Fig. S5 FTIR spectra of CTzDa.

Fig. S6 PXRD patterns of TzDa.
Fig. S7 PXRD pattern of CTzDa.

Fig. S8 PXRD patterns of CTzDa after immersing in various solvents.

Fig. S9 TGA curves of TzDa and CTzDa.
Fig. S10 TEM images: (a) TzDa; (b) CTzDa.

Fig. S11 SEM images: (a) TzDa; (b) CTzDa.

Fig. S12 $N_2$ adsorption-desorption isotherms and the pore size distribution: (a, b) TzDa; (c, d) CTzDa.
Fig. S13 Effect of dosage on the adsorption capacity at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser.

Fig. S14 Effect of pH on the adsorption efficiency at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser.
Fig. S15 Time-dependent adsorption on TzDa at 293 K: (a) Trp (50 mg L\(^{-1}\)); (b) His (20 mg L\(^{-1}\)); (c) Asp (20 mg L\(^{-1}\)); (d) Ser (20 mg L\(^{-1}\)).

Fig. S16 Time-dependent adsorption of AAs at different initial concentrations on CTzDa at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser .
Fig. S17 Plots of pseudo-first-order kinetics for the adsorption of AAs at different initial concentrations on CTzDa at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser.

Fig. S18 Plots of pseudo-second-order kinetics for the adsorption of AAs at different initial concentrations on CTzDa at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser.

Fig. S19 Adsorption isotherms on CTzDa in the range of 293–323 K: (a) Trp; (b) His; (c) Asp; (d) Ser.
Fig. S20 Effect of eluents on the desorption efficiency for AAs from CTzDa: (a) Trp; (b) His; (c) Asp; (d) Ser.

Fig. S21 Recyclable adsorption on CTzDa: (a) Trp; (b) His; (c) Asp; (d) Ser.

Fig. S22 (a) XRD patterns and (b) FT-IR spectra of CTzDa after 5 times reuse.
**Fig. S23** Plots of $\ln \left( \frac{q_e}{C_e} \right)$ against $q_e$ at various temperatures for AAs.

**Fig. S24** Plots of $\ln K_0$ against $1/T$ for AAs.
Supporting Tables

Table S1 Zeta data of TzDa and CTzDa.

| COFs  | Zeta potential (mV) |
|-------|---------------------|
| TzDa  | -8.2                |
| CTzDa | -47.3               |

Table S2 Nitrogen adsorption-desorption data of TzDa and CTzDa.

