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Supporting Information for

Thermo-responsive polymer-tethered and Pd NPs loaded UiO-66 NMOF for biphasic CBs dechlorination

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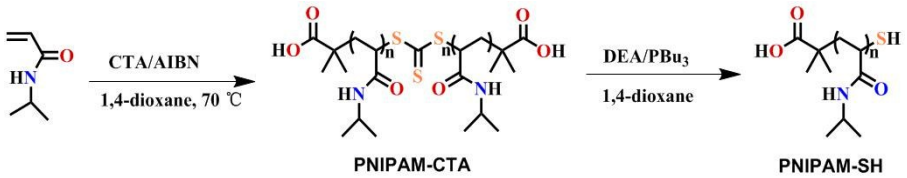
1. Synthesis and characterization of PNIPAM-CTA and PNIPAM-SH



Scheme S1 The synthesis of PNIPAM-CTA and PNIPAM-SH.

Synthesis of PNIPAM-CTA. The trithiocarbonate-containing polymer of PNIPAM-CTA was prepared according to the modified literature method.[1] Briefly, *N*-isopropyl acrylamide (NIPAM) monomer (6.12 g, 53 mmol) and 1,4-dioxane (16 mL) was added to a Schlenk flask and purged with high purity nitrogen in a dry ice bath for 15 min. The headspace of the flask was then purged with high purity nitrogen for 10 min. Then, AIBN (8.7 mg, 0.053 mmol) and S,S'-bis(α,α'-dimethylacetic acid) trithiocarbonate (CTA) (0.299 g, 1.06 mmol) were weighed into a separate Schlenk flask and exposed to three vacuum and nitrogen purge cycles to remove air. The NIPAM/1,4-dioxane solution was then transferred to the AIBN/CTA flask via cannula and reacted for 24 h at 70 °C. The polymerization was quenched by rapid cooling upon immersion of the flask into iced water. The synthesized polymer was precipitated in cold diethyl ether, and the precipitate was dried under vacuum at 80 °C overnight to afford a yellow powder of PNIPAM-CTA in 83 % yield. FTIR (KBr, cm^{-1}): 3297 (s), 2973 (m), 2877 (m), 1708 (m) 1655 (s), 1536 (s) 1473 (m), 1386 (m), 1375 (m), 1179 (m). ^{13}C NMR (DMSO-d_6, δ): (-CH_3, 22.76 ppm), (-*C*H-$(CH_3)_2$, 43.50 ppm), (-(CH_2-*C*H)$_n$-, 60.11-73.31 ppm), (>*C*=O, 161.65 ppm), (>*C*=S, 166.91 ppm), (>*C*=O, 173.81 ppm).

Synthesis of PNIPAM-SH. A mixture of PNIPAM-CTA (5.0 g, 1.0 mmol), 1,4-dioxane (16 mL), ethanolamine (1.2 mL, 10 mmol), and tributyl phosphine (530 μL, 1 mmol) was stirred at room temperature for 2 h under nitrogen to facilitate reduction of the trithiocarbonate linkage to thiol groups in the polymer. After precipitating in diethyl ether and drying under vacuum at 80 °C overnight, 5.6 g of sulfhydryl-terminated PNIPAM (PNIPAM-SH) was obtained as a white powder in 88 % yield. FTIR (KBr, cm^{-1}): 3301 (s), 2974(m), 2877(m), 1645(s), 1473 (m), 1386(m), 1376(m), 1166(m). ^{13}C NMR (DMSO-d_6, δ): (-CH_3, 22.60 ppm), (-*C*H-$(CH_3)_2$, 41.50 ppm), (-(CH_2-*C*H)$_n$-, 59.93-73.87 ppm), (>*C*=O, 163.455 ppm), (>*C*=O, 173.87 ppm).

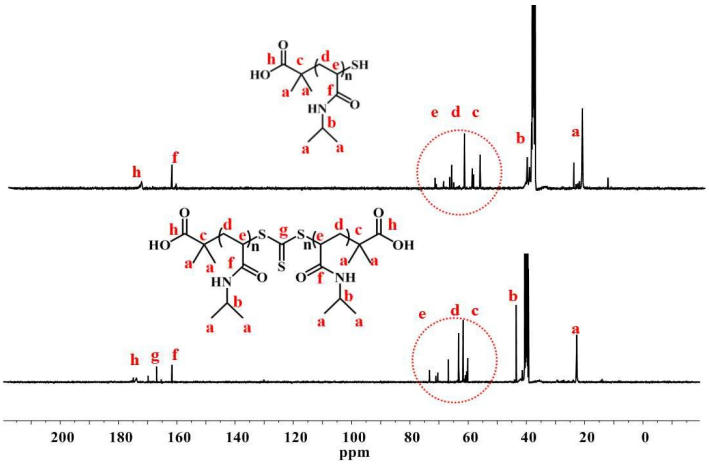


Fig. S1 ^{13}C spectra (in DMSO-d_6) of PNIPAM-CTA and PNIPAM-SH. Disappearance of the peak at 169.91 ppm belonging to the >C=S coupling groups indicated the successful synthesis of PNIPAM-SH chains.

