Electronic Supplementary Information (ESI)

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

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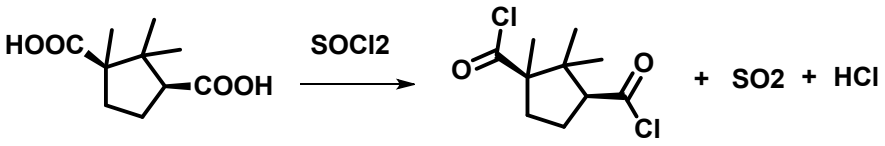
Supporting Methods

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. N_2 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).



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 works[1, 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 (ΔG_{bind}). The binding constants (K_{bind}) was further obtained using $K_{bind}=\exp(\Delta G_{bind}/RT)$ 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:

$$q_e = \frac{C_e q_m b}{C_e b + 1} \qquad (1)$$

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:

$$logq_e = logK + \frac{1}{n} logC_e \qquad (2)$$

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 (ΔG, kJ mol^{-1}), enthalpy change (ΔH, kJ mol^{-1}), and entropy change (ΔS, J mol^{-1} K^{-1}). They were calculated by the following equations:

$$K_0 = \frac{q_e}{C_e} \quad (3)$$

$$\Delta G = -RT\ln K_0 \quad (4)$$

$$\ln K_0 = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

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 (q_e/C_e) versus q_e. ΔH and ΔS 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:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

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

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

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

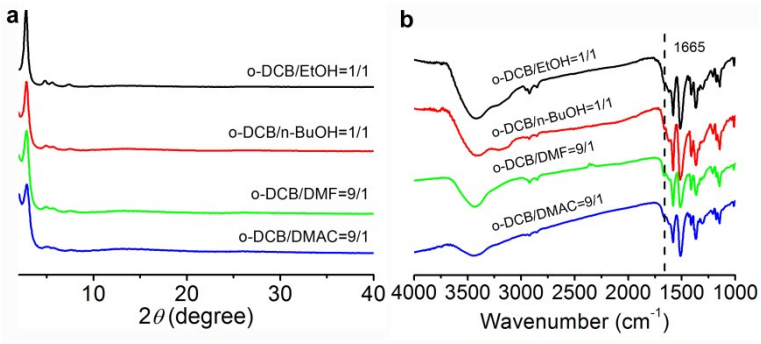


Fig. S1 (a) PXRD patterns and (b) FT-IR spectra of TzDa synthesized under different conditions at room temperature.

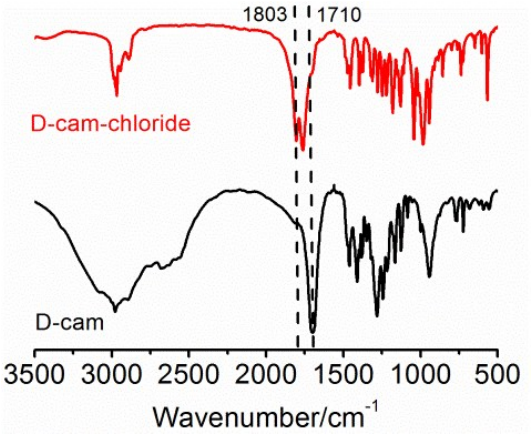


Fig. S2 FTIR spectra of D-cam-chloride and D-cam.

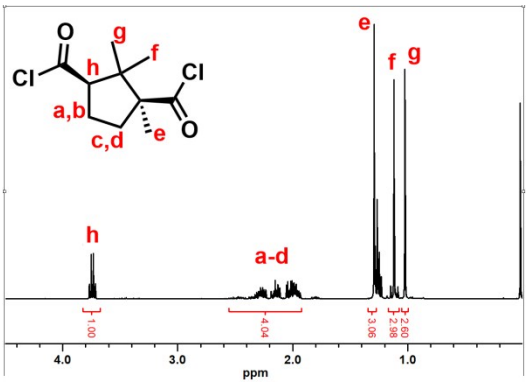


Fig. S3 ^{1}H NMR of D-cam-chloride.

