Supporting Information

CO_2-driven reversible transfer of the amine-functionalized ZIF-90 between organic and aqueous phases

Xiaoyan Pei,[*a] Chunyu Tian,[a] Yanning Wang,[a] Zhenzhen Li,[a] Zhiyan Xiong,[a] Huiyong Wang,[b] Xiantao Ma,[a] Xinhua Cao[a] and Zhiyong Li[*b]

[a.] *College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang, Henan 464000, P. R. China.*

[b] *Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, P. R. China.*

E-mail: xiaoyanpei2009@163.com; yli@htu.edu.cn

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1. Experimental section

Synthesis of ZIF-90

Typically, imidazole-2-carboxyaldehyde (1.38 g, 14.4 mmol) and triethylamine (1.46 g, 14.4 mmol) were mixed in 60 mL of methanol under stirring for 5 min at room temperature. Then, aqueous solution (30 mL) of $Zn(CH_3COO)_2 \cdot 2H_2O$ (1.58 g, 7.2 mmol) was added into the above mixture and stirred for 12 h. The precipitation was separated through centrifugation (9000 rpm, 3 min) and then washed with methanol three times and dried at 60 °C for 24 h under vacuum to obtain ZIF-90.

Synthesis of the amine-functionalized ZIF-90

Amine-functionalized ZIF-90 was prepared as follows. As an example, 0.80 g of the as-prepared ZIF-90 and 0.15 g of DAB were successively added into methanol (40 mL). After 12 h of reaction at 25 °C, the product was parted by centrifugation (9000 rpm, 3 min) and washed with methanol. Then, ZIF-90-DAB was obtained by drying under vacuum at 70 °C for 12 h. Similar process has been used for preparation of the other amine-functionalized ZIF-90, such as ZIF-90-DAE, ZIF-90-DAH and ZIF-90-DAO.

Trans-esterification reaction

The typical procedure for the trans-esterification of organic esters and n-butanol catalyzed by the functionalized ZIF-90 is shown as follows. A known amount of the amine-functionalized ZIF-90 was added to n-butanol and sonicated for 5 min until a homogenous dispersion was obtained. Then, an ester was added to the above mixture. The reaction was carried out at 100 ^oC for 8 h under the atmosphere of nitrogen. After reaction completed, the system was cooled to room temperature and the functionalized ZIF-90 was transferred to the lower aqueous phase through bubbling of CO_2. At the same time, the product stayed at the n-butanol phase for further purification, and n-butanol was then collected for the next cycles. Upon removal of CO_2, the amine-functionalized ZIF-90 could return to the organic phase. When a new substrate was added, the same reaction carried out again.

2. Tables S1-S6

Table S1 Surface chemical composition of the amine-functionalized ZIF-90 (in at.%).

ZIFs	Zn	C	N	O
ZIF-90	7.23	57.01	19.56	15.71
ZIF-90-DAE	5.08	60.92	23.99	9.56
ZIF-90-DAB	4.92	64.74	21.61	8.73
ZIF-90-DAH	5.25	65.55	21.95	7.25
ZIF-90-DAO	4.44	65.34	20.84	9.38

Table S2 The values of water contact angle and zeta potential of the amine-functionalized ZIF-90 before and after bubbling of CO_2.

Sample	Contact angel/^{o}		Zeta potential/mV	
	Before CO_2	After CO_2	Before CO_2	After CO_2
ZIF-90-DAE	56	22	21	35
ZIF-90-DAB	62	30	28	42
ZIF-90-DAH	68	39	30	40
ZIF-90-DAO	94	49	35	39

Table S3 Trans-esterification reaction of (phenylthio)acetic acid ethyl ester and n-butanol catalyzed by ZIF-90-DAB at different reaction times

Entry	MOF	Time	Yield (%)
1	ZIF-90-DAB	2 h	52
2	ZIF-90-DAB	4 h	75
3	ZIF-90-DAB	6 h	86
4	ZIF-90-DAB	8 h	99
5	ZIF-90-DAB	10 h	91
6	ZIF-90-DAB	12 h	89

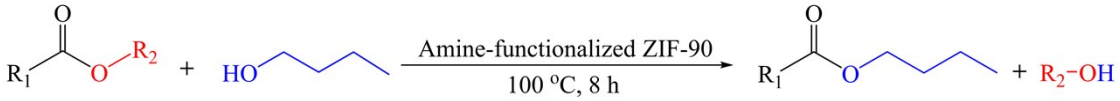
Reaction conditions: 100 ^{o}C, refluxing n-butanol (1.5 mL), substrate = 1 mmol

Table S4 Trans-esterification reaction of (phenylthio)acetic acid ethyl ester and n-butanol.

Entry	MOF	Yield (%)
1	No ZIF	1
2	Pristine ZIF-90	23
3	ZIF-90-DAE	97
4	ZIF-90-DAB	99
5	ZIF-90-DAH	35
6	ZIF-90-DAO	10

Reaction conditions: 100 °C, 8 h, refluxing n-butanol (1.5 mL), substrate = 1 mmol.

Table S5 Isolated yields for the reactions of esters with alcohol catalyzed by ZIF-90-DAB.



