Supporting Information

Yolk-shell smart Pickering nanoreactors for base-free one-pot cascade Knoevenagel-Hydrogenation with high catalytic efficiency in water

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Experimental Section

Synthesis of 2,5-Bis[(E)-2-(triethoxysilyl)vinyl]pyridine

2,5-Bis(trimethylsilylethynyl)pyridine. A suspension of 2,5-diiodopyridine (10 g, 30.2 mmol), $PdCl_2(PPh_3)_2$ (0.85 g, 1.21 mmol) and CuI (0.12 g, 0.60 mmol) in iPr_2NH (120 ml) and THF (40 ml) was cooled with an ice bath, and then to this suspension was added trimethylsilylacetylene (11.8 g, 121 mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 16 h. The resulting mixture was filtered to remove insoluble matter, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/AcOEt = 10:1) to give 2,5-bis(trimethylsilylethynyl)pyridine (7.4 g, 90%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.26 (9 H, s), 0.27 (9 H, s), 7.38 (1 H, d, J = 8.24 Hz), 7.68 (1 H, dd, 8.24 Hz), 8.62 (1

H, s); ^{13}C NMR (100MHz, CDCl$_3$): δ -0.1, 0.0, 97.3, 100.5, 101.4, 103.6, 119.8, 126.7, 139.0, 141.9, 152.9. The ^{1}H and ^{13}C NMR data were identical to those reported in the literature.

2,5-Diethynylpyridine. To a THF (160 mL) solution of 2,5-bis(trimethylsilylethynyl)pyridine (7.4g, 27.1 mmol) was added n-Bu$_4$NF (1.0 M THF solution, 60 mL, 60 mmol) and a few drops of H$_2$O subsequently. The reaction mixture was stirred for 4 h at room temperature, concentrated, and diluted with ether/H$_2$O. The separated ether layer was washed with brine, dried over MgSO$_4$, and then the solvent was completely evaporated. The residue was chromatographed on silica gel (hexane/AcOEt = 3:1) to give 2,5-diethynylpyridine (3.0 g, 88%). ^{1}H NMR (400 MHz, CDCl$_3$): δ3.26 (1 H, s), 3.31 (1 H, s), 7.45 (1 H, dd, J = 7.32 Hz), 7.75 (1 H, dd, J = 10.52 Hz), 8.68-8.69 (1 H, m); ^{13}C NMR (100 MHz, CDCl$_3$): δ 79.1, 79.9, 82.3, 82.4, 119.0, 126.7, 139.2, 141.5, 152.9. The ^{1}H and ^{13}C NMR data were identical to those reported in the literature.

2,5-Bis[(E)-2-(triethoxysilyl)vinyl] pyridine. To a CH$_3$CN (27 mL) solution of 2,5-diethynylpyridine (0.30 g, 2.36 mmol), [Rh(cod)Cl]$_2$ (23 mg, 0.047 mmol), PPh$_3$ (50 mg, 0.19mmol) was added triethoxysilane (1.55 g, 9.44 mmol) under an argon atmosphere. The reaction mixture was stirred at 100 ºC for 24 h. After cooling to room temperature, the reaction mixture was filtered through charcoal and Celite bed, and then the solvent was completely evaporated. The residue was purified by Kugelrohr distillation at 190–200 ºC/30 Pa to give 2,5-Bis[(E)-2-(triethoxysilyl)vinyl]pyridine (0.47 g, 44%) as a yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.25–1.29 (18 H, m),

3.86−3.92 (12 H, m), 6.27 (1 H, d, J = 19.68 Hz),6.70 (1 H, d, J = 19.68 Hz), 7.19 (1 H, d, J = 19.68 Hz), 7.28 (1 H, d, J = 19.20 Hz), 7.40 (1 H, d, J= 8.24 Hz) 7.77−7.79 (1 H, m), 8.64 (1 H, d, J = 2.28 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 18.2,58.7, 120.9, 121.7, 123.3, 132.4, 133.5, 145.0, 147.9, 148.9, 155.1;

Synthesis of 1,4-bis-((E)-2-(triethoxysilyl)vinyl)-benzene

In a typical synthesis 30.12 g (0.128 mol) of 1,4-dibromobenzene was dissolved in 220 mL of dimethylformamide in a 500 mL three-necked-flask. To this solution 55 mL (0.261 mol) of vinyltriethoxysilane, 70 mL (0.512 mol) of triethylamine, and 0.493 g (4.27 × 10^{-4} mol) of tetrakis(triphenylphosphine)-palladium were added. After the reaction mixture was stirred for 4d at 110 °C under an argon atmosphere, the resulting solution was cooled to 0 °C to complete the precipitation of the formed salt (HNEt$_3$Br). After removal of the salt by filtration, the solvent was removed under reduced pressure. The obtained raw product was purified by Kugelrohr distillation. For further purification of the precursor this distillation step was repeated twice: 41.7 g (0.092mol, yield: 71%) of the organosilane precursor was obtained as a slightly yellow transparent liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ1.27 (t, J) 6.89 Hz, 18 H), 3.89 (q, J) 6.89 Hz, 12 H), 6.19 (d, J) 19.2 Hz, 2 H), 7.20 (d, J) 19.2 Hz, 2 H), 7.46 (s, 4 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 18.2, 58.5, 118.2, 126.9, 137.9, 148.3.