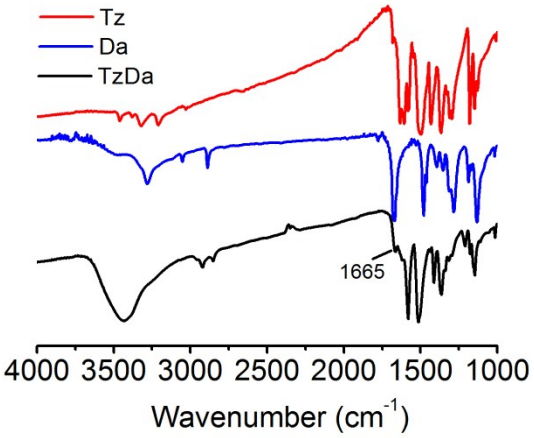


Fig. S4 FTIR spectra of Tz, Da and TzDa.

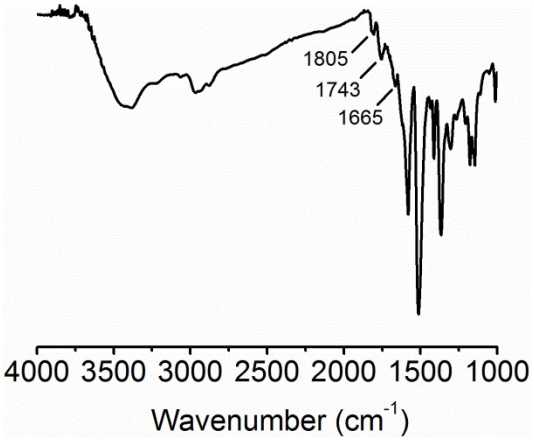


Fig. S5 FTIR spectra of CTzDa.

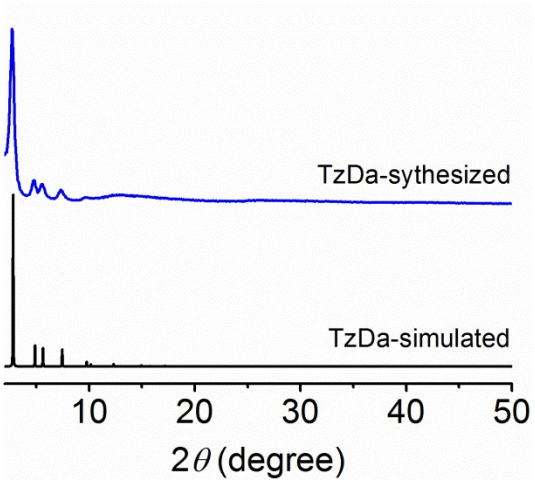


Fig. S6 PXRD patterns of TzDa.

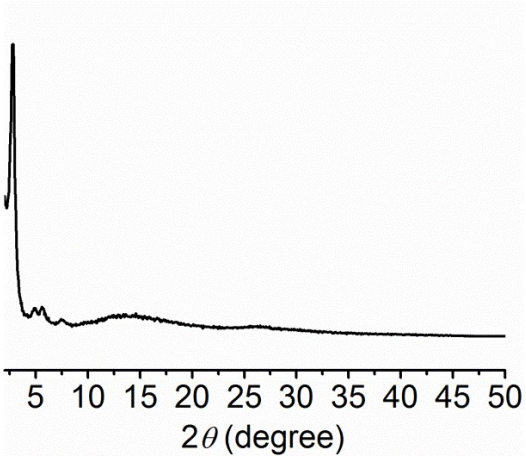


Fig. S7 PXRD pattern of CTzDa.

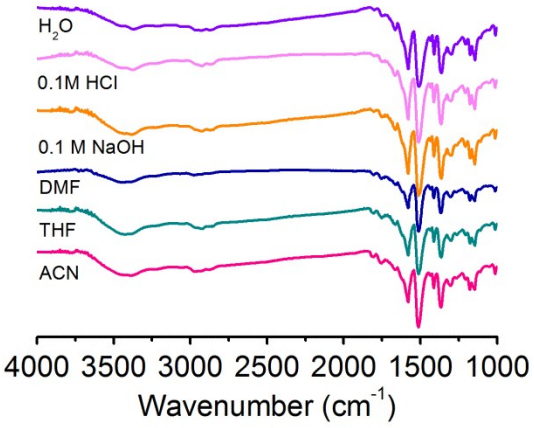


Fig. S8 PXRD patterns of CTzDa after immersing in various solvents.