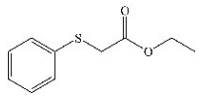
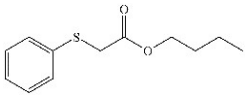
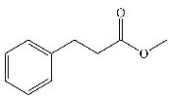
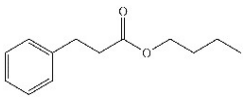
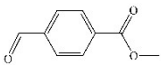
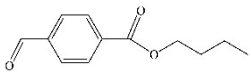
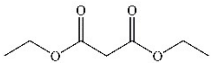
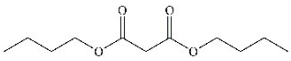
Entry	Ester	alcohol	Product	Yield (%)
1				99
2				89
3				82
4				86

Table S6 Trans-esterification reaction of 3-phenylpropionic acid methyl ester and n-butanol catalyzed by different catalysts

Entry	Catalyst	Yield (%)	Ref.
1	$Zn(OAc)_2$	72	1
2	K-10 montmorillonite	47	2
3	HB zeolite	59	3
4	ZIF-90-DAB	89	This work

3. Figures S1-S23

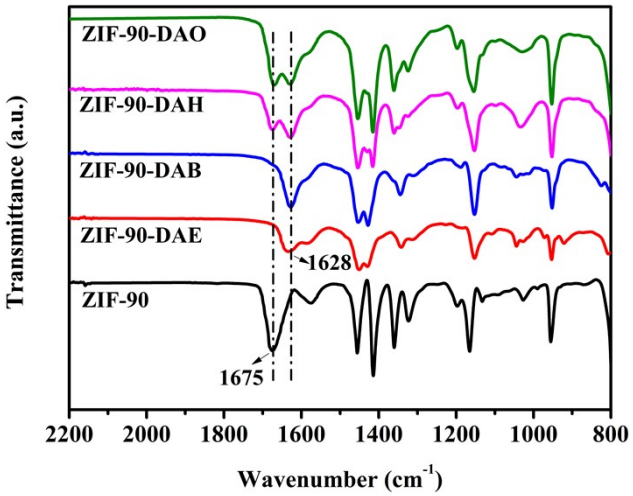


Figure S1 FT-IR spectrum of the pristine and amine-functionalized ZIF-90.

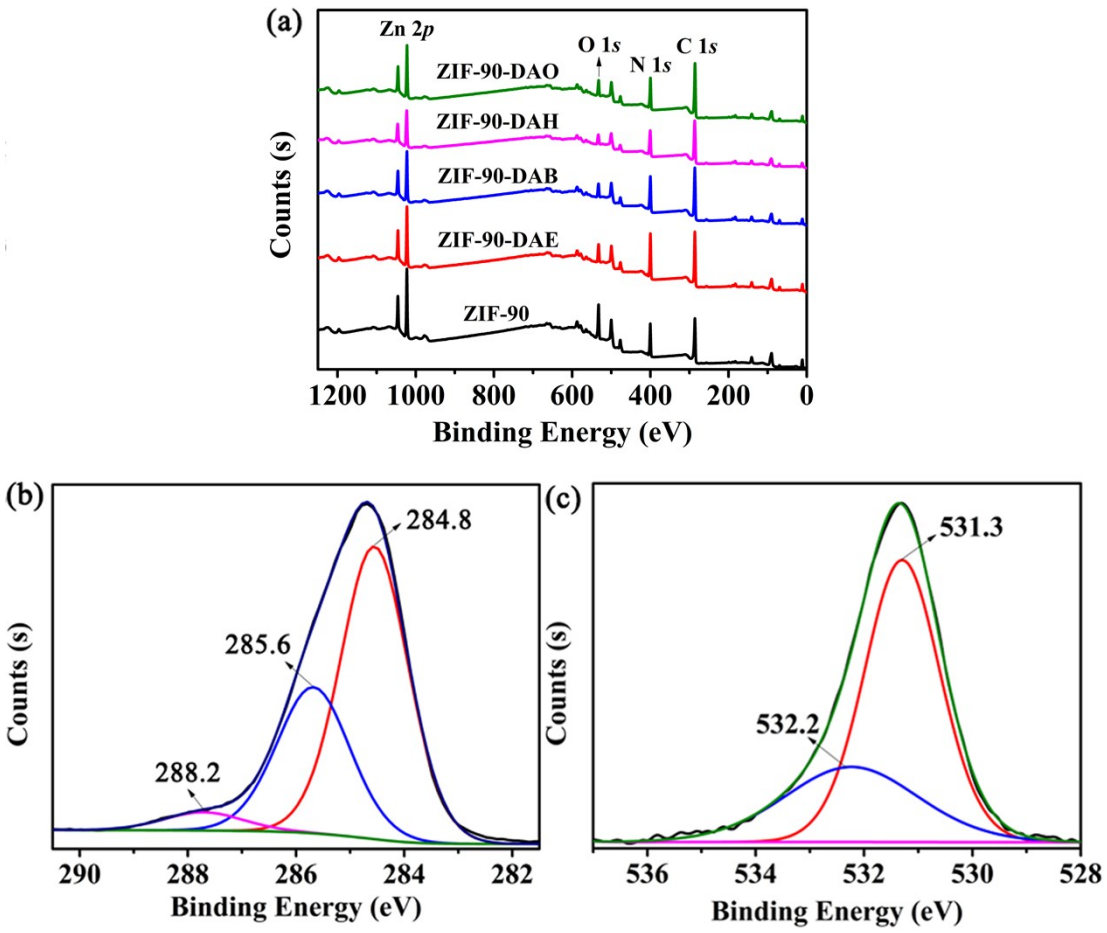


Figure S2 XPS spectrum of the amine-functionalized ZIF-90 (a), high-resolution XPS spectrum of C 1*s* (b) and O 1*s* (c) of ZIF-90-DAB.

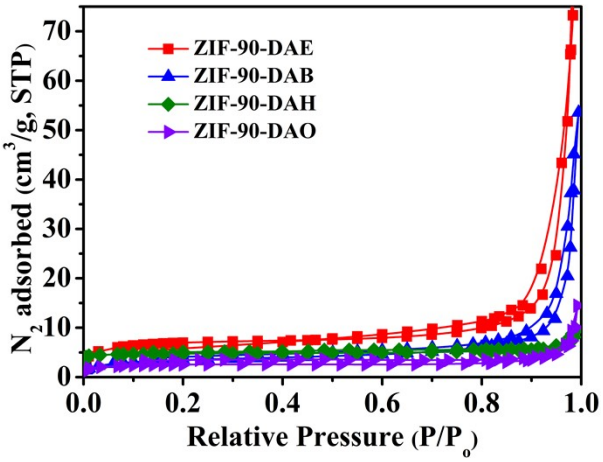


Figure S3 N_2 adsorption isotherms of the amine-functionalized ZIF-90.

