Supplementary Information

Theoretical and experimental studies on the separation of cinnamyl acetate and cinnamaldehyde by adsorption onto a β-cyclodextrin polyurethane polymer

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Summary

Table S1 BET-surface areas, pore volumes and sizes of β-CD and CDPU

Samples	BET Surface Area ($m^2 \cdot g^{-1}$)	BJH adsorption cumulative volume of pores ($cm^3 \cdot g^{-1}$)	Adsorption average pore width (nm)
CDPU	10.19	0.0574	24.54
β−CD	0.63	0.0027	35.72

Table S2 Deconvoluted components for XPS signals (C1s, O1s) of fresh CDPU and CDPU adsorbing CA or CAc

XPS signals	Sample	XPS species	Binding energy (eV)	Area percentage (%)
C1s	CDPU	C*−C/C*−H	284.73	38.74
		C*−NH−C=O	285.63	5.72
		C*−OH/C−O−C*	286.23	45.56
		N−C*(O)=O	288.64	9.98
	CDPU/CA	C*−C/C*−H/C*=C	284.76	52.02
		C*−NH−C=O	285.60	5.18
		C*−OH/C−O−C*	286.47	32.17
		N−C*(O)=O/C−C*=O	288.62	9.23
		O−C*=O	288.00	1.40
	CDPU/CAc	C*−C/C*−H/C*=C	284.69	45.84
		C*−NH−C=O	285.62	2.24
		C*−OH/C−O−C*	286.22	41.58
		N−C*(O)=O/O−C*(O)=O	288.80	10.34
O1s	CDPU	C−NH−C=O*	531.50	10.16
		C−O*H/C−O*−C	533.14	89.84
	CDPU/CA	C−NH−C=O*	531.50	12.34
		O−C=O*	532.30	4.44
		C−O*H/C−O*−C	533.06	83.22
	CDPU/CAc	C−NH−C=O*/O−C=O*	531.40	14.51
		C−O*H/C−O*−C	532.92	85.49
N1s	CDPU	C−N*H−C=O	400.12	100
	CDPU/CA	C−N*H−C=O	400.06	100
	CDPU/CAc	C−N*H−C=O	399.83	100

Table S3 Numbers, types, bond lengths (*r*) and bond angles (*A*) of intermolecular hydrogen bonds between CDPU and adsorbates calculated by DMol3

Adsorption positions	Complexes	Numbers	Types	*r* (Å)[a]	*A* (°)[b]
CA on crosslink unit	-	4	O10···H21−O10 (II)	3.270	147.697
			O10···H18−C9 (I)	2.944	108.954
			C7−H16···O20 (I)	3.113	91.344
			C6−H15···O36 (I)	3.283	111.478
CAc on crosslink unit	-	7	C11−H25···O10 (II)	3.026	117.263
			C22···H21−O10 (II)	3.419	142.520
			O3···H24−C22 (II)	3.258	139.770
			O10···H20−O10 (II)	2.656	162.820
			O12···H21−C10 (I)	2.977	93.289
			O12···H21−C10 (I)	2.977	102.095
			C9−H21···O10 (I)	3.407	103.174
CA in cyclodextrin cavity	up	10	C6−H15···O10 (IV)	3.184	123.738
			C5−H14···O8 (IV)	3.273	115.562C
			C1−H11···O8 (IV)	3.231	161.301
			C8−H17···O8 (VI)	3.302	98.158
			C8−H17···O8 (III)	3.452	101.389
			C8···H39−O8 (III)	3.452	175.270
			C9−H18···O8 (VI)	3.180	110.288
			O10···H15−C6 (VI)	3.155	121.711
			O10···H16−O7 (VII)	3.310	111.433
			O10···H14−C5 (VII)	3.092	120.592
CAc in cyclodextrin cavity	up	13	C2−H14···O10 (II)	3.448	101.114
			C2···H21−O10 (II)	3.448	97.674
			C3−H15···O10 (II)	3.154	122.558
			C3···H21−O10 (II)	3.154	90.737
			C5−H16···O2 (II)	3.076	94.043