|         | BET surface area [m$^2$ g$^{-1}$] | Pore volume [cm$^3$ g$^{-1}$] | Pore size [nm] |
|---------|-----------------------------------|-------------------------------|----------------|
| TzDa    | 1380                              | 1.22                          | 3.2            |
| CTzDa   | 403                               | 0.46                          | 1.8            |
|        | C₀  | qₑ(exp)  | qₑ(cal)  | k₂          | R²      |
|--------|-----|----------|----------|-------------|---------|
|        | [mg L⁻¹] | [mg g⁻¹] | [mg g⁻¹] | [g mg⁻¹ min⁻¹] |
| D-Trp 15 | 10.3 ± 0.2 | 10.4 ± 0.1 | 0.0867 | 0.9998 |
|        25 | 14.7 ± 0.3 | 14.7 ± 0.2 | 0.0689 | 0.9997 |
|        50 | 21.7 ± 0.3 | 21.7 ± 0.2 | 0.0659 | 0.9998 |
| L-Trp 15 | 17.6 ± 0.5 | 17.8 ± 0.2 | 0.0448 | 0.9996 |
|        25 | 24.6 ± 0.4 | 24.8 ± 0.2 | 0.0336 | 0.9998 |
|        50 | 30.5 ± 0.2 | 30.6 ± 0.3 | 0.0371 | 0.9997 |
| D-His 10 | 5.47 ± 0.03 | 5.47 ± 0.02 | 0.780  | 0.9999 |
|        20 | 13.7 ± 0.1 | 13.7 ± 0.2 | 0.548  | 0.9996 |
|        50 | 14.7 ± 0.2 | 14.8 ± 0.1 | 0.131  | 0.9998 |
| L-His 10 | 11.0 ± 0.1 | 11.0 ± 0.1 | 0.291  | 0.9998 |
|        20 | 21.9 ± 0.3 | 21.8 ± 0.3 | 0.149  | 0.9995 |
|        50 | 24.7 ± 0.2 | 24.9 ± 0.1 | 0.0541 | 0.9999 |
| D-Asp 10 | 4.93 ± 0.09 | 4.95 ± 0.08 | 0.414  | 0.9991 |
|        20 | 9.40 ± 0.09 | 9.45 ± 0.07 | 0.232  | 0.9998 |
|        50 | 9.86 ± 0.16 | 9.95 ± 0.17 | 0.111  | 0.9992 |
| L-Asp 10 | 9.02 ± 0.11 | 8.99 ± 0.14 | 0.161  | 0.9993 |
|        20 | 19.2 ± 0.1 | 19.2 ± 0.1 | 0.151  | 0.9999 |
|        50 | 20.9 ± 0.1 | 20.9 ± 0.1 | 0.0856 | 0.9999 |
| D-Ser 10 | 4.71 ± 0.09 | 4.75 ± 0.06 | 0.472  | 0.9995 |
|        20 | 6.56 ± 0.11 | 6.61 ± 0.10 | 0.279  | 0.9993 |
|        50 | 7.71 ± 0.17 | 7.84 ± 0.14 | 0.0867 | 0.9990 |
| L-Ser 10 | 6.51 ± 0.02 | 6.53 ± 0.04 | 0.165  | 0.9999 |
|        20 | 11.1 ± 0.1 | 11.1 ± 0.1 | 0.144  | 0.9999 |
|        50 | 13.6 ± 0.2 | 13.7 ± 0.2 | 0.0674 | 0.9995 |
| Analyte | T (K) | $q_m$ (mg g$^{-1}$) | b (L mg$^{-1}$) | $R^2$ | $K_F$ | $1/n$ | $R^2$ |
|--------|------|------------------|----------------|-------|-------|-------|-------|
| D-Trp  | 293  | 29.1 ± 0.8       | 0.0757 ± 0.0018 | 0.998 | 12.3 ± 1.1 | 0.155 ± 0.018 | 0.944 |
|        | 303  | 24.1 ± 0.2       | 0.0530 ± 0.0040 | 0.990 | 8.20 ± 0.96 | 0.191 ± 0.023 | 0.946 |
|        | 313  | 20.0 ± 0.1       | 0.0512 ± 0.0026 | 0.997 | 4.59 ± 0.63 | 0.266 ± 0.027 | 0.972 |
|        | 323  | 17.9 ± 0.7       | 0.0351 ± 0.0021 | 0.990 | 1.92 ± 0.13 | 0.418 ± 0.022 | 0.970 |
| L-Trp  | 293  | 44.3 ± 0.7       | 0.1210 ± 0.0050 | 0.995 | 13.4 ± 1.0  | 0.241 ± 0.020 | 0.966 |
|        | 303  | 41.7 ± 0.7       | 0.0857 ± 0.0034 | 0.997 | 9.05 ± 1.20 | 0.327 ± 0.040 | 0.919 |