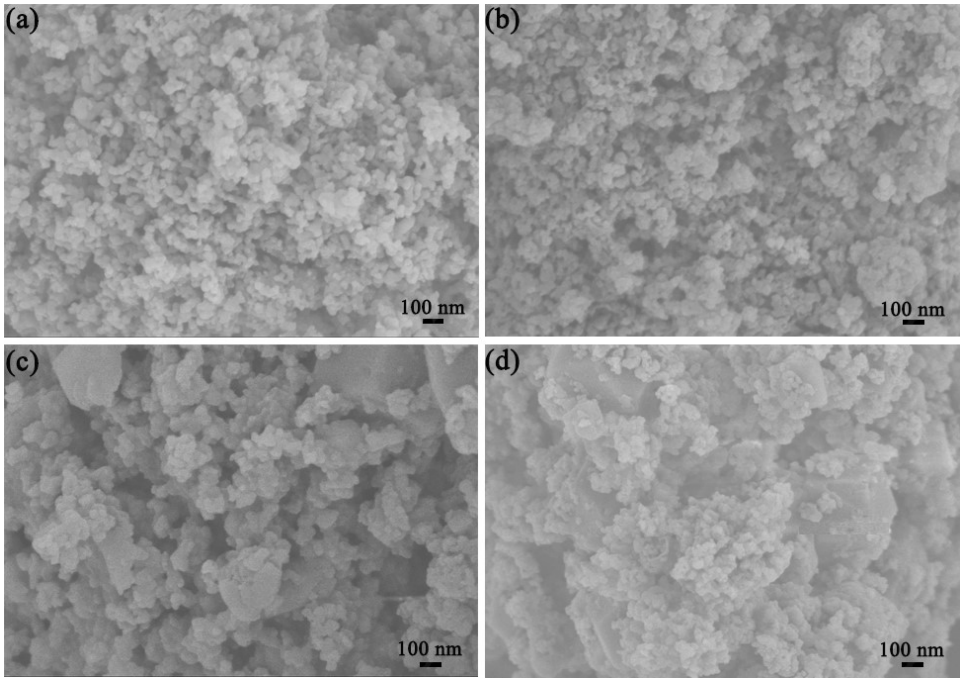


Figure S4 SEM images of ZIF-90 (a), ZIF-90-DAE (b), ZIF-90-DAH (c) and ZIF-90-DAO (d).

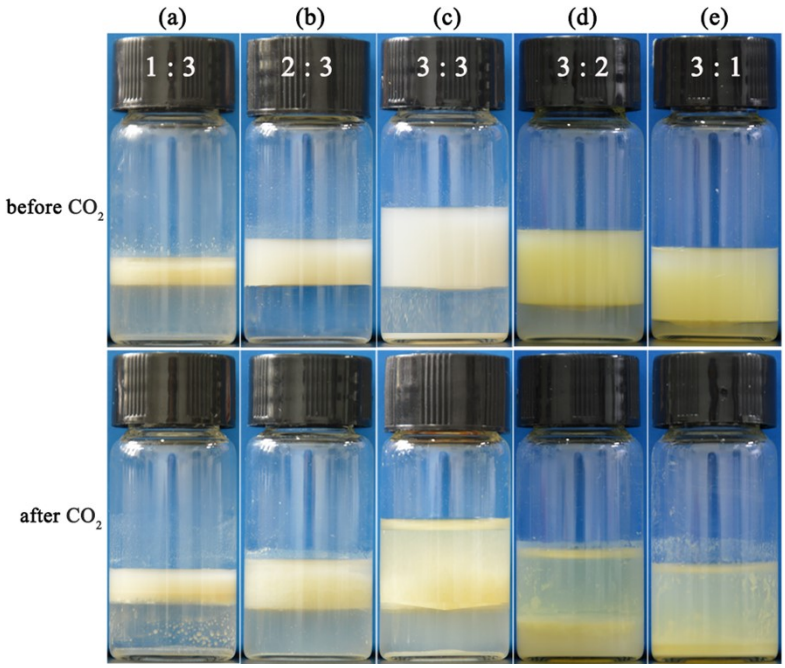


Figure S5 Phase behavior of ZIF-90-DAE between n-butanol and aqueous phases before and after bubbling of CO_2.

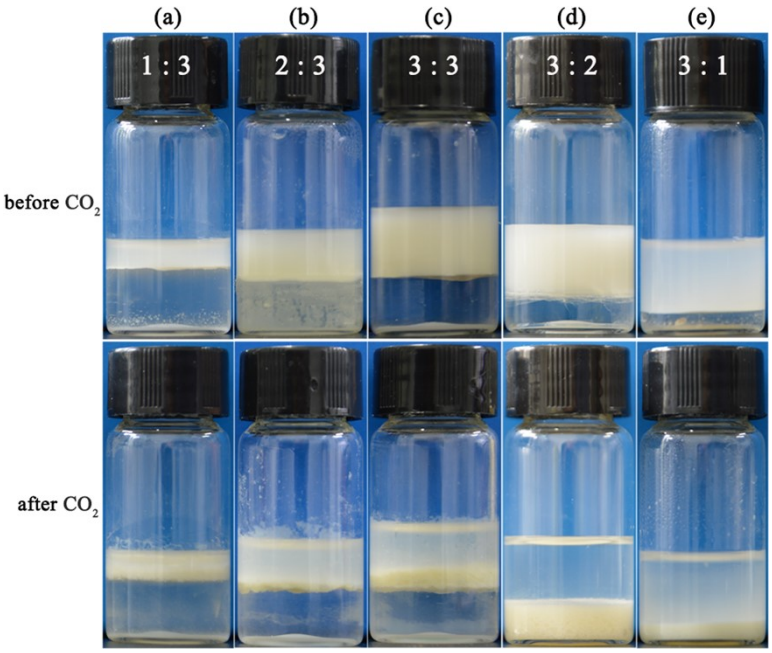


Figure S6 Phase behavior of ZIF-90-DAB between n-butanol and aqueous phases before and after bubbling of CO_2.