Table S1. The calculated molecular weight and dispersion index of PNIPAM-CTA, PNIPAM-SH, and the freed PNIPAM chains obtained by digesting **UiO-66-S-PNIPAM** from GPC curves.

Specimen	M_n	M_w	M_p	PDI
PNIPAM-CTA	4824	5837	5362	1.21
PNIPAM-SH	2416	2972	2635	1.23
UiO-66-S-PNIPAM	2554	3167	2814	1.24

2. Additional characterization for UiO-66-based materials

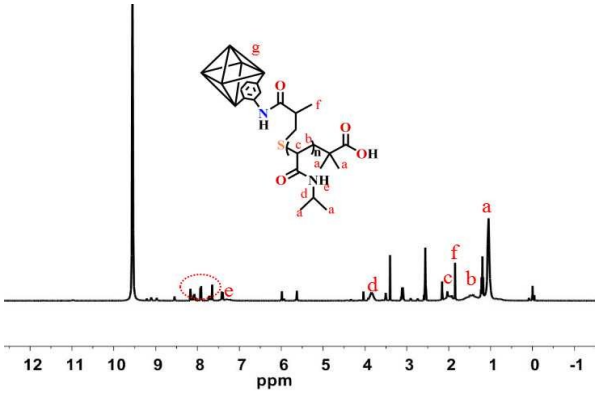


Fig. S2 ^{1}H NMR spectrum of **UiO-66-S-PNIPAM**.

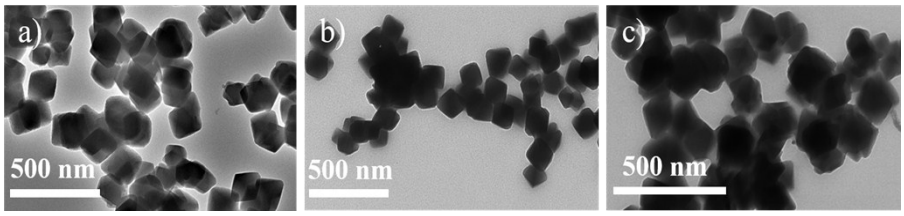


Fig. S3 TEM images of a) UiO-66-NH_2, b) UiO-66-Met, and c) **UiO-66-S-PNIPAM**.

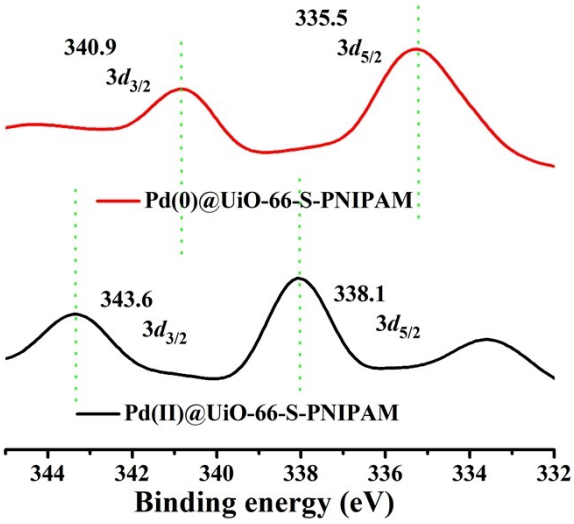


Fig. S4 XPS spectra of Pd(II)@UiO-66-S-PNIPAM and **Pd@UiO-66-S-PNIPAM**.