			C9−H20···O8 (IV)	3.254	125.424
			C9···H39−O8 (IV)	3.254	108.862
			C9−H21···O40 (II)	3.369	138.596
			O10···H16−O7 (VII)	3.497	104.447
			O12···H39−O8 (III)	2.609	169.560
			O12···H15−C6 (III)	3.475	91.635
			C22−H25···O8 (VI)	3.263	164.253
			C22−H23···O7 (VII)	3.253	166.724
CA in cyclodextrin cavity	down	6	O10···H17−C9 (II)	3.285	144.177
			C8−H17···O8 (IV)	3.170	168.195
			C7−H16···O10 (II)	3.172	135.327
			C2···H39−O8 (III)	3.046	153.699
			C3−H13···O8 (IV)	3.138	161.176
			C3···H39−O8 (IV)	3.138	96.018
CAc in cyclodextrin cavity	down	12	C6−H17···O7 (I)	3.294	171.158
			C1−H13···O8 (III)	3.128	92.060
			C1···H39−O8 (III)	3.128	151.522
			C2−H14···O8 (III)	3.074	137.540
			C2···H39−O8 (III)	3.074	95.886
			C2−H14···O8 (VI)	3.072	92.335
			C2···H39−O8 (V)	3.252	102.973
			C2−H14···O8 (V)	3.252	127.973
			C3−H15···O8 (V)	3.441	111.500
			C3···H39−O8 (V)	3.441	104.047
			C3−−H15···O8 (IV)	3.152	148.093
			C3···H16−O7 (IV)	3.152	94.064

[a] The bond angle of ∠OHO or ∠CHO.

[b] The bond length between C···O or O···O.

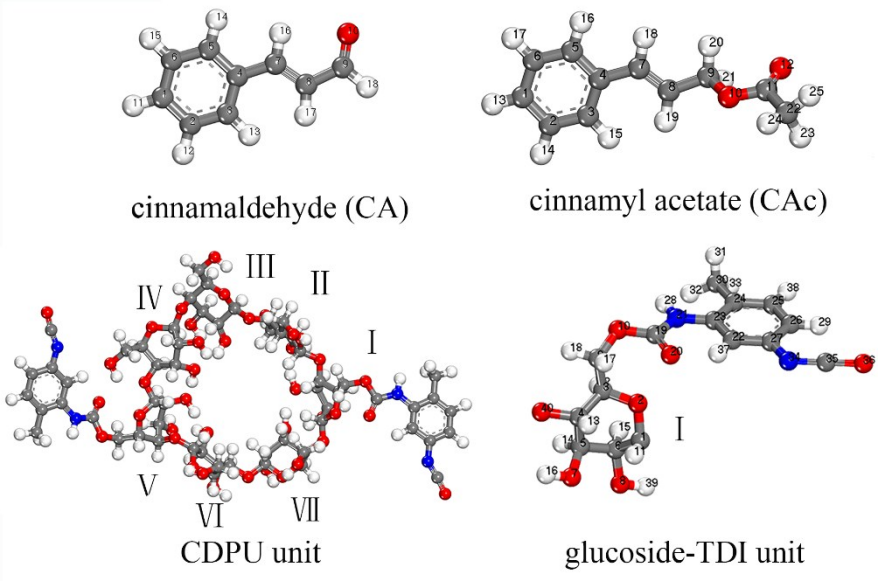

Fig. S1 The atom numbers of CA, CAc, CDPU unit and glucoside-TDI unit.

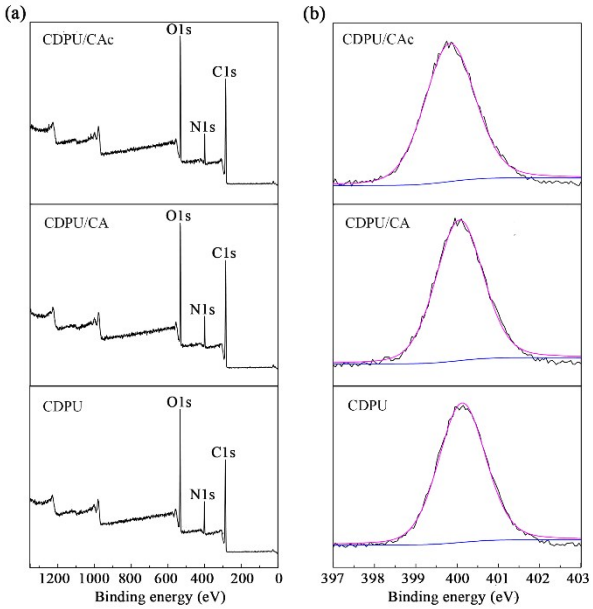

Fig. S2 XPS spectra of survey scan (a) and N1s (b) of CDPU before and after adsorption of CA and CAc.