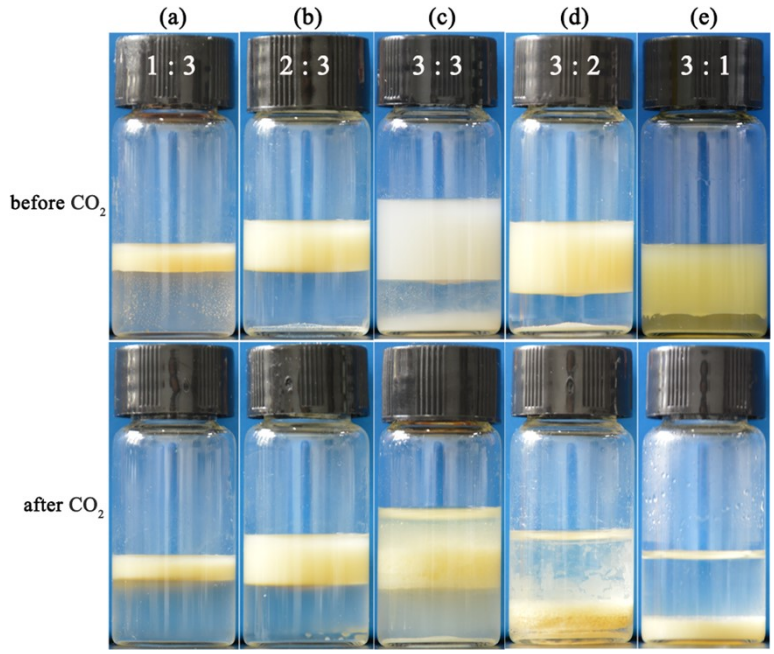


Figure S7 Phase behavior of ZIF-90-DAH between n-butanol and aqueous phases before and after bubbling of CO_2.

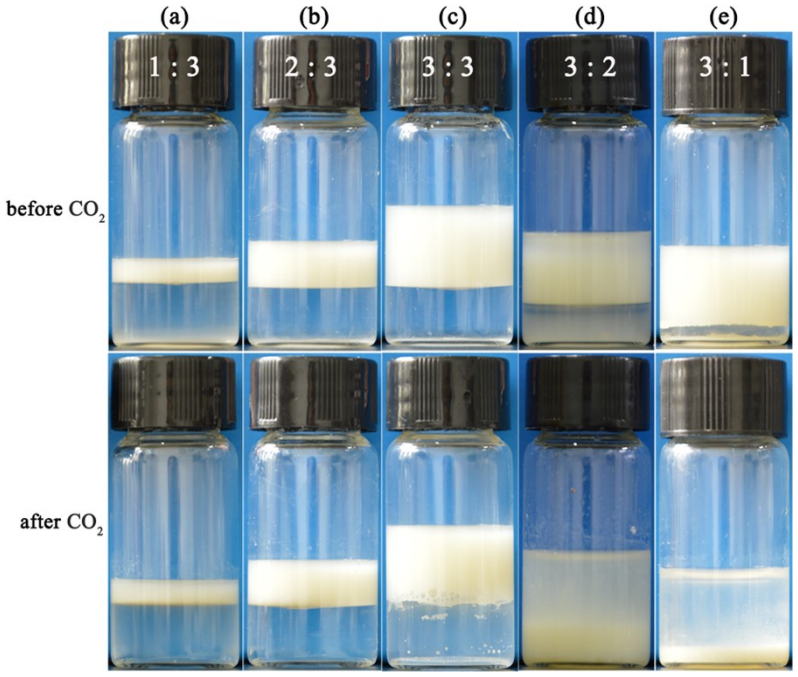


Figure S8 Phase behavior of ZIF-90-DAO between n-butanol and aqueous phases before and after bubbling of CO_2.

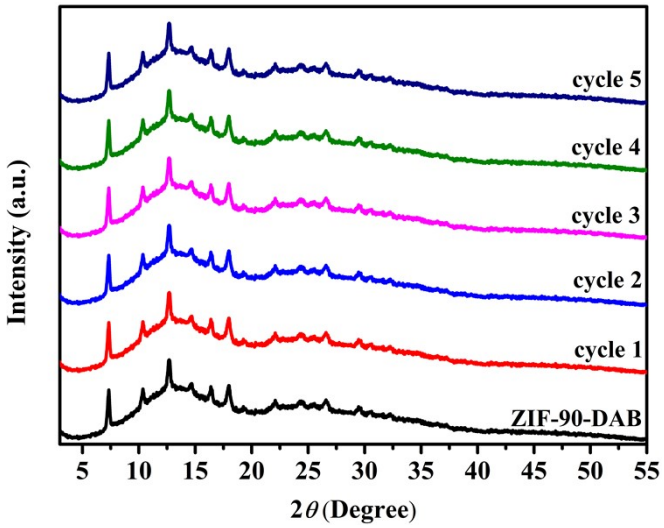


Figure S9 XRD patterns of the ZIF-90-DAB after five phase transfer cycles.