Dispersion process of Pickering Pd@Py-PMO nanoreactors in water or organic solvents

6 mg Pd@Py-PMO nanoparticles were added into 5 ml water, toluene, styrene,

nitrobenzene and 3-nitrostyrene respectively. After ultrasonic treatment for 5 minutes, the solution was placed for 5 hours before the phenomenon was observed.

Equilibrium adsorption isotherms of Pd@Py-PMO nanoparticles

Different amounts of styrene, nitrobenzene and 3-nitrostyrene (50 μL, 150 μL, 250 μL, 350 μL and 450 μL) were added to 25 mL of water containing 100 mg of Pd@Py-PMO nanoparticles at 293 K, 298 K, 303 K and 308 K, respectively. The adsorption was carried out in a sealed glass vial by equilibrating the mixture for 6 h on a magnetic stirring apparatus. After adsorption, the materials were directly removed from solution by filtration. The styrene, nitrobenzene and 3-nitrostyrene in water were extracted by ethyl acetate for 3 times. Then, the amounts of styrene, nitrobenzene and 3-nitrostyrene in ethyl acetate was measured with an external standard method by gas chromatography.

Equilibrium adsorption isotherms of Pd@Ph-PMO nanoparticles

Different amounts of styrene (50 μL, 150 μL, 250 μL, 350 μL and 450 μL) were added to 25 mL of water containing 100 mg of Pd@Ph-PMO nanoparticles at 293 K, 298 K, 303 K and 308 K, respectively. The adsorption was carried out in a sealed glass vial by equilibrating the mixture for 6 h on a magnetic stirring apparatus. After adsorption, the materials were directly removed from solution by filtration. The styrene in water were extracted by ethyl acetate for 3 times. Then, the amount of styrene in ethyl acetate was measured with an external standard method by gas chromatography.

Equilibrium adsorption isotherms of Pd@V-Ph-PMO nanoparticles

Different amounts of nitrobenzene (50 μL, 150 μL, 250 μL, 350 μL and 450 μL) were added to 25 mL of water containing 100 mg of Pd@V-Ph-PMO nanoparticles at 293 K, 298 K, 303 K and 308 K, respectively. The adsorption was carried out in a sealed glass vial by equilibrating the mixture for 6 h on a magnetic stirring apparatus. After adsorption, the materials were directly removed from solution by filtration. The nitrobenzene in water were extracted by ethyl acetate for 3 times. Then, the amount of nitrobenzene in ethyl acetate was measured with an external standard method by gas chromatography.

To obtain the working curve of styrene, nitrobenzene and 3-nitrostyrene in ethyl acetate, the different known styrene, nitrobenzene and 3-nitrostyrene in ethyl acetate was measured under the same condition by gas chromatography. A well-fitted linear equation, $A = 94.15 \cdot C + 6.01$, was obtained with a correlation coefficient (R^2) of 0.9998, where C is the concentration of styrene, nitrobenzene and 3-nitrostyrene in ethyl acetate, A is the peak area corresponding to different concentrations. The adsorption capacities of the materials were calculated according to the equation of $Q_e = (C_0 - C_e) V/m$, where C_0 and C_e represent the initial and equilibrium concentrations (mg/g), where V is the volume of the solution (mL), and m is the amount of the materials (mg).

Calculation of Adsorption Enthalpy

250μL of styrene, nitrobenzene or 3-nitrostyrene were added to 25 mL of water containing 100 mg of Pd@Py-PMO, Pd@Ph-PMO or Pd@V-Ph-PMO at different

temperatures (293 K, 298 K, 303 K and 308 K). The processing steps were the same as above. The adsorption enthalpy was calculated following the derivative Clausius-Clapeyron equation, $lnCe=\Delta H/(RT)+lnK$, where ΔH is the adsorption enthalpy (KJ/mol), T is the absolute temperature (K), R is the ideal gas constant [8.314 J/(mol·K)], and K is a constant.