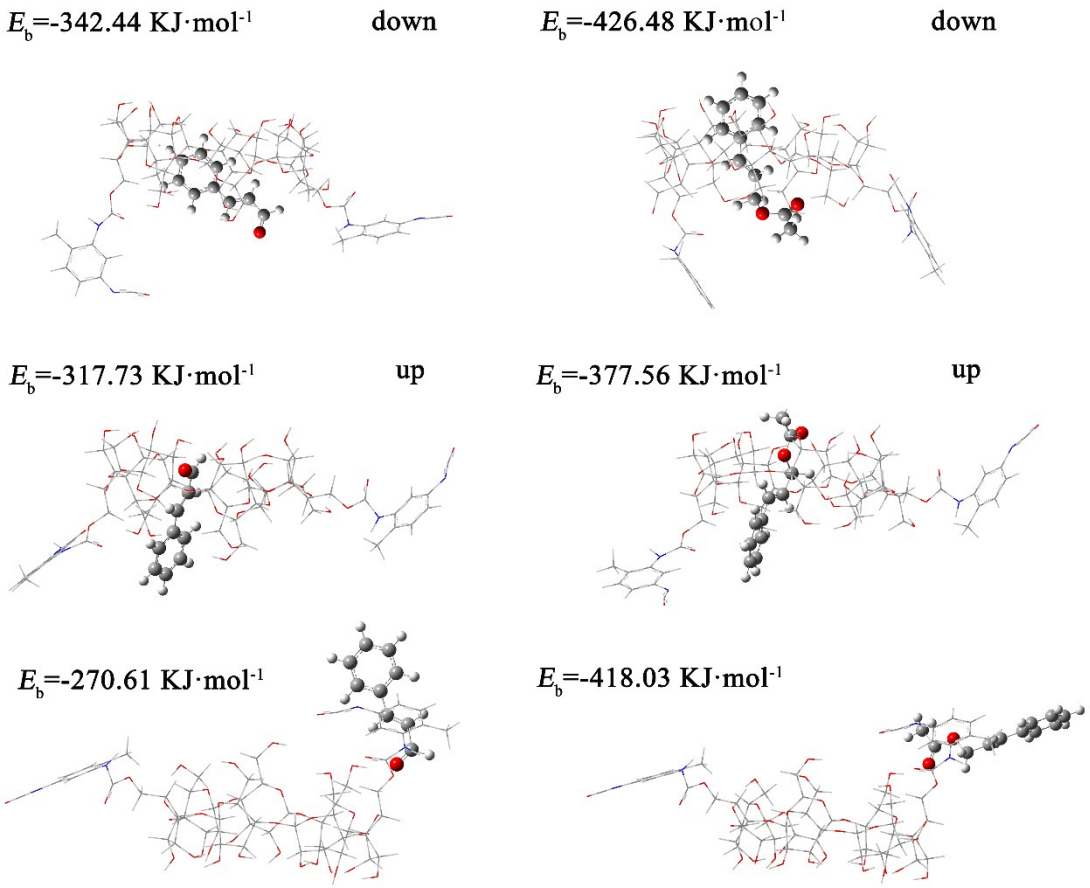

Fig. S3 Optimized geometries and binding energy between CDPU and guests obtained by Gaussian.

Text S1 Effects of different types of co-solvents on the adsorption of CDPU to CAc and CA.

According to the principle of easy availability and low toxicity, we chose five organic solvents (including methanol, dimethyl sulfoxide, ethanol, acetone and 2-propanol) as cosolvent to improve the concentrations of CAc and CA in the aqueous solution. All solvents were analytical grade and used as received from Chengdu Kelong Chemical Reagent Co. Ltd., China. To investigate the influence of varying the cosolvents on the adsorptive performance of CDPU, 70 $mmol \cdot L^{-1}$ of equimolar CAc and CA solution was prepared by dissolving certain amount of equimolar mixture of CAc and CA in different types of 40% organic-water solution (v/v). Then the adsorption experiment was conducted by the procedure as described in Section 2.5.3.

As shown in Fig. S4a, the adsorption capacity of CDPU and CAc/CA selectivity both increased with increasing the solvent polarity of solution, as the dielectric constant of five organic solvents are in the order of DMSO (48.9) > methanol (33.1) > ethanol (23.8) > acetone (20.7) > 2-propanol (18.3). And CDPU exhibited the best adsorptive performance in the 40% of DMSO solution (v/v). Using DMSO as cosolvent, in the premise of dissolving all of the substances in the 70 $mmol \cdot L^{-1}$ of equimolar CAc-CA solution, adsorption experiment was carried out in DMSO aqueous solutions with different volume percentages of DMSO (40~60%). The adsorption capacity of CDPU declined rapidly as the volume percentage of DMSO increasing, meanwhile the CAc/CA selectivity also decreased (Fig. S4b). This can be explained that the decrease of polarity weakened the hydrophobic interaction, resulting in less adsorbate molecules enter the hydrophobic cavities of the CDPU. Therefore, we chose 40 % DMSO aqueous solution (v/v) as the solvent in further

experiments.