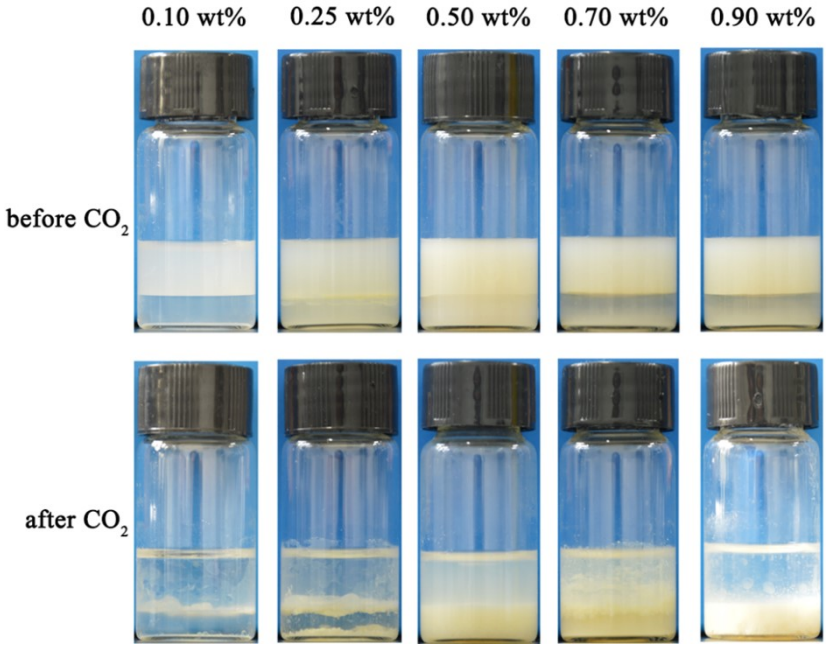


Figure S10 Phase transfer of the different amounts of ZIF-90-DAE between n-butanol and aqueous phases before and after bubbling of CO_2.

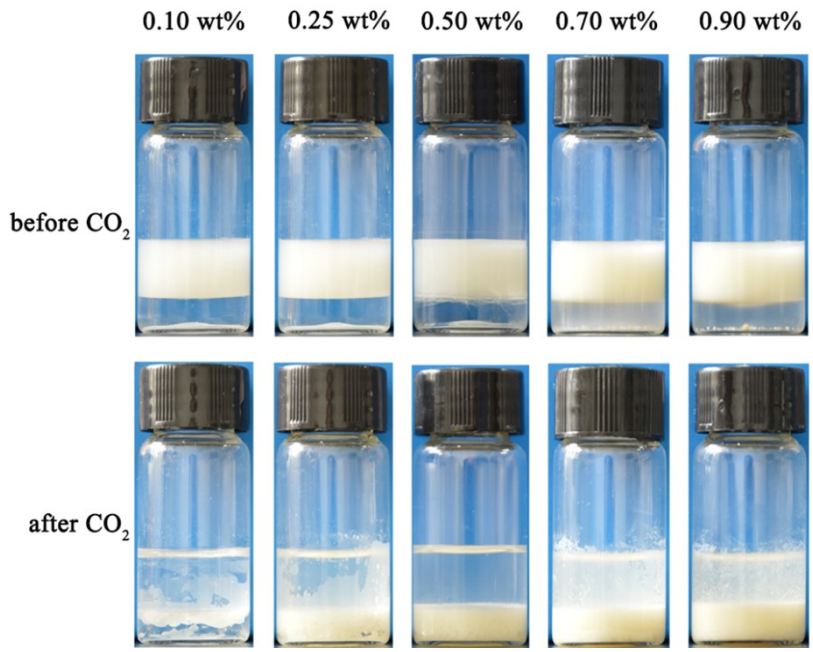


Figure S11 Phase transfer of the different amounts of ZIF-90-DAB between n-butanol and aqueous phases before and after bubbling of CO_2.

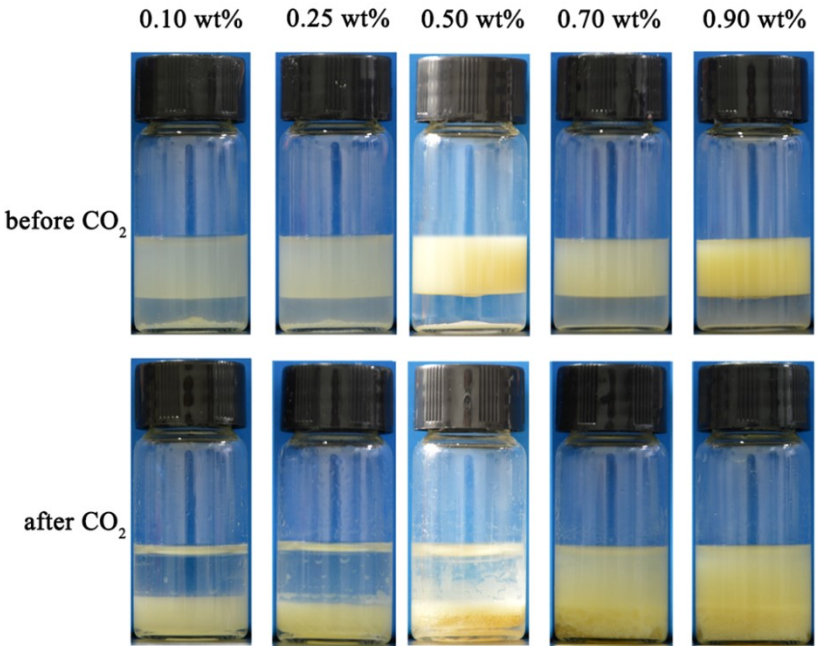


Figure S12 Phase transfer of the different amounts of ZIF-90-DAH between n-butanol and aqueous phases before and after bubbling of CO_2.