Hydrogenation reaction of intermediate tests using porous structured Pd@Py-PMO, Pd@Ph-PMO and Pd@V-Ph-PMO nanospheres

We did controlled experiments using porous structured Pd@Py-PMO, Pd@Ph-PMO and Pd@V-Ph-PMO nanoparticles. In a typical controlled experiment, 25mg of the controlled nanoparticles, 0.6 mmol of intermediate B, 1.0 mL of diethyl malonate and 3.0 mL of H_2O were added in a 50 mL Schlenk tube equipped with a magnetic stirrer. The above reaction system was performed at 298 K in hydrogen of ordinary pressure under the stirring condition to complete the Hydrogenation reaction. After completion of the Hydrogenation reaction, the solid nanospheres were recovered by centrifugation and the product was extracted by ethyl acetate 3 times. The liquid phase was subsequently analyzed by using a gas chromatography-mass spectrum Shimadzu GCMS-QP2010 Plus with a flame ionization detector (FID), using dodecane as an internal standard. The column was GsBP-1 ms (30 m); the initial temperature was 50 °C, the heating rate was 10 °C min^{-1}, and the final temperature was 280 °C, the temperature of the FID detector was 250 °C.

Supplementary Figures and Legends
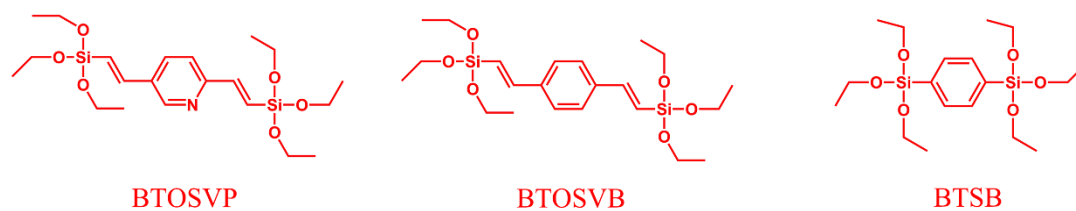
Figure S1. Structural formula of 2,5-Bis[(E)-2-(triethoxysilyl)vinyl]pyridine (BTOSVP), 1,4-bis-[(E)-2-(triethoxysilyl)vinyl]-benzene (BTOSVB) and 1,4-Bis(triethoxysilyl)benzene (BTSB).
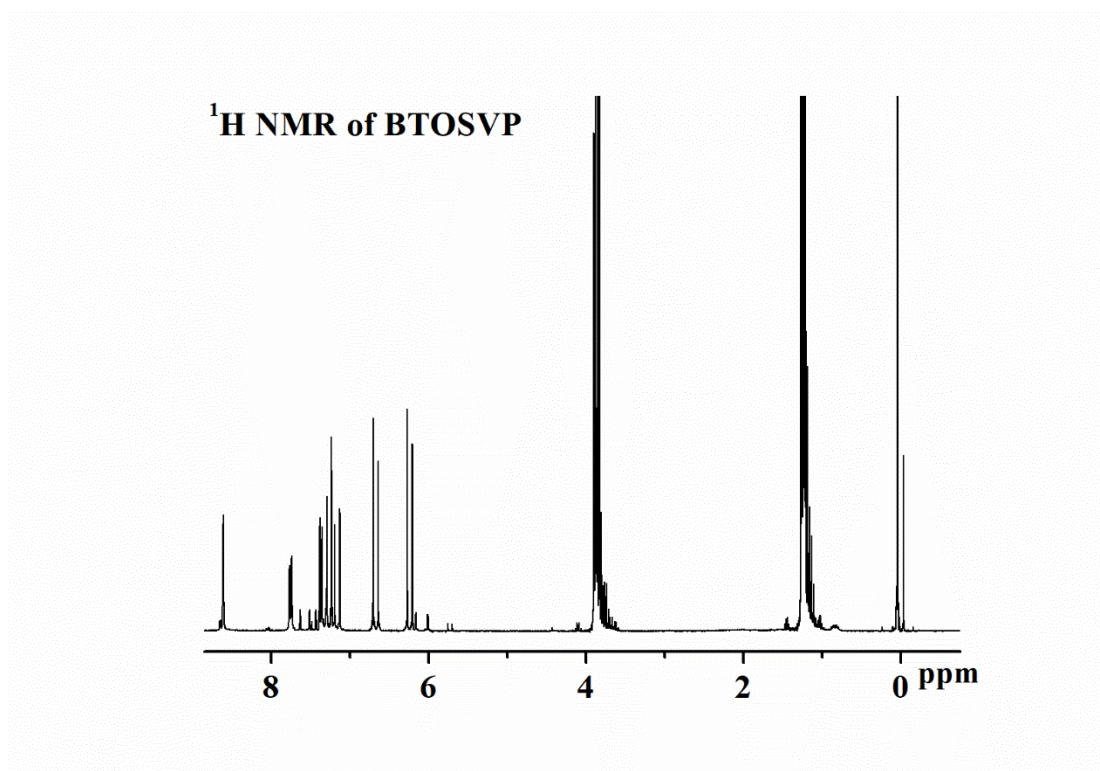
Figure S2. ^{1}H NMR spectra of 2,5-bis[(E)-2-(triethoxysilyl)vinyl]pyridine.
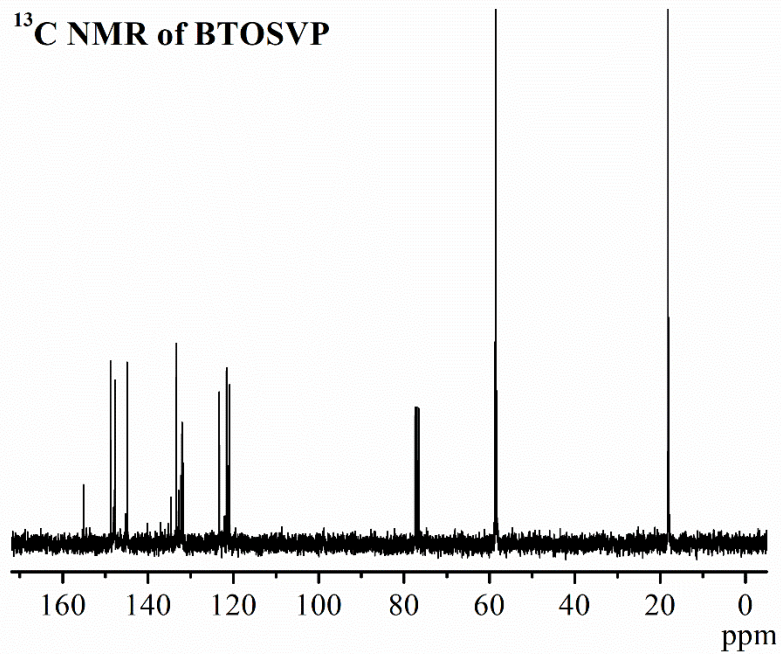
Figure S3. ^{13}C NMR spectras of 2,5-bis[(E)-2-(triethoxysilyl)vinyl]pyridine.
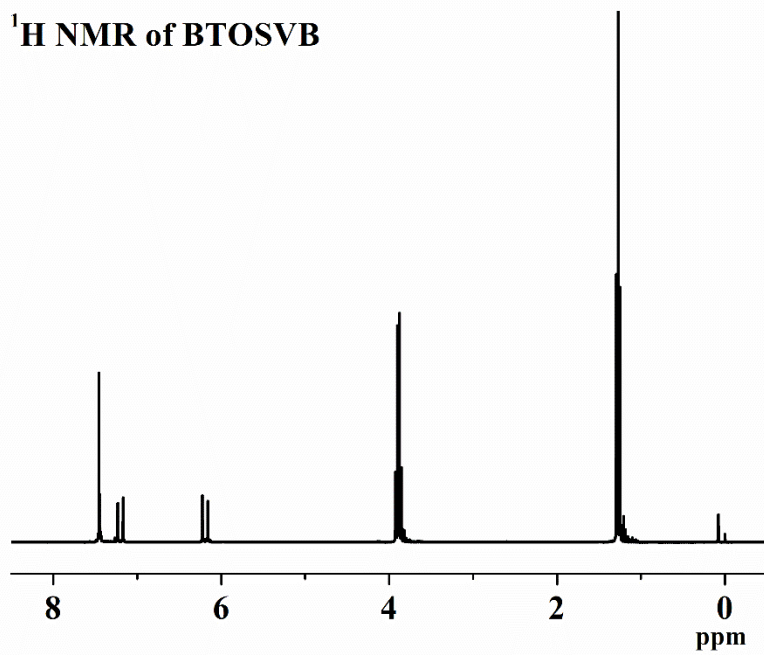
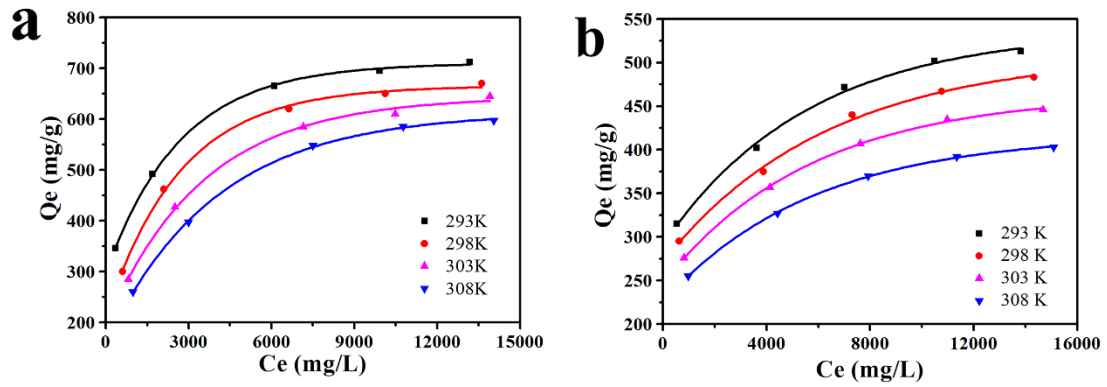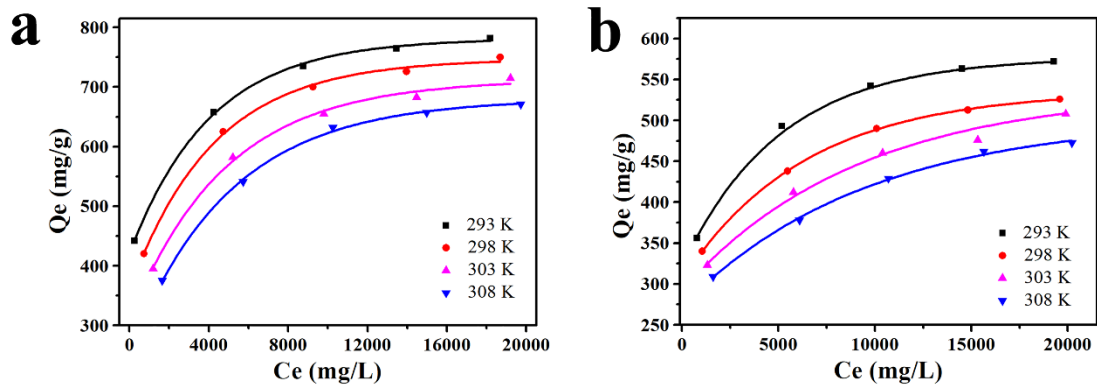**Figure S4.** ^{1}H NMR spectras of 1,4-bis-((E)-2-(triethoxysilyl)vinyl)-benzene.
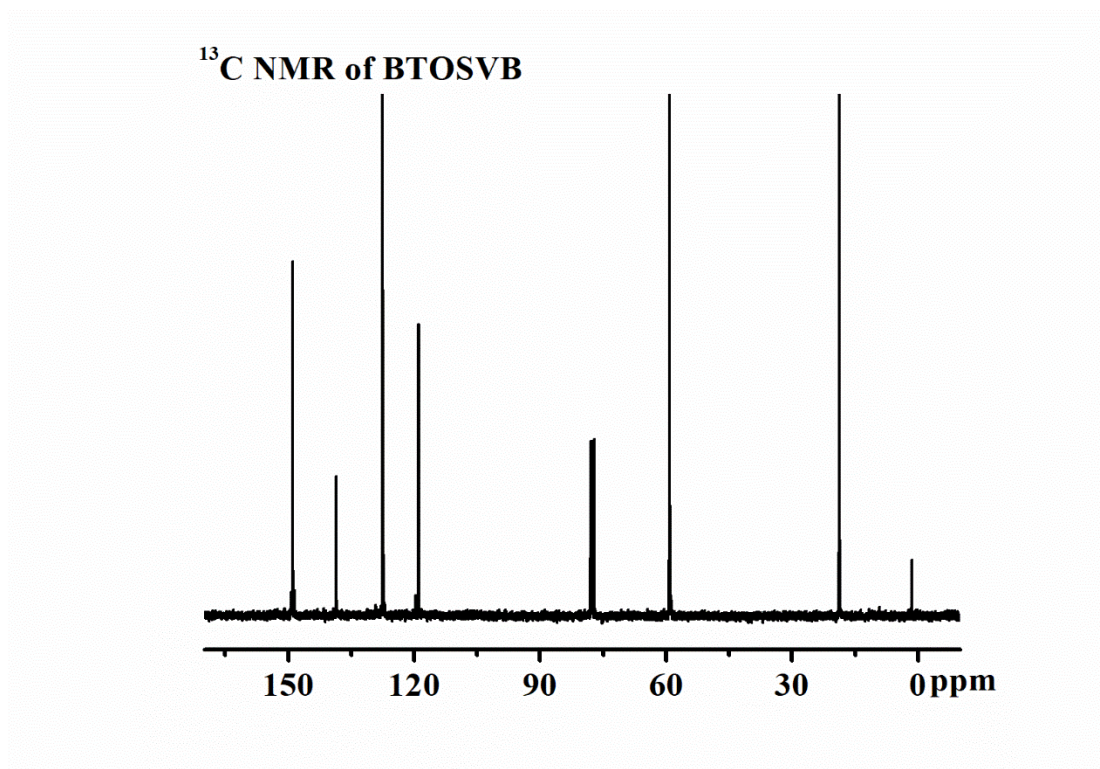