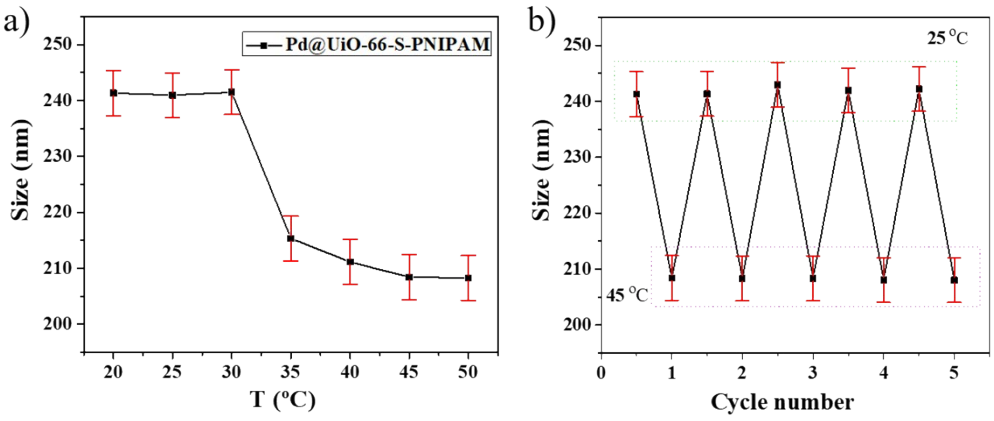


Fig. S5 a) Hydrodynamic diameters of **Pd@UiO-66-S-PNIPAM** in dilute aqueous solution at different temperatures. b) Five heating-cooling cycles in the range of 20 to 50 °C.

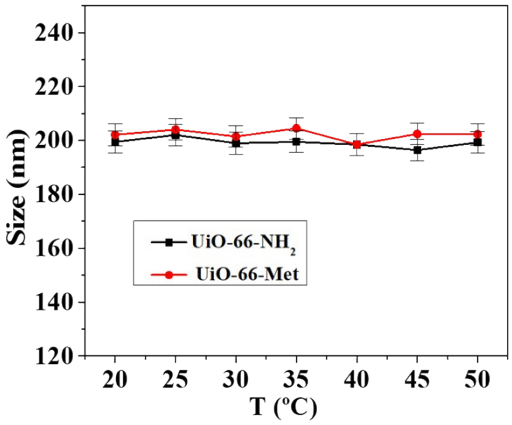


Fig. S6 Hydrodynamic diameters of UiO-66-NH_2 and UiO-66-Met in dilute aqueous solution of at different temperatures.

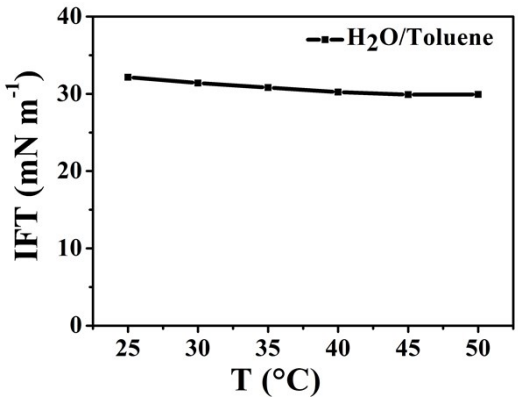


Fig. S7 IFT data of pure water/toluene measured at different temperatures.

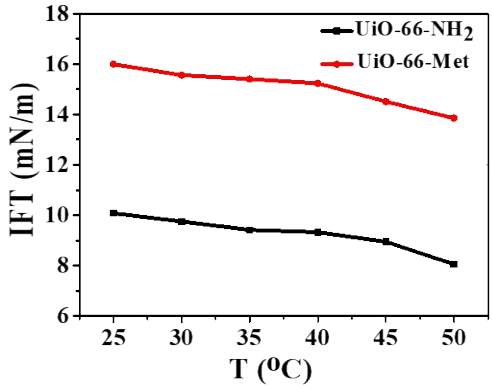


Fig. S8 IFT data of UiO-66-NH_2, and UiO-66-Met measured at different temperatures.

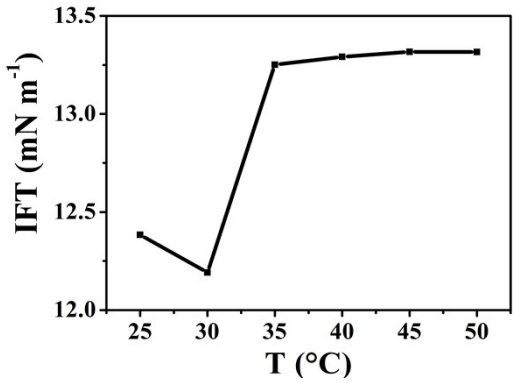


Fig. S9 IFT data of PNIPAM-SH measured at different temperatures.