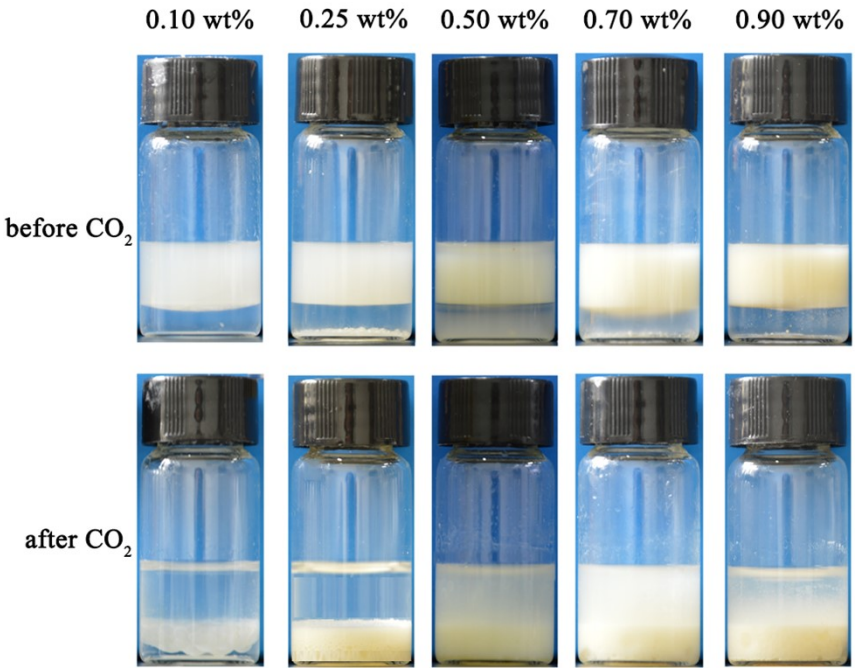


Figure S13 Phase transfer of the different amounts of ZIF-90-DAO between n-butanol and aqueous phases before and after bubbling of CO_2.

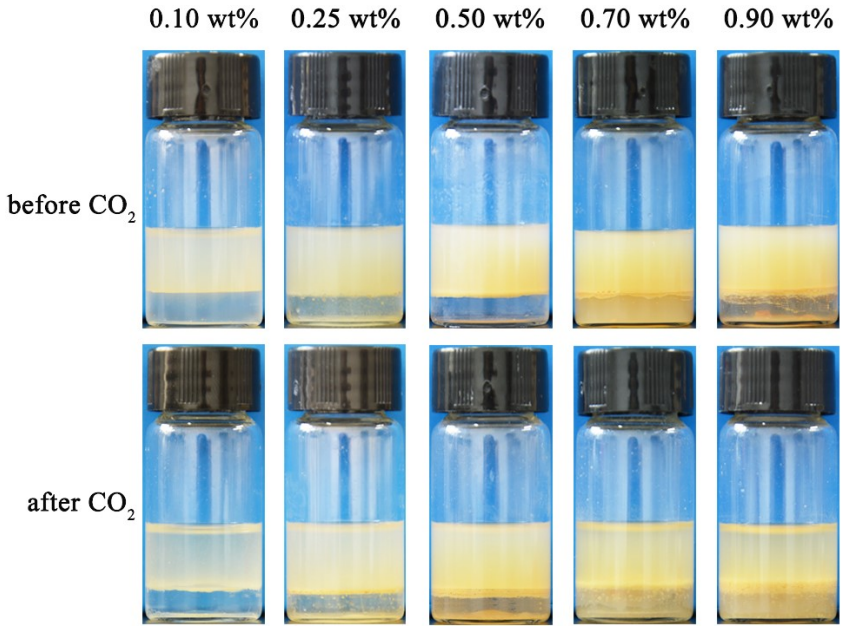


Figure S14 Phase transfer of the different amounts of the pristine ZIF-90 from n-butanol to water before and after bubbling of CO_2.

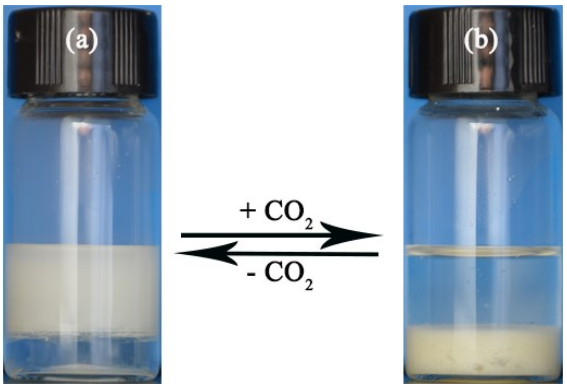


Figure S15 Reversible phase transfer of ZIF-90-DAB between n-pentanol and aqueous phases ($V_{\text{n-pentanol}}/V_{\text{water}}$ = 3:2) before and after bubbling of CO_2, as well as removal of CO_2.

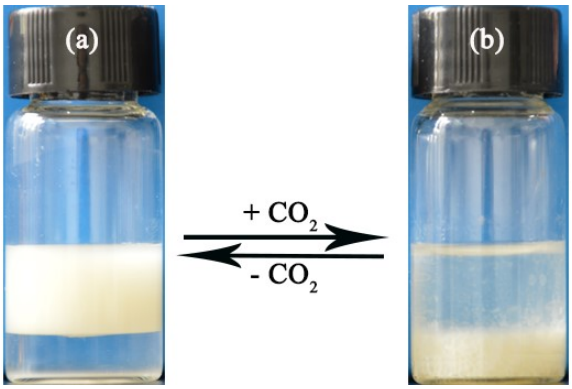


Figure S16 Reversible phase transfer of ZIF-90-DAB between n-hexanol and aqueous phases ($V_{\text{n-hexanol}}/V_{\text{water}}$ = 3:2) before and after bubbling of CO_2, as well as removal of CO_2.