Figure S5. ^{13}C NMR spectras of 1,4-bis-((E)-2-(triethoxysilyl)vinyl)-benzene.
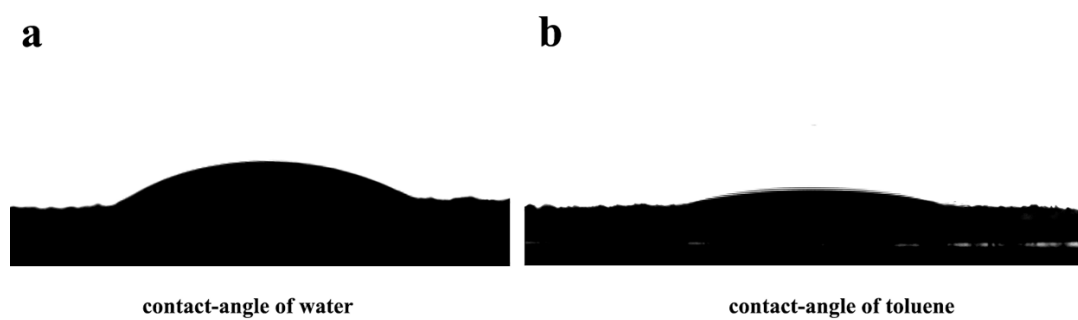
Figure S6. Water contact-angle (a) and oil contact-angle (b) of the Pd@Py-PMO nanoreactors.
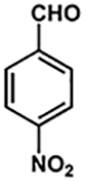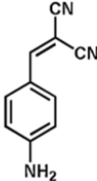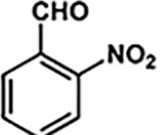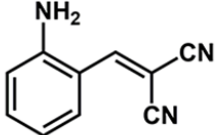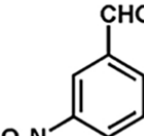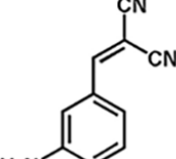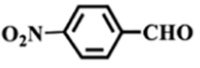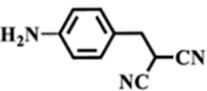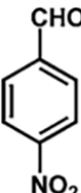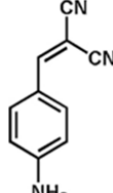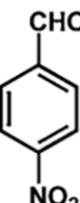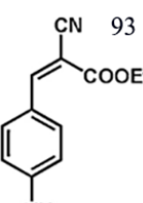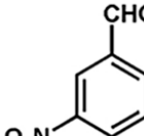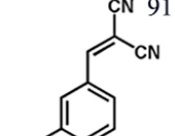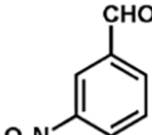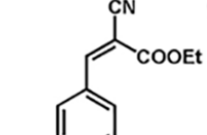
**Figure S7.** Adsorption Isotherms of Pd@Py-PMO to styrene (a) and Pd@Ph-PMO to styrene (b).