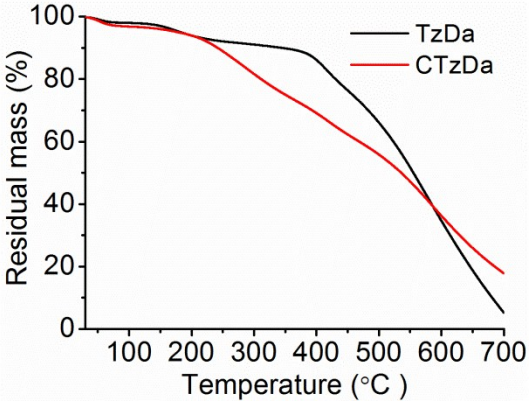


Fig. S9 TGA curves of TzDa and CTzDa.

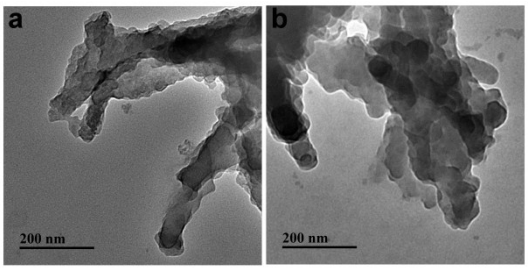


Fig. S10 TEM images: (a) TzDa; (b) CTzDa.

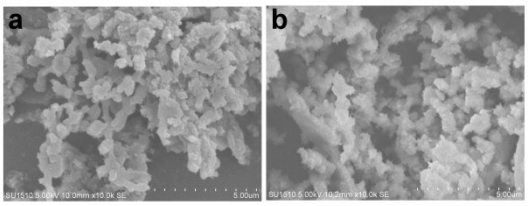


Fig. S11 SEM images: (a) TzDa; (b) CTzDa.

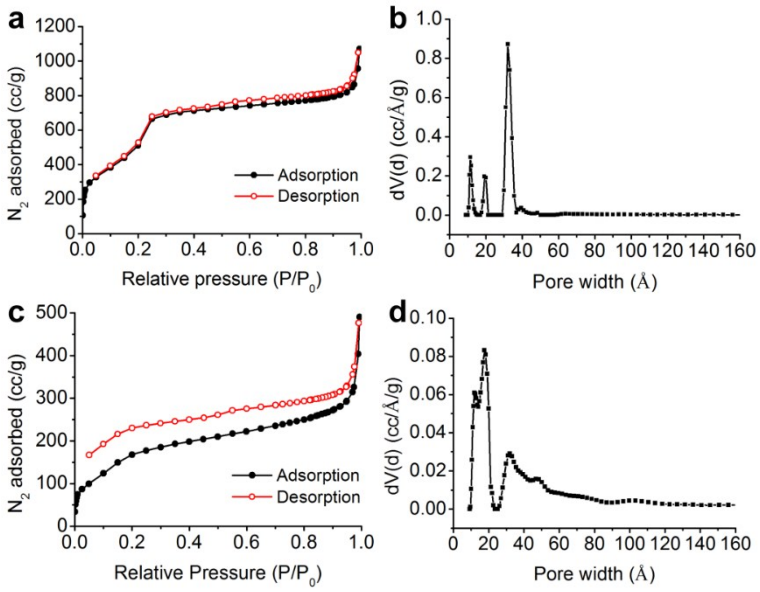


Fig. S12 N_2 adsorption-desorption isotherms and the pore size distribution: (a, b) TzDa; (c, d) CTzDa.