3. Additional characterization of Pickering emulsion

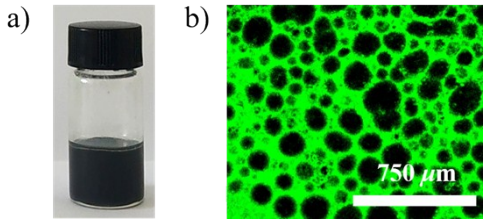


Fig. S10 a) Visual and b) confocal microscopy images of **Pd@UiO-66-S-PNIPAM** (2.0 wt%, toluene-to-water = 3:1, v/v)-stabilized toluene-in-water Pickering emulsion after two weeks storage.

4. Characterization for the dechlorination reaction

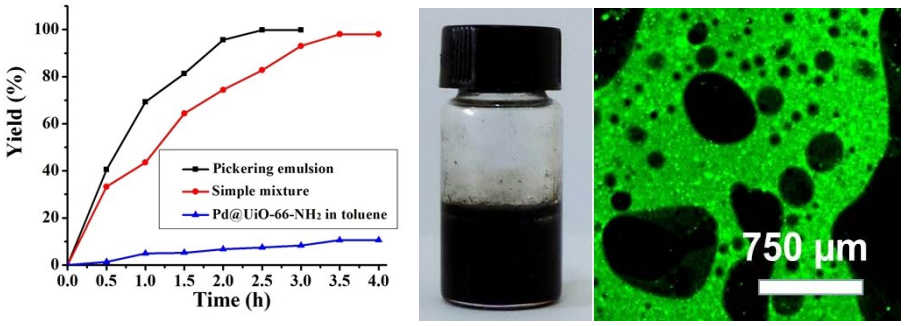


Fig. S11 Left: Comparison on the catalytic performance of Pickering emulsion (2.25 mL of toluene, 0.75 mL of H_2O) with that of simple water-toluene mixture (2.25 mL of toluene, 0.75 mL of H_2O) over **Pd@UiO-66-S-PNIPAM** and the monophasic toluene solution (3.00 mL of toluene) over **Pd@UiO-66-NH$_2$**. Reaction conditions for Pickering emulsion and simple water-toluene mixture: *p*-chloroacetophenone (1.0 mmol), HCO_2NH_4 (10 mmol), **Pd@UiO-66-S-PNIPAM** (58 mg, 2 mol % Pd NPs equiv), room temperature, in air. Reaction condition for monophasic toluene solution: *p*-chloroacetophenone (1.0 mmol), HCO_2NH_4 (10 mmol), 3.00 mL of toluene, **Pd@UiO-66-NH$_2$** (56 mg containing 2.2 mg of Pd, 2 mol % Pd NPs equiv), room temperature, magnetic stirring with a constant speed of 500 rpm, in air. The yields for the water-toluene mixture and monophasic toluene solution were 82 % and 9.8 % at 2.5 h, respectively. Right: Visual and confocal microscopy images of the simple water-toluene mixture after magnetic stirring.

