Supporting Information

Polyhedral Metal-Organic Framework Monolayer Colloidal Crystals with Sharpened and Crystal Facet-Dependent Selectivity for Organic Vapor Sensing

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EXPERIMENTAL

Chemicals and materials. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was purchased from Alfa Aesar. Hexahydrate zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 2-methylimidazole ($C_4H_6N_2$) were purchased from Sigma-Aldrich Company. 1-methylimidazole ($C_4H_6N_2$) and cetyltrimethylammonium bromide (CTAB, $C_{16}H_{33}(CH_3)_3NBr$) were purchased from Macklin Company. Polyvinylpyrrolidone (PVP, K30) was purchased from Yuanye Biological Company. Methanol (CH_3OH, 99%), ethanol (C_2H_5OH, 99%), n-propanol (C_3H_7OH, 99%), n-butanol (C_4H_9OH, 99%), n-pentanol ($C_5H_{11}OH$, 99%), isopropanol (C_3H_7OH, 99%), isobutanol (C_3H_7OH, 99%), tert-butanol (C_4H_9OH, 99%), n-pentanol ($C_5H_{11}OH$, 99%), n-hexanol ($C_6H_{13}OH$, 99%), n-heptanol ($C_7H_{15}OH$, 99%), n-octanol ($C_8H_{17}OH$, 99%), n-pentane (C_5H_{12}, 99%), n-hexane (C_6H_{14}, 99%), n-heptane (C_7H_{16}, 99%), n-octane (C_8H_{18}, 99%) and 2,2,4-trimethylpentane (isooctane, C_8H_{18}, 99%) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. 2-methyl-2-butanol ($C_5H_{11}OH$, 99%), 2,2-dimethyl-1-butanol ($C_5H_{11}OH$, 99%), 2-ethyl-1-butanol ($C_6H_{13}OH$, 99%), 2-methyl-1-pentanol ($C_6H_{13}OH$, 99%), 2,2-dimethylbutane (C_6H_{14}, 99%), 2,3-dimethylbutane (C_6H_{14}, 99%), 2-methylpentane (C_6H_{14}, 99%), n-hexene (C_6H_{12}, 99%), n-heptene (C_7H_{14}, 99%) and n-octene (C_8H_{16}, 99%) were purchased from Aladdin Company. 2-ethyl-1-butene (C_6H_{12}, 99%), 3-methyl-1-pentene (C_6H_{12}, 99%), 3-ethyl-2-pentene (C_7H_{14}, 99%), 2-methyl-1-hexene (C_7H^{14}, 99%), 2-ethyl-1-hexene (C_8H_{16}, 99%) and 2-methyl-1-heptene (C_8H_{16}, 99%) were purchased from Beijing Bailingwei Company. 2,2-dimethylpentane (C_7H_{16}, 99%), 2,3-dimethylpentane (C_7H_{16}, 99%) and 2-methylhexane (C_7H_{16}, 99%) were purchased from Anaiji Company. 3-ethyl-3-pentanol ($C_7H_{15}OH$, 99%), 2-methyl-3-hexanol ($C_7H_{15}OH$, 99%), 2-ethyl-1-hexanol ($C_8H_{17}OH$, 99%), 3-methyl-1-heptanol ($C_8H_{17}OH$, 99%), 2,2-dimethylpropane (C_5H_{12}, 99%), 2-methylbutane (C_5H_{12}, 99%), 2,4-dimethylhexane (C_8H_{18}, 99%) and 2-methylheptane (C_8H_{18}, 99%) were purchased from TCI. The water used in the experiment is all Milli-Q Reference ultrapure water (≥18.2 MΩ).

Preparation of monodisperse rhombic dodecahedral (RD) ZIF-8 nanoparticles.

RD ZIF-8 particles were synthesized according to a previously reported method with some modifications.[1] Specifically, 0.875 g of Zn $(CH_3COO)_2 \cdot 2H_2O$ and 1.313 g of 2-methylimidazole were dissolved in 200 mL of methanol under vigorous strring. After they are completely dissolved, the solution was kept at a water bath and allowed to stand at 25 °C for 24 h. The precipitate was centrifuged and washed with methanol and ethanol several times to obtain RD ZIF-8 crystals with a particle size of ~667 nm. To synthesize 590 nm- and 745 nm-sized RD ZIF-8 crystals, the amount of 2-methylimidazole was adjusted to 1.614 g and 0.985 g, respectively, while other conditions remained unchanged.

Preparation of monodisperse slightly truncated cubes (TC) ZIF-8 nanoparticles. CB ZIF-8 particles were synthesized according to a previously reported method with