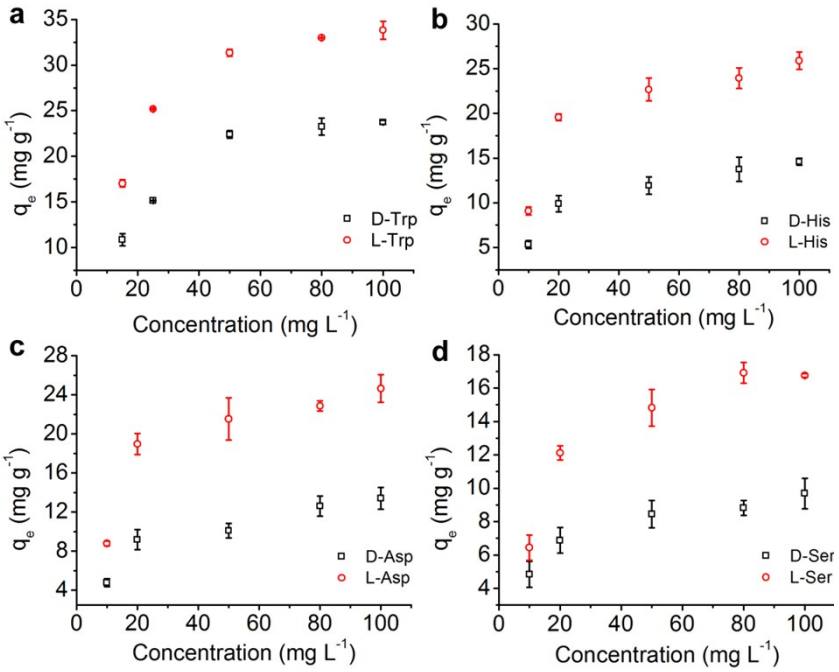


Fig. S13 Effect of dosage on the adsorption capacity at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser.

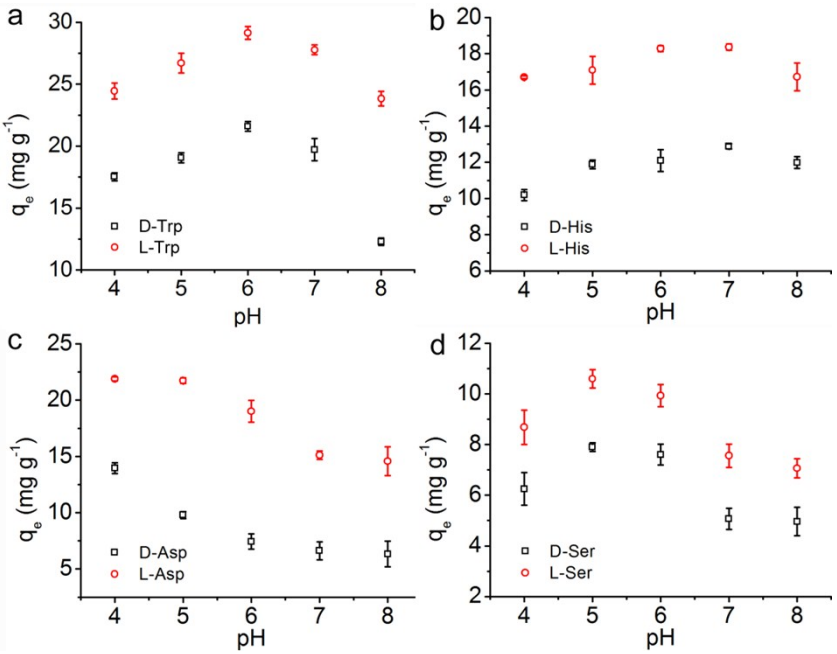


Fig. S14 Effect of pH on the adsorption efficiency at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser.