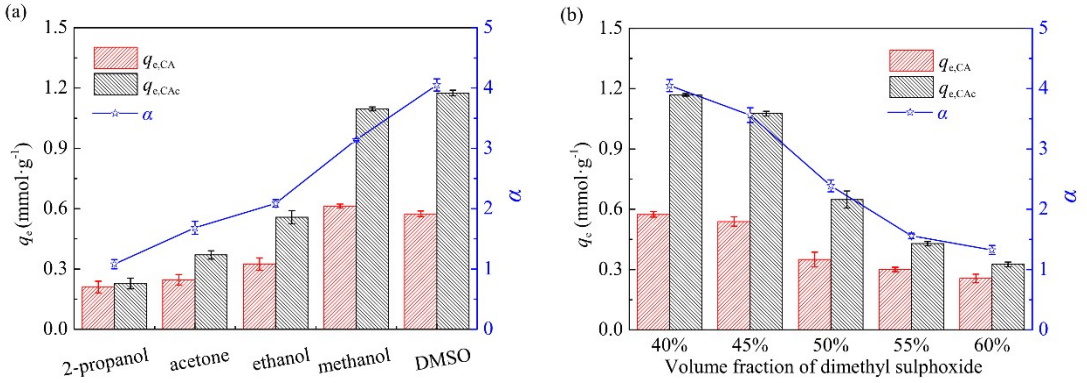

Fig. S4 The adsorptive performances of CDPU in (a) different types of solvent aqueous solutions and (b) DMSO aqueous solutions with different volume fractions of DMSO at 25 °C.

Text S2 Effects of degree of crosslinking of polymer on the adsorption of CDPU to CAc and CA.

To determine the influence of the degree of crosslinking of polymer onto the adsorption performance of CDPU, 0.2 g of CDPU with various degrees of crosslinking was added into 10 mL of equimolar CAc-CA solutions (70 $mmol \cdot L^{-1}$), being shaken at 25 ^{o}C for 4 h. After attaining equilibrium, the equilibrium concentrations of CA and CAc in the supernatant were analyzed by the procedure as described in Section 2.4.

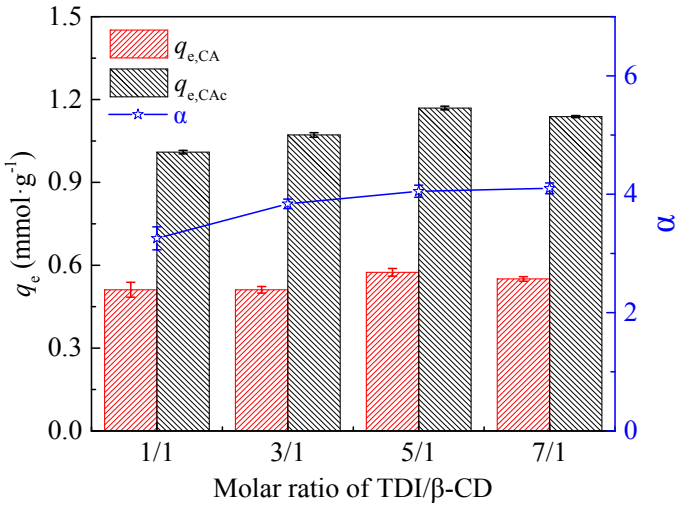

Fig. S5 The adsorptive performances of CDPU prepared in different molar ratio of TDI/β-CD.

Text S3 Information for the adsorbent used for comparison in this study.

For comparison, four adsorbents including the commercial bentonite and activated carbon (abbreviated as AC), β-CD crosslinked hexamethylene diisocyanate (HDI) polymer (abbreviated as CHP) and β-CD crosslinked epichlorohydrin (EPI) polymer (abbreviated as CEP) were employed. The specific information of these materials are as follows:

Bentonite and AC were obtained from J&K Chemical Co. Ltd., (China). The general characteristics of bentonite were: BET surface area (76 $m^2 g^{-1}$), pore size (106 Å), pore volume (0.20 $cm^3 g^{-1}$), and for AC (as provided by the supplier): particle size (10~24 mesh), BET surface area (500~1000 $m^2 g^{-1}$). The two adsorbents were used as received without purification.

CHP was prepared by crosslinking β-CD with HDI as crosslinking agent. For synthesizing CHP, the molar ratio of HDI to β-CD was 5/1, and the synthesis procedure was the same as that used for the preparation of CDPU in this study.

CEP was prepared by crosslinking CD with EPI as crosslinking agent. Experimental procedure for the synthesis of CEP was the same as the method previously described in literature [1].

1. J. Huang, P. Su, B. J. Zhao and Y. Yang, *Anal. Methods*, 2015, **7**, 2754-2761.