|        | 313  | 37.0 ± 0.7       | 0.0614 ± 0.0033 | 0.993 | 8.93 ± 0.88 | 0.264 ± 0.024 | 0.958 |
|        | 323  | 31.9 ± 0.4       | 0.0520 ± 0.0048 | 0.988 | 9.02 ± 2.20 | 0.230 ± 0.049 | 0.860 |
| D-His  | 293  | 17.1 ± 0.3       | 0.0608 ± 0.0039 | 0.998 | 2.66 ± 0.37 | 0.377 ± 0.033 | 0.986 |
|        | 303  | 14.5 ± 0.3       | 0.0583 ± 0.0028 | 0.998 | 2.32 ± 0.46 | 0.380 ± 0.053 | 0.949 |
|        | 313  | 13.8 ± 0.3       | 0.0532 ± 0.0038 | 0.997 | 1.90 ± 0.39 | 0.418 ± 0.053 | 0.966 |
|        | 323  | 11.6 ± 0.3       | 0.0525 ± 0.0019 | 0.998 | 1.31 ± 0.12 | 0.468 ± 0.042 | 0.950 |
| L-His  | 293  | 30.8 ± 1.4       | 0.0806 ± 0.0063 | 0.995 | 4.94 ± 1.10 | 0.417 ± 0.094 | 0.812 |
|        | 303  | 28.9 ± 0.4       | 0.0795 ± 0.0026 | 0.999 | 5.83 ± 0.97 | 0.336 ± 0.050 | 0.926 |
|        | 313  | 25.5 ± 0.6       | 0.0693 ± 0.0028 | 0.998 | 3.81 ± 0.60 | 0.416 ± 0.057 | 0.919 |
|        | 323  | 21.0 ± 0.9       | 0.0557 ± 0.0051 | 0.992 | 3.21 ± 0.76 | 0.390 ± 0.073 | 0.883 |
| D-Asp  | 293  | 14.5 ± 2.4       | 0.0764 ± 0.0300 | 0.864 | 2.80 ± 0.10 | 0.354 ± 0.110 | 0.745 |
|        | 303  | 11.5 ± 1.4       | 0.0639 ± 0.0210 | 0.914 | 1.98 ± 0.39 | 0.368 ± 0.053 | 0.945 |
|        | 313  | 10.2 ± 1.0       | 0.0485 ± 0.0190 | 0.920 | 1.55 ± 0.17 | 0.375 ± 0.025 | 0.992 |
|        | 323  | 9.28 ± 1.40      | 0.0474 ± 0.0210 | 0.857 | 1.41 ± 0.17 | 0.380 ± 0.030 | 0.984 |
| L-Asp  | 293  | 28.4 ± 0.5       | 0.0806 ± 0.0024 | 0.999 | 4.69 ± 0.71 | 0.387 ± 0.057 | 0.896 |
|        | 303  | 25.5 ± 1.0       | 0.0667 ± 0.0580 | 0.993 | 3.72 ± 0.45 | 0.412 ± 0.035 | 0.974 |
|        | 313  | 19.9 ± 0.8       | 0.0518 ± 0.0051 | 0.994 | 2.61 ± 0.44 | 0.420 ± 0.045 | 0.969 |
|        | 323  | 14.9 ± 0.7       | 0.0483 ± 0.0037 | 0.993 | 1.57 ± 0.23 | 0.471 ± 0.053 | 0.931 |
| D-Ser  | 293  | 11.1 ± 1.6       | 0.0629 ± 0.0200 | 0.849 | 2.28 ± 0.28 | 0.322 ± 0.038 | 0.946 |
|        | 303  | 10.6 ± 1.3       | 0.0597 ± 0.0200 | 0.888 | 2.17 ± 0.68 | 0.322 ± 0.086 | 0.817 |
|        | 313  | 9.97 ± 1.20      | 0.0591 ± 0.0150 | 0.913 | 1.89 ± 0.28 | 0.344 ± 0.051 | 0.912 |
|        | 323  | 9.54 ± 0.35      | 0.0588 ± 0.0046 | 0.994 | 1.44 ± 0.16 | 0.393 ± 0.033 | 0.973 |
| L-Ser  | 293  | 18.7 ± 0.1       | 0.0939 ± 0.0018 | 0.999 | 4.16 ± 0.45 | 0.309 ± 0.025 | 0.990 |
|        | 303  | 14.6 ± 0.3       | 0.0837 ± 0.0034 | 0.998 | 2.91 ± 0.31 | 0.337 ± 0.032 | 0.965 |
|        | 313  | 13.7 ± 0.2       | 0.0755 ± 0.0024 | 0.998 | 2.43 ± 0.07 | 0.353 ± 0.011 | 0.995 |
|        | 323  | 13.0 ± 0.4       | 0.0563 ± 0.0045 | 0.996 | 1.99 ± 0.52 | 0.384 ± 0.067 | 0.923 |
Table S5 Adsorption enantioselectivity of CTzDa for AAs