Figure S8. Adsorption Isotherms of Pd@Py-PMO to nitrobenzene (a) and Pd@V-Ph-PMO to nitrobenzene (b).


$$q_e = (C_0 - C_e) \, V/m$$
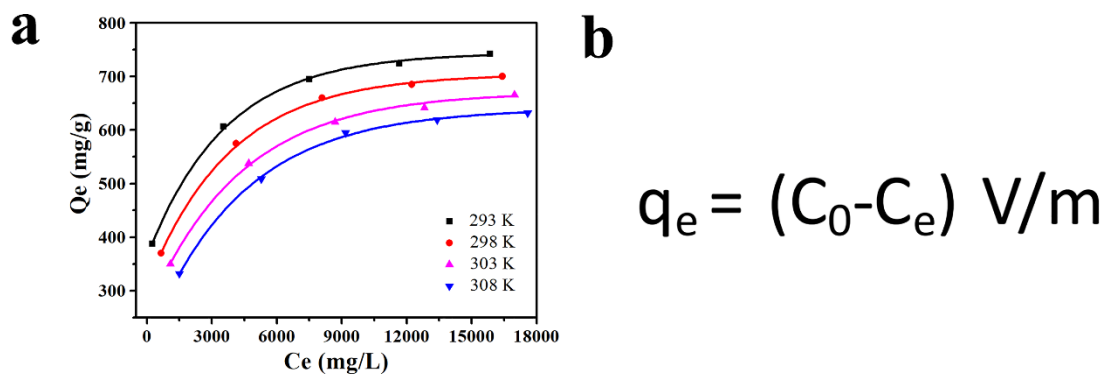
Figure S9. Adsorption Isotherm of Pd@Py-PMO to 3-nitrostyrene (a) and (b) The equation of Clausius−Clapeyron to calculate the adsorption capacities of the materials.