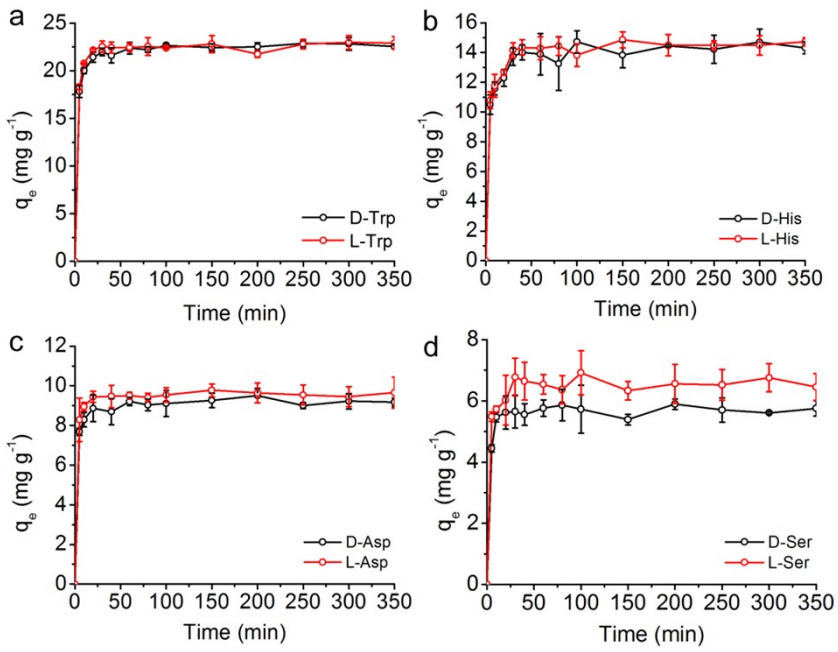


Fig. S15 Time-dependent adsorption on TzDa at 293 K: (a) Trp (50 mg L^{-1}); (b) His (20 mg L^{-1}); (c) Asp (20 mg L^{-1}); (d) Ser (20 mg L^{-1}).

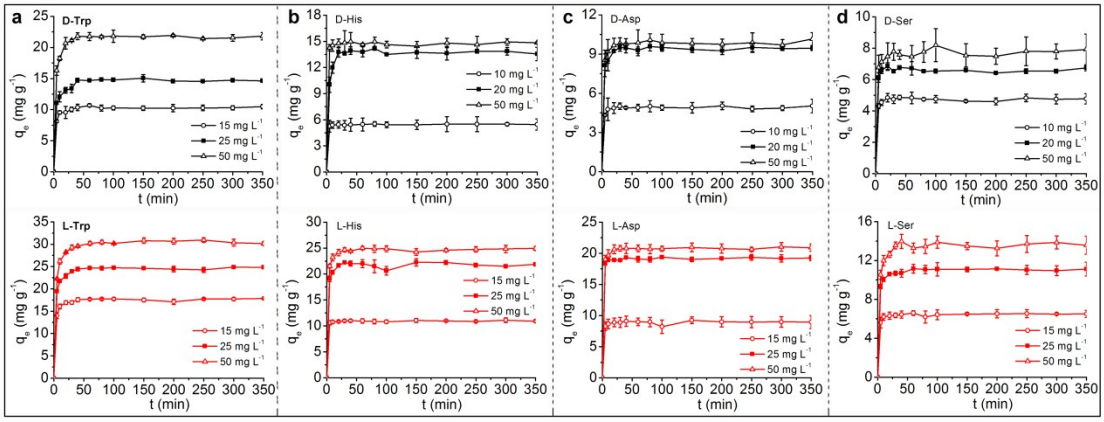


Fig. S16 Time-dependent adsorption of AAs at different initial concentrations on CTzDa at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser .

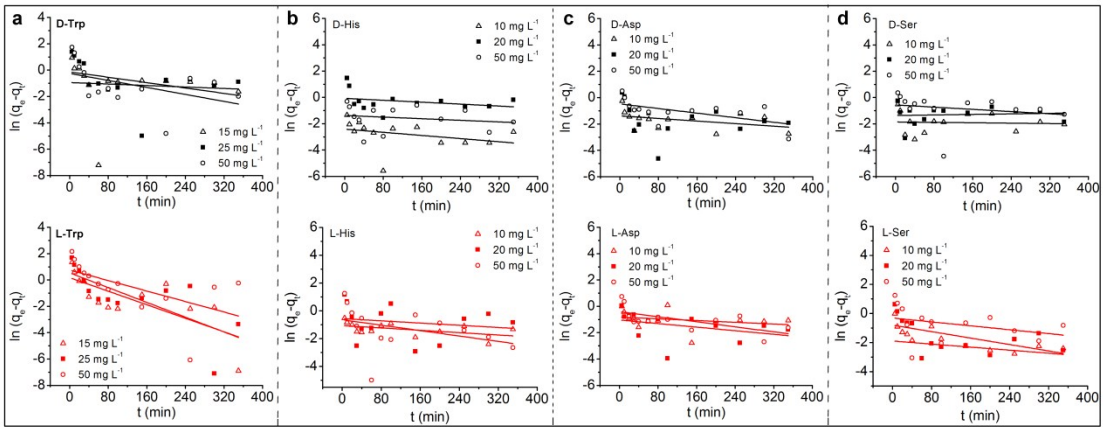


Fig. S17 Plots of pseudo-first-order kinetics for the adsorption of AAs at different initial concentrations on CTzDa at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser.