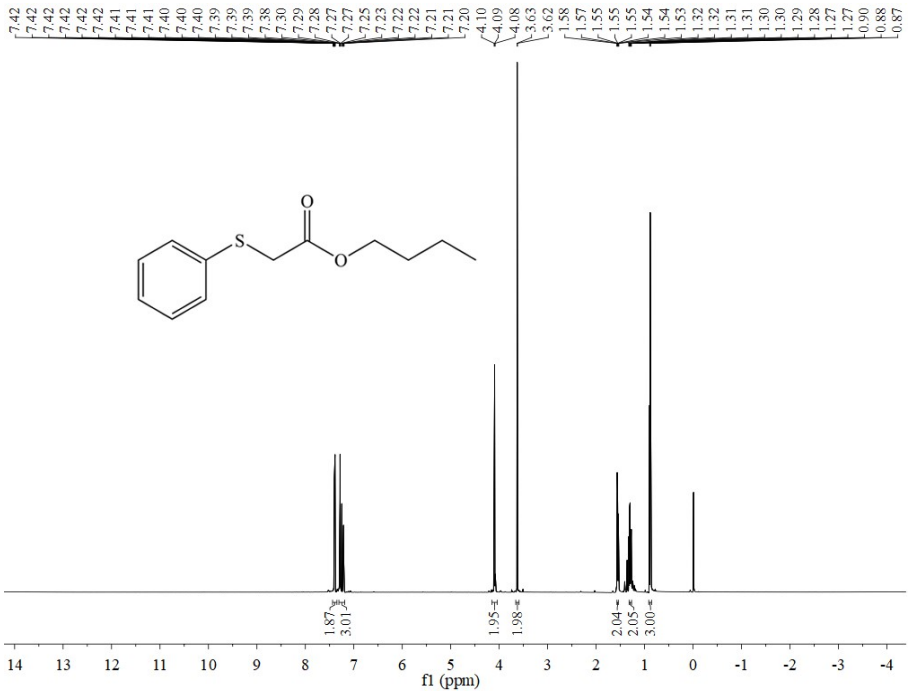


Figure S17 ^{1}H NMR spectra of (phenylthio)acetic acid butyl ester.

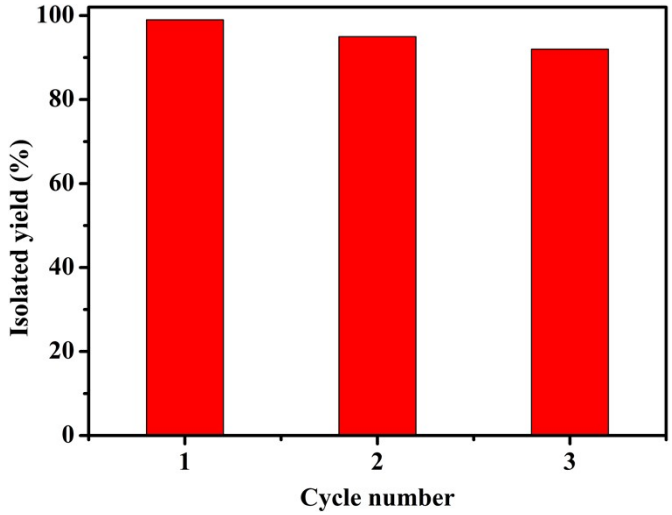


Figure S18 The recyclability of ZIF-90-DAB in the formation of (phenylthio)acetic acid butyl ester.

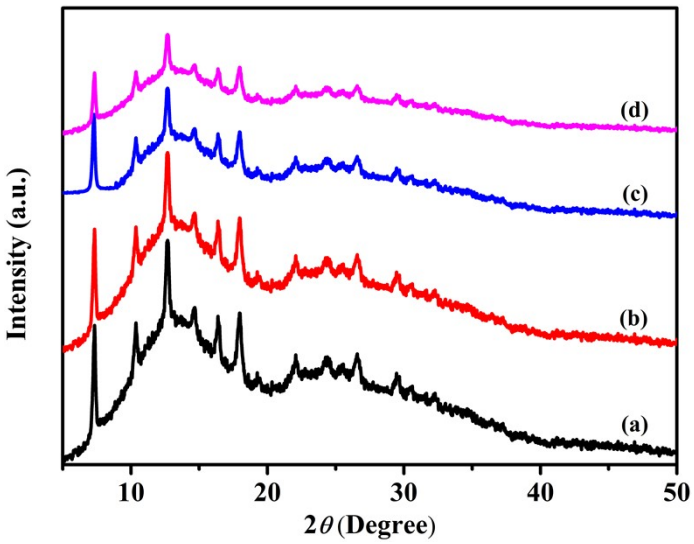


Figure S19 XRD patterns of the ZIF-90-DAB (a), the first recycled ZIF-90-DAB (b), the second recycled ZIF-90-DAB (c), and the third recycled ZIF-90-DAB (d).

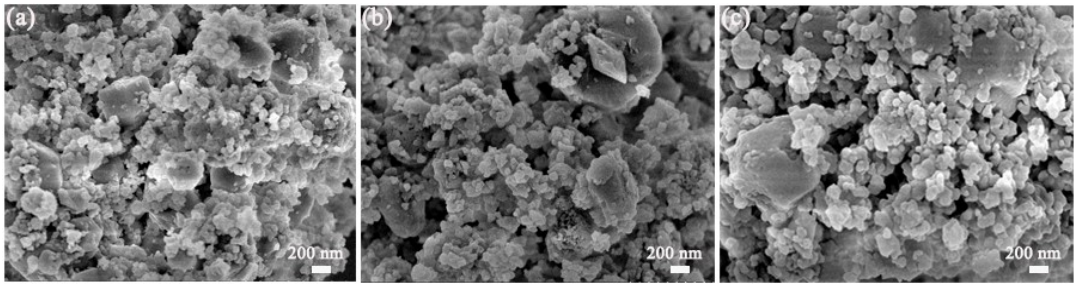


Figure S20 SEM images of the first recycled ZIF-90-DAB (a), the second recycled ZIF-90-DAB (b), and the third recycled ZIF-90-DAB (c).