| catalyst	Substrate	T (K)	Time (h)	Solvent	Product	Yield (%)
Pd@ MOF-3 [1]		298	3.5	Toluene -Water		95
		298	3.5	Toluene -Water		91
		298	3.5	Toluene -Water		62
Fe₃O₄@ CFR- SPNIPAM₃ @ Pd/CDs [2]		298	24.5	Water		71.2
Pd/DETA- APP [3]		333	6	Ethanol		95
		333	6	Ethanol		93
		333	6	Ethanol		91
		333	6	Ethanol		91

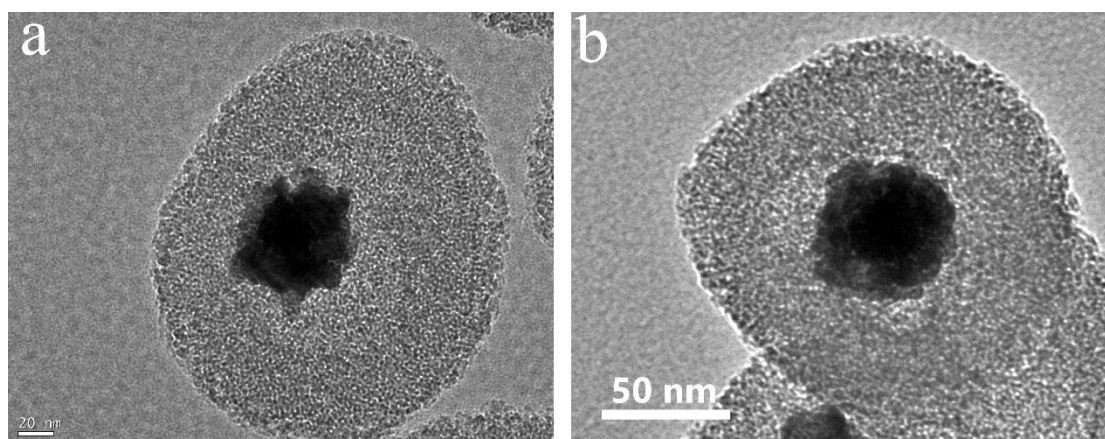**Figure S10.** The Knoevenagel-Hydrogenation reactions catalyzed by reported catalysts.[1,2,3]
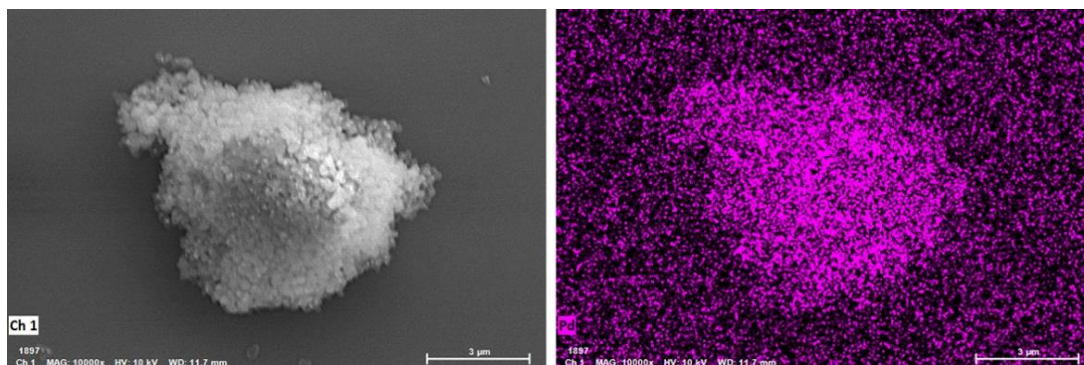
Figure S11. Elemental mapping of Pd of the recovered Pd@Py-PMO nanoreactors.
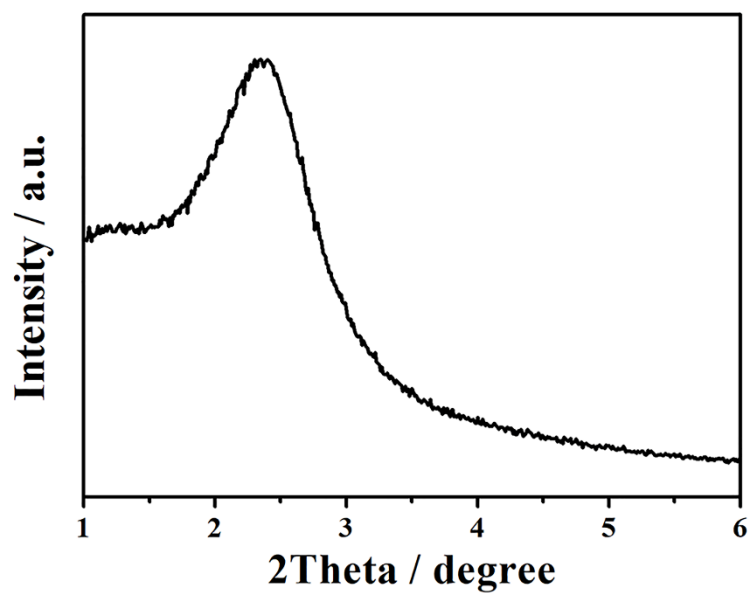
Figure S12. The small-angle XRD of the novel smart Pd@Py-PMO nanoreactor after being reused for eight times
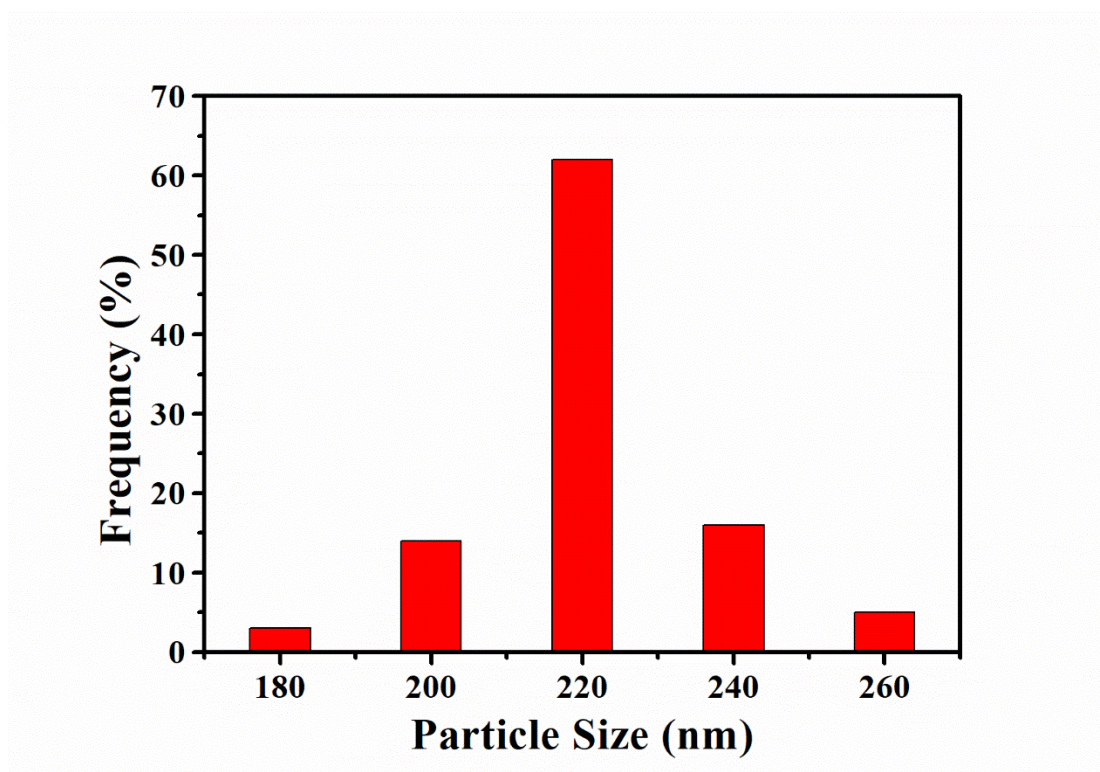
Figure S13. Particle size distribution of Pd@Py-PMO nanoparticles.

Figure S14. TEM images of control materials Pd@V-Ph-PMO (a) and Pd@Ph-PMO (b).

Notes and references

1. W.-L. Jiang, Q.-J. Fu, B.-J. Yao, L.-G. Ding, C.-X. Liu, and Y.-B. Dong, Smart pH-Responsive Polymer-Tethered and Pd NP-Loaded NMOF as the Pickering Interfacial Catalyst for One-Pot Cascade Biphasic Reaction, *ACS Appl. Mater. Interfaces*, 2017, **9**, 36438-36446.

2. Y. Yang, W. J. Zhu, B. F. Shi and C. l. Lu, Construction of a thermo-responsive polymer brush decorated Fe_3O_4@catechol-formaldehyde resin core–shell nanosphere stabilized carbon dots/PdNP nanohybrid and its application as an efficient catalyst, *J. Mater. Chem. A*, 2020, **8**, 4017-4029.

3. P. Puthiaraj, K. Yu, S.-H. Baeck and W.-S. Ahn, Cascade Knoevenagel condensation-chemoselective transfer hydrogenation catalyzed by Pd nanoparticles stabilized on amine-functionalized aromatic porous polymer, *Catalysis Today*, 2020, **352**, 298-307.