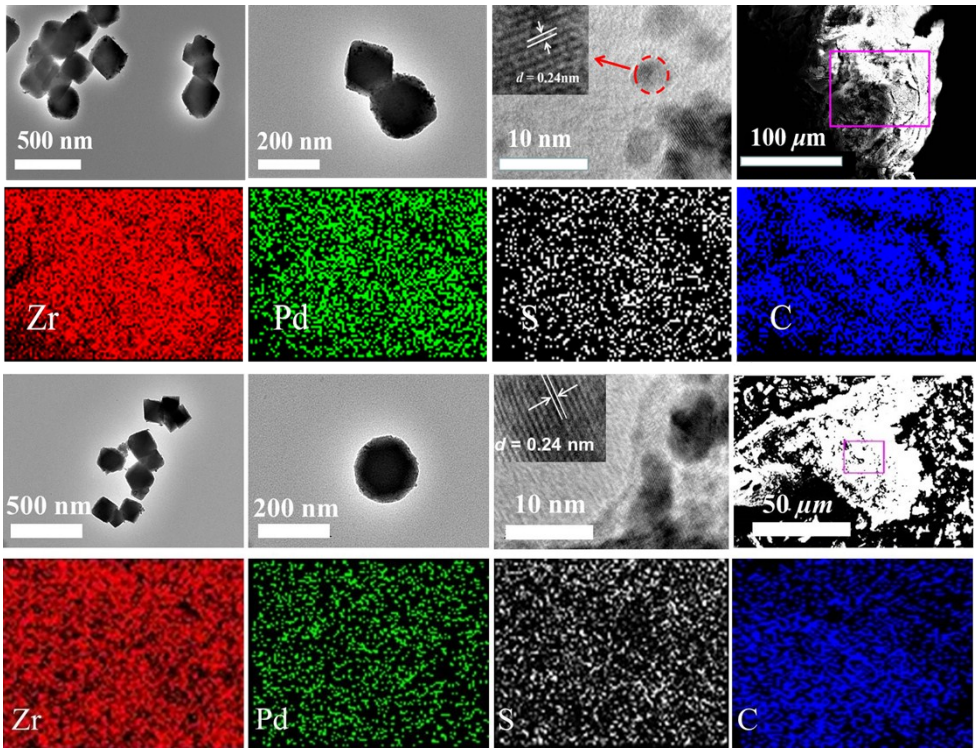


Fig. S12 HRTEM and SEM-EDX images of **Pd@UiO-66-S-PNIPAM** after five (top) and eight (bottom) catalytic runs.

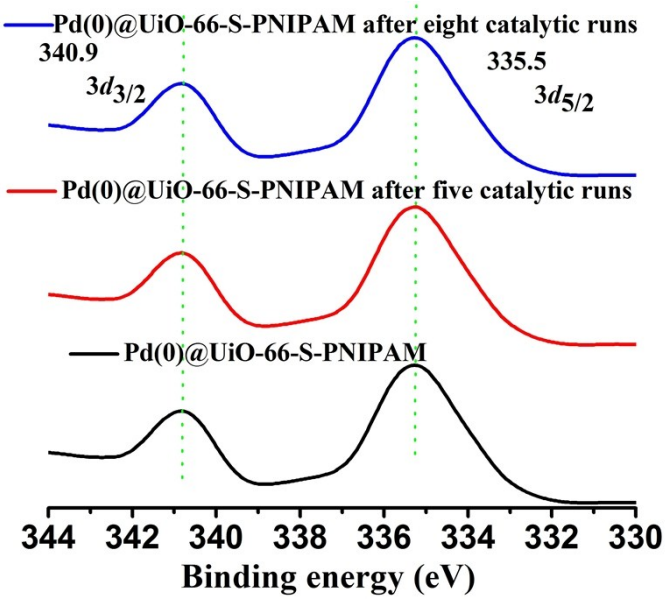


Fig. S13 XPS spectra of **Pd@UiO-66-S-PNIPAM** before and after five and eight catalytic runs.

Table S2. ICP results of UiO-66-NH_2, UiO-66-NH_2, UiO-66-Met, **UiO-66-S-PNIPAM**, and **Pd@UiO-66-S-PNIPAM** and it after five catalytic runs.

sample	Zr (wt %)	Pd (wt %)
UiO-66-NH_2	26.87	--
UiO-66-Met	23.06	--
UiO-66-S-PNIPAM	19.64	--
Pd@UiO-66-S-PNIPAM	17.68	3.81
Pd@UiO-66-S-PNIPAM after five catalytic runs	17.08	3.75
Pd@UiO-66-S-PNIPAM after eight catalytic runs	17.01	3.72

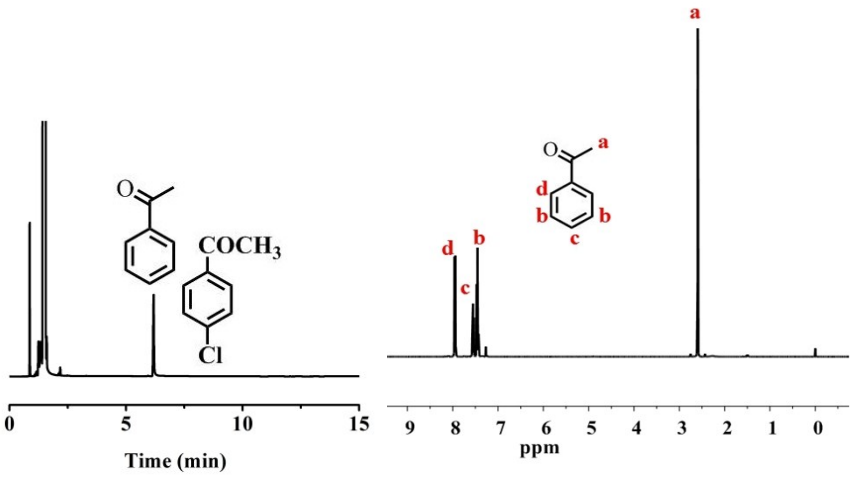


Fig. S14 GC and ^{1}H NMR ($CDCl_3$) spectra for the dechlorinating reaction of *p*-chloroacetophenone catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 2.5 h. The yield is ≥99 %.