| Analyte   | $K_0^a$ (L g$^{-1}$) | Adsorption enantioselectivity$^b$ |
|-----------|----------------------|----------------------------------|
| L-Trp/D-Trp | 28.8/6.86            | 4.20                             |
| L-His/D-His  | 5.06/1.95            | 2.59                             |
| L-Asp/D-Asp  | 4.53/1.74            | 2.60                             |
| L-Ser/D-Ser   | 4.39/2.72            | 1.61                             |

$^a$ *Distribution coefficient.*

$^b$ Defined as the ratio of $K_0$ for L-AAs to that for D-AAs.
| Adsorbent                        | analyte | Adsorption Enantioselectivity | Ref.                               |
|---------------------------------|---------|-----------------------------|------------------------------------|
| Hyper-cross-linked chiral porous polymers | Trp     | 1.30                        | Micropor. Mesopor. Mat., 2020, 294, 109892 |
| L-histidine imprinted salicylic acid functionalized resin | His     | 1.95                        | React. Funct. Polym., 2018, 128, 104-113 |
| L-tryptophan imprinted microspheres | Trp     | 2.45                        | J. Colloid Interf. Sci., 2015, 445, 371-379 |
| Cross-linked chitosan/glyoxal molecularly imprinted resin | Asp     | 2.0                         | Biochem. Eng. J., 2010, 51, 140-146  |
| CTzDa                            | Trp     | 4.20                        | This work                          |
|                                  | His     | 2.59                        |                                    |
|                                  | Asp     | 2.60                        |                                    |
| Analyte | T (K) | lnK₀ | ΔG (kJ mol⁻¹) | ΔH (kJ mol⁻¹) | ΔS(J mol⁻¹ K⁻¹) |
|---------|-------|------|---------------|---------------|-----------------|
| D-Trp   | 293   | 1.93 | -4.69         | -39.87        | -119.3          |
|         | 303   | 1.58 | -3.99         |               |                 |
|         | 313   | 1.01 | -2.63         |               |                 |
|         | 323   | 0.423| -1.14         |               |                 |
|         | 333   | 0.358| -0.992        |               |                 |
| L-Trp   | 293   | 3.36 | -8.19         | -56.28        | -163.8          |
|         | 303   | 2.73 | -6.87         |               |                 |
|         | 313   | 1.89 | -4.93         |               |                 |
|         | 323   | 1.25 | -3.36         |               |                 |
|         | 333   | 0.476| -1.32         |               |                 |
| D-His   | 293   | 0.669| -1.63         | -15.16        | -46.43          |
|         | 303   | 0.418| -1.05         |               |                 |
|         | 313   | 0.183| -0.476        |               |                 |
|         | 323   | 0.109| -0.291        |               |                 |
| L-His   | 293   | 1.62 | -3.95         | -27.49        | -79.42          |
|         | 303   | 1.47 | -3.71         |               |                 |
|         | 313   | 1.14 | -2.96         |               |                 |
|         | 323   | 0.557| -1.50         |               |                 |
| D-Asp   | 293   | 0.555| -1.35         | -13.81        | -43.13          |
|         | 303   | 0.202| -0.510        |               |                 |
|         | 313   | 0.0765| -0.199       |               |                 |
|         | 323   | 0.0183| -0.0491      |               |                 |
| L-Asp   | 293   | 1.51 | -3.67         | -35.34        | -108.1          |
|         | 303   | 1.06 | -2.66         |               |                 |
|         | 313   | 0.496| -1.29         |               |                 |
|         | 323   | 0.200| -0.537        |               |                 |
| D-Ser   | 293   | 1.00 | -2.43         | -27.06        | 83.22           |
|         | 303   | 0.887| -2.23         |               |                 |
|         | 313   | 0.382| -0.995        |               |                 |
|         | 323   | 0.0146| -0.0392      |               |                 |
| L-Ser   | 293   | 1.48 | -3.61         | -31.75        | 95.84           |
|         | 303   | 1.04 | -2.62         |               |                 |
|         | 313   | 0.833| -2.17         |               |                 |
|         | 323   | 0.201| -0.538        |               |                 |
**Table S8** Bonding energy and adsorption equilibrium constant of D-AAs and L-AAs on CTzDa

| Analyte | BE (kcal mol\(^{-1}\)) |
|---------|---------------------|
| D-Trp   | -4.0                |
| L-Trp   | -4.4                |
| D-His   | -2.4                |
| L-His   | -2.7                |
| D-Asp   | -2.0                |
| L-Asp   | -2.1                |
| D-Ser   | -1.7                |
| L-Ser   | -1.9                |

**References**

1. E. T. Kang, K. L. Tan, K. Kato, Y. Uyama and Y. Ikada, *Macromolecules*, 1996, **29**, 6872-6879.
2. S. N. Zhang, Y. L. Zheng, H. D. An, B. Aguila, C. X. Yang, Y. Y. Dong, W. Xie, P. Cheng, Z. J. Zhang, Y. Chen and S. Q. Ma, *Angew. Chem. Int. Edit.*, 2018, **57**, 16754-16759.
3. E. Zor, H. Bingol, A. Ramanaviciene, A. Ramanavicius and M. Ersoz, *Analyst*, 2015, **140**, 313-321.
4. T. Wang, J. Wang, C. Zhang, Z. Yang, X. Dai, M. Cheng and X. Hou, *Analyst*, 2015, **140**, 5308-5316.