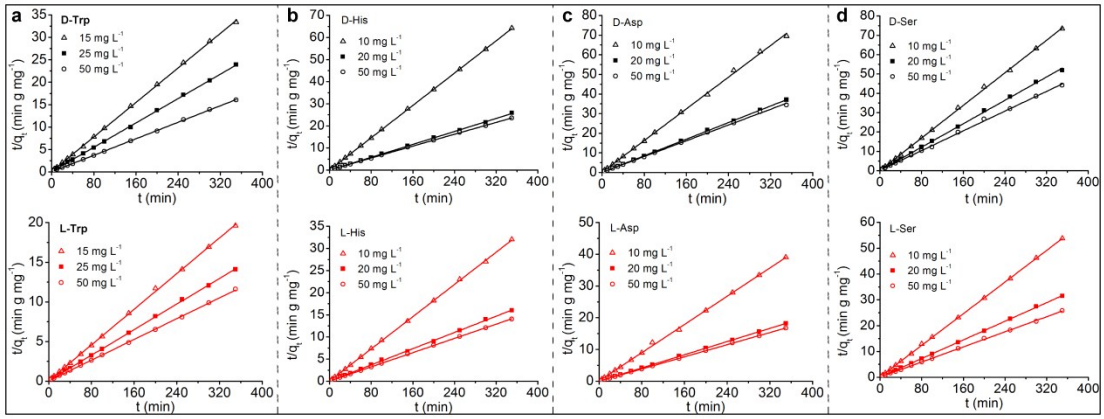


Fig. S18 Plots of pseudo-second-order kinetics for the adsorption of AAs at different initial concentrations on CTzDa at 293 K: (a) Trp; (b) His; (c) Asp; (d) Ser.

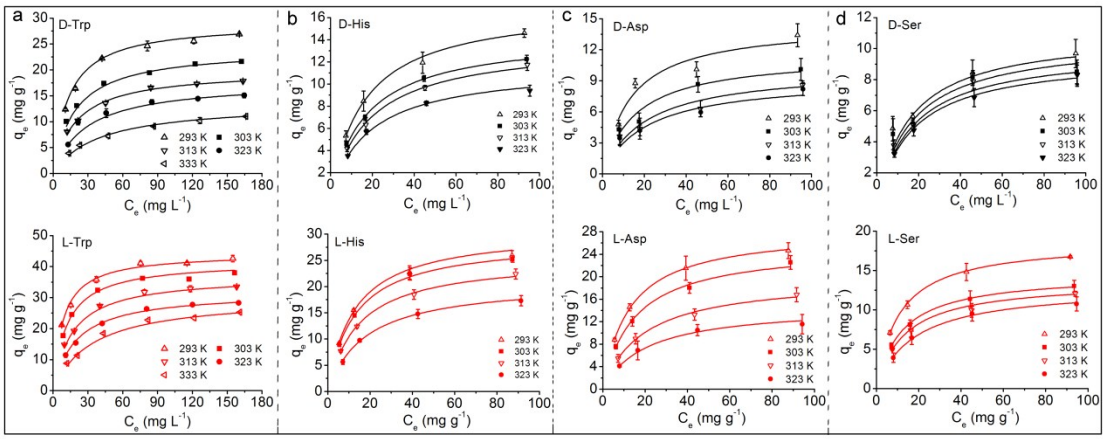


Fig. S19 Adsorption isotherms on CTzDa in the range of 293−323 K: (a) Trp; (b) His; (c) Asp; (d) Ser.