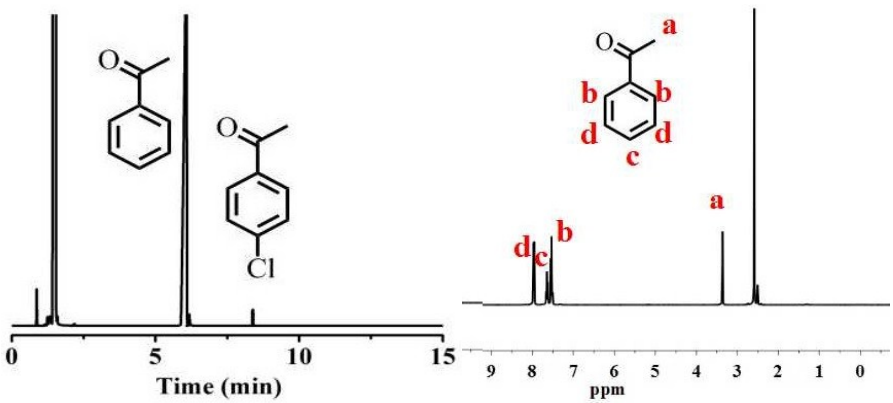


Fig. S15 GC and ^{1}H NMR ($CDCl_3$) spectra for the dechlorinating reaction of *p*-chloroacetophenone catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 2.5 h for five catalytic runs. The yield is 96 %.

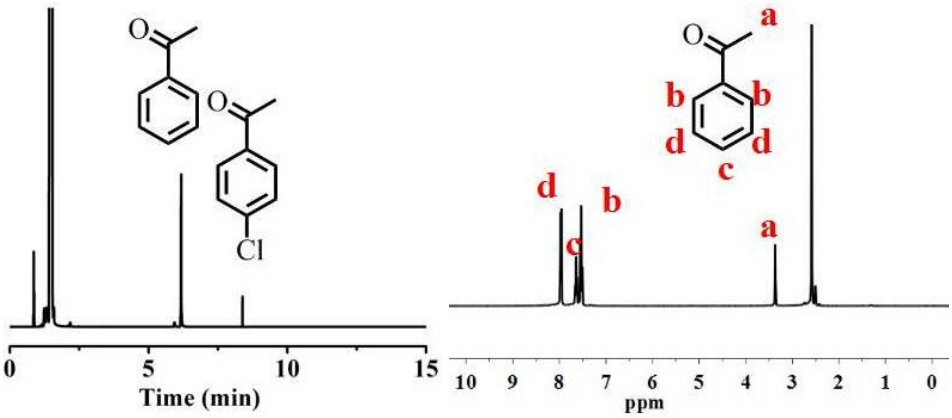


Fig. S16 GC and ^{1}H NMR ($CDCl_3$) spectra for the dechlorinating reaction of *p*-chloroacetophenone catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 2.5 h for eight catalytic runs. The yield is 93 %.

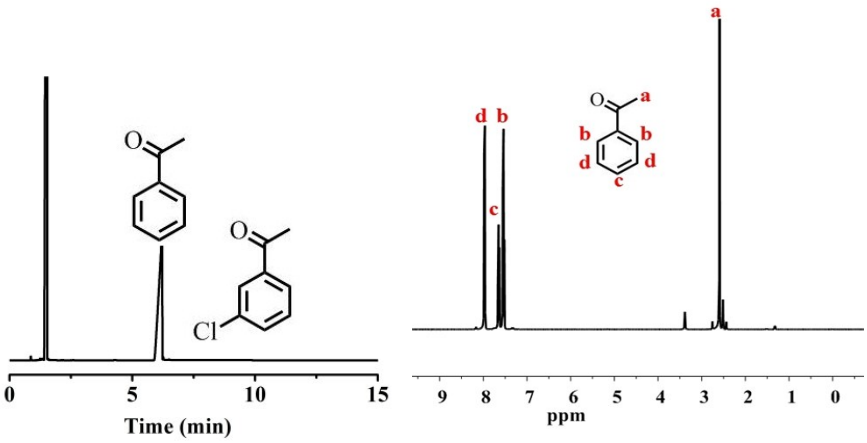


Fig. S17 GC and ^{1}H NMR (DMSO-d_6) spectra for the dechlorinating reaction of *m*-chloroacetophenone catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 2.5 h. The yield is ≥99 %.