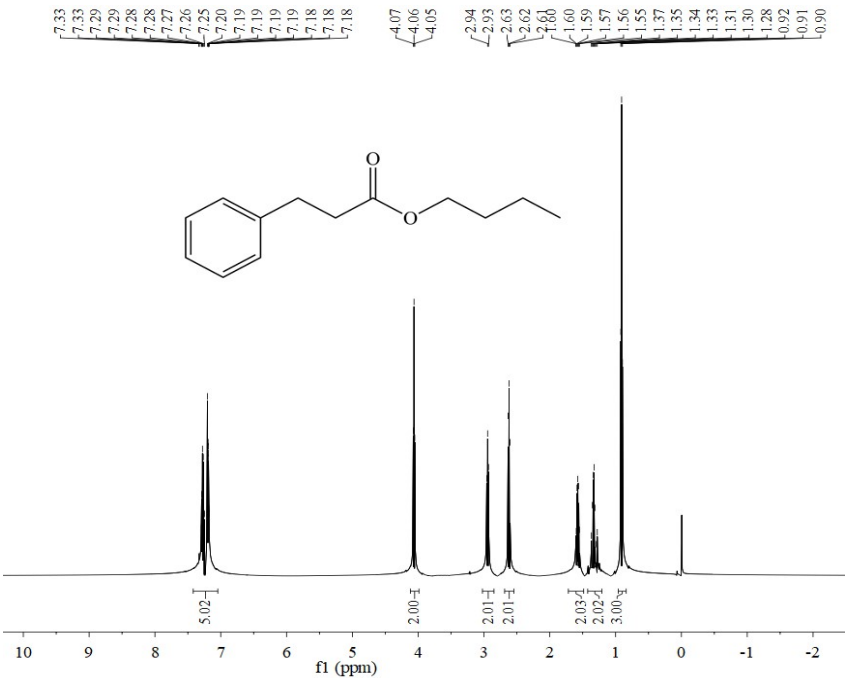


Figure S21 ^{1}H NMR spectra of 3-phenylpropionic acid butyl ester.

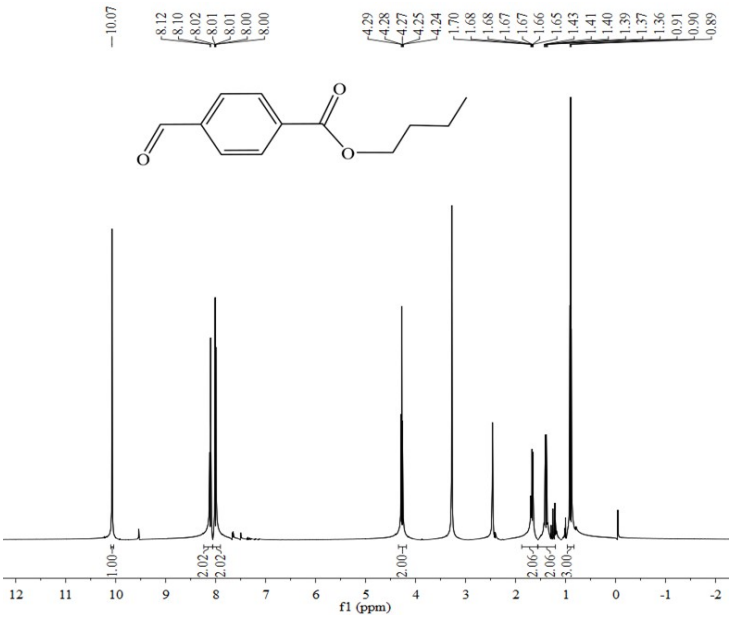


Figure S22 ^{1}H NMR spectra of butyl 4-formylbenzoate.

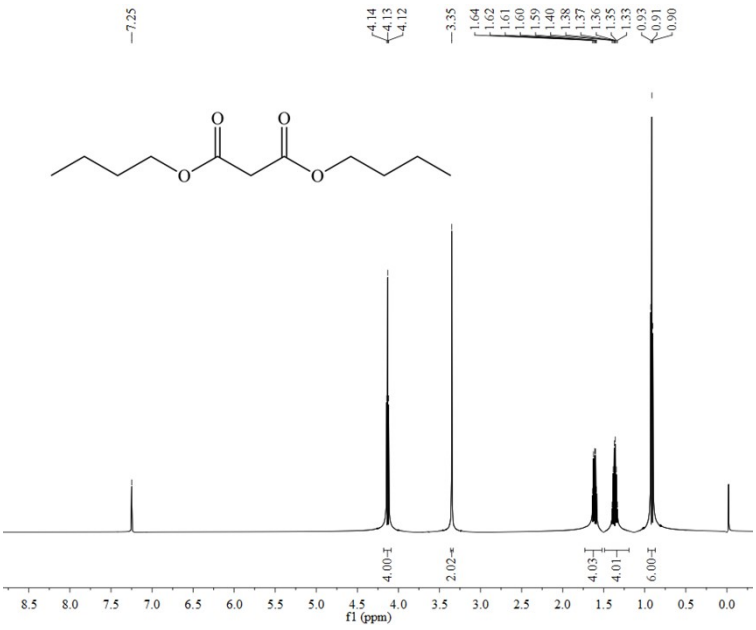


Figure S23 ^{1}H NMR spectra of dibutyl malonate.

4. References

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3 S. K. Karmee, A. Chadha, *Bioresour. Technol.*, 2005, **96**, 1425-1429.