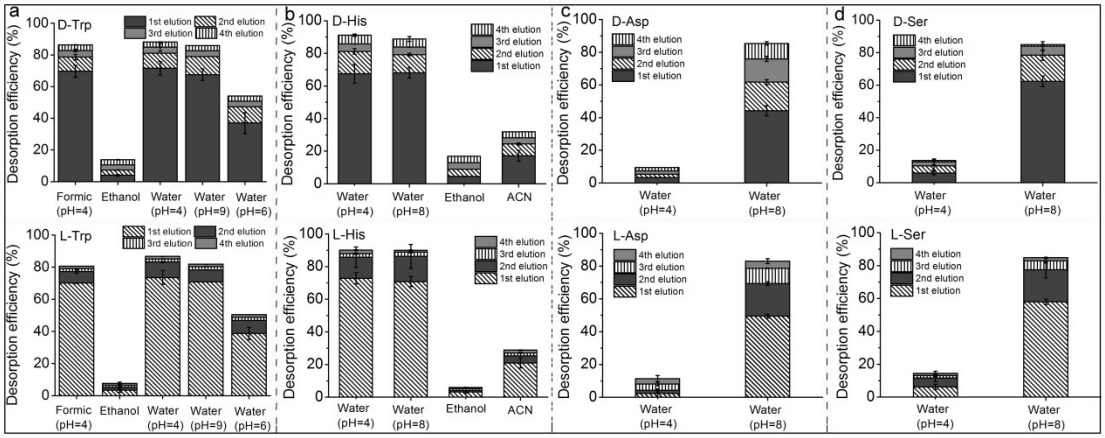


Fig. S20 Effect of eluents on the desorption efficiency for AAs from CTzDa: (a) Trp; (b) His; (c) Asp; (d) Ser.

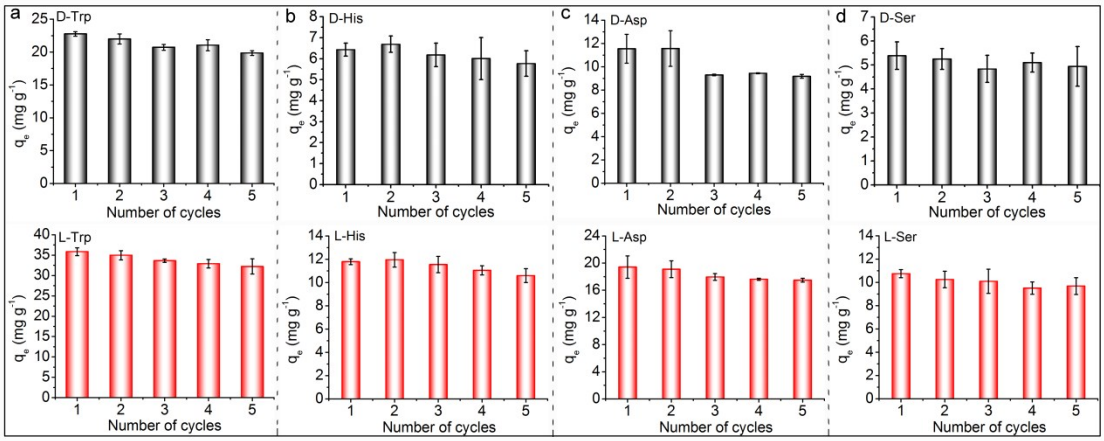


Fig. S21 Recyclable adsorption on CTzDa: (a) Trp; (b) His; (c) Asp; (d) Ser.

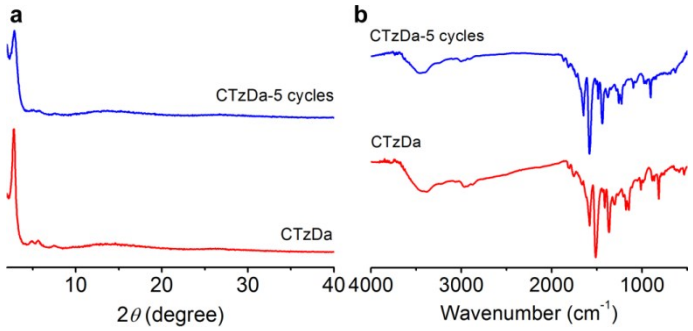


Fig. S22 (a) XRD patterns and (b) FT-IR spectra of CTzDa after 5 times reuse.