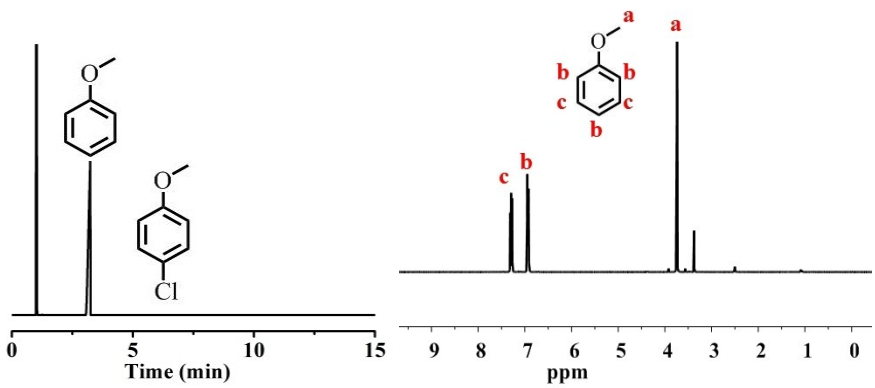


Fig. S18 GC and ^{1}H NMR (DMSO-d_6) spectra for the dechlorinating reaction of *p*-chlorophenyl ether catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 2.5 h. The yield is ≥99 %.

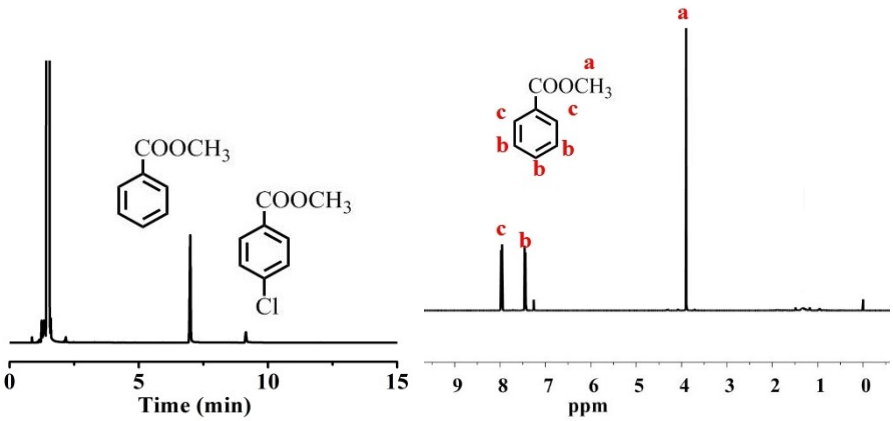


Fig. S19 GC and ^{1}H NMR ($CDCl_3$) spectra for the dechlorinating reaction of methyl *p*-chlorobenzoate catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 4 h. The yield is 94 %.

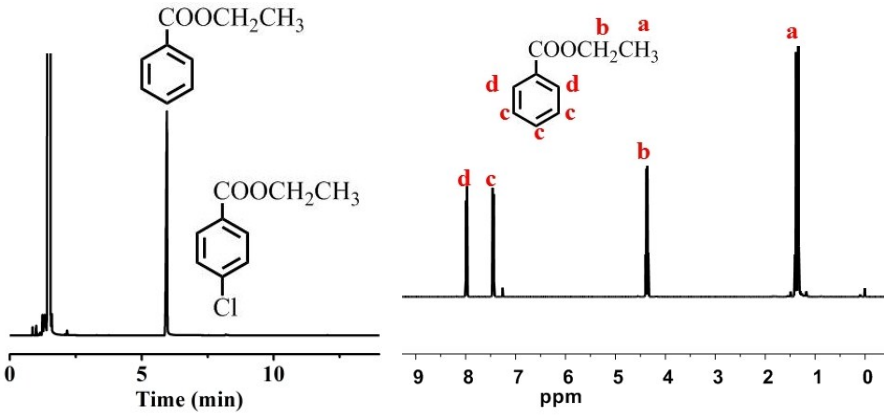


Fig. S20 GC and ^{1}H NMR ($CDCl_3$) spectra for the dechlorinating reaction of ethyl 4-chlorobenzoate catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 4 h. The yield is 99 %.

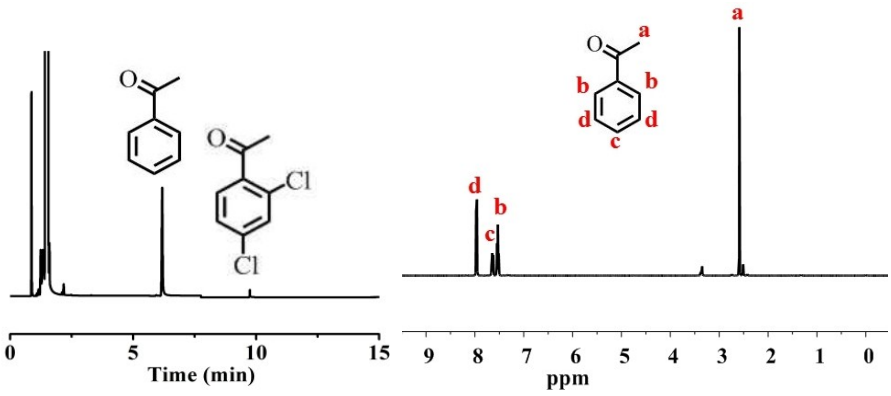


Fig. S21 GC and ^{1}H NMR (DMSO-d_6) spectra for the dechlorinating reaction of 2,4-dichoroacetophenone catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 4 h. The yield is 97 %.

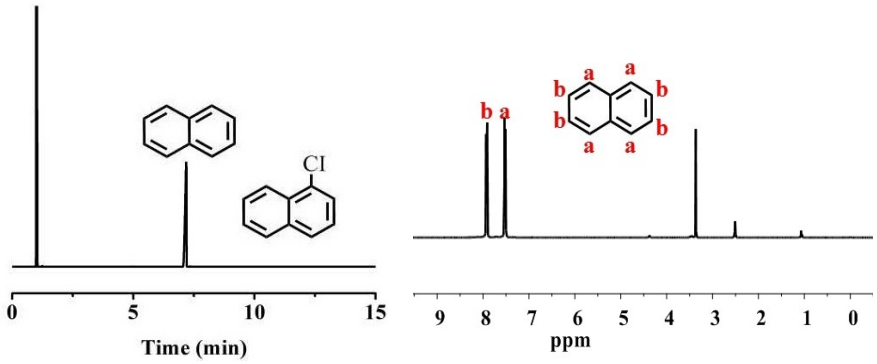


Fig. S22 GC and ^{1}H NMR (DMSO-d_6) spectra for the dechlorinating reaction of 1-chloronaphthalene catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 4 h. The yield is 99 %.

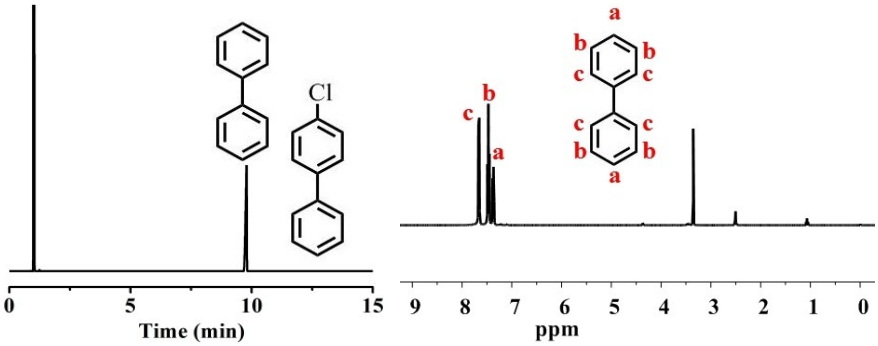


Fig. S23 GC and ^{1}H NMR (DMSO-d_6) spectra for the dechlorinating reaction of 4-chlorobiphenyl catalyzed by **Pd@UiO-66-S-PNIPAM**-stabilized Pickering emulsion at 4 h. The yield is 98 %.

5. Samples abbreviation

Table S3. Abbreviation of the sample names in the manuscript.

Samples	Abbreviation
Methacrylamide group decorated UiO-66-MOF NPs	UiO-66-Met
trithiocarbonate-containing poly(*N*-isopropyl acrylamide)	PNIPAM-CAT
Thiol-terminated poly(*N*-isopropyl acrylamide)	PNIPAM-SH
Poly(*N*-isopropyl acrylamide) sulfide (PNIPAM-S-) brushes-tethered UiO-66-MOF NPs	UiO-66-S-PNIPAM
Poly(*N*-isopropyl acrylamide) sulfide (PNIPAM-S-) brushes-tethered and Pd nano particles (NPs) loaded UiO-66-MOF NPs	Pd@UiO-66-S-PNIPAM
chlorobenzenes	CBs
chlorinated aromatic compounds	ArCl

6. References

[1] M. Li, P. De, S. R. Gondi, B. S. Sumerlin, *J. Polym. Sci., Part A: Polymer Chemistry*, 2008, **46**, 5093–5100.