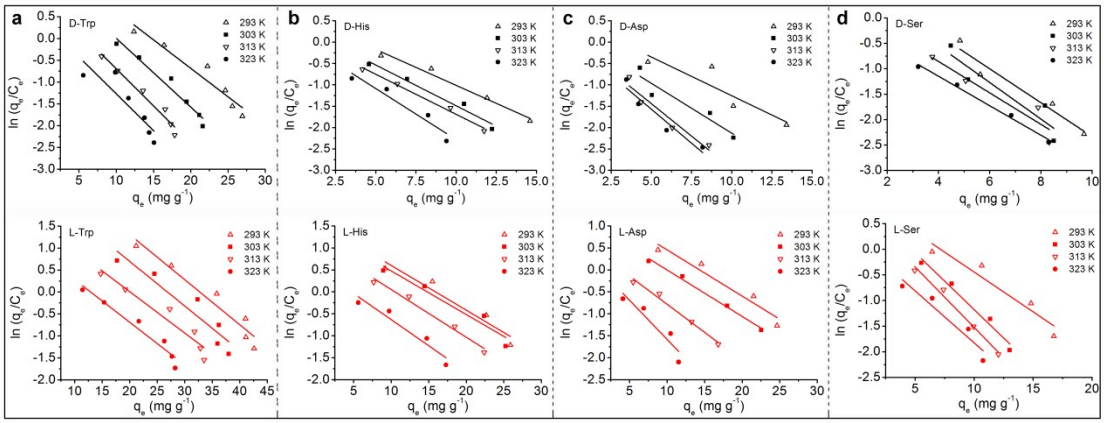


Fig. S23 Plots of ln (q_e/C_e) against q_e at various temperatures for AAs.

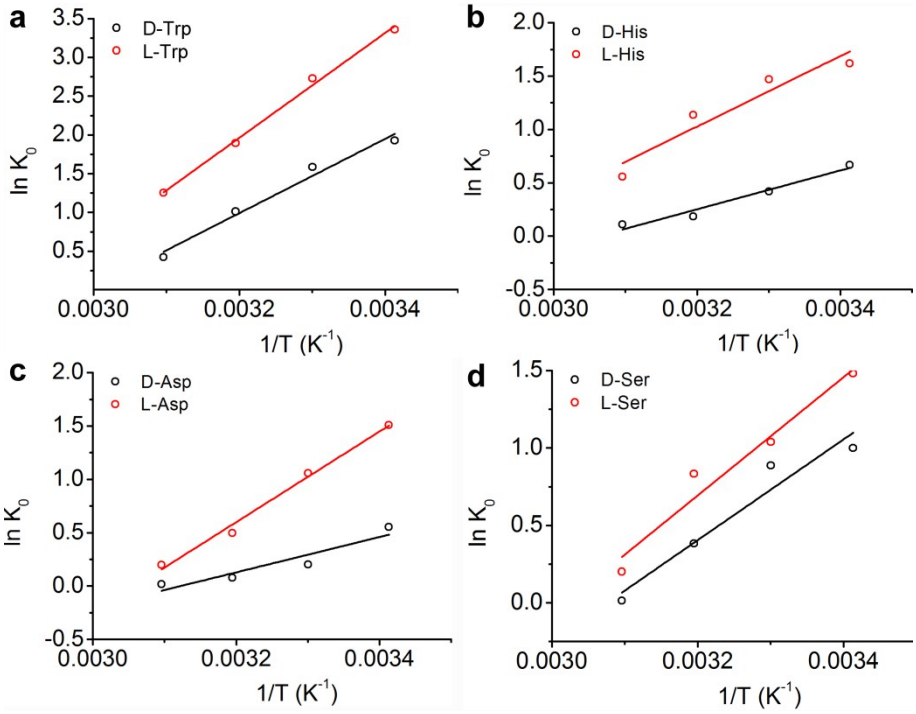


Fig. S24 Plots of lnK_0 against 1/T for AAs.

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

Table S3 Kinetic parameters for the adsorption of AAs on CTzDa

	C_0 [mg L^{-1}]	qe(exp) [mg g^{-1}]	qe(cal) [mg g^{-1}]	k_2 [g mg^{-1} min^{-1}]	R^2
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

Table S4 Parameters of Langmuir and Freundlich models for the adsorption of AAs on CTzDa

Analyte	T (K)	Langmuir			Freundlich		
		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.

Table S6 Comparison of the adsorption enantioselectivity of CTzDa with other adsorbents

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	

Table S7 Thermodynamic parameters for the absorption of AAs on CTzDa

		Thermodynamic parameters			
Analyte	T (K)	$\ln K_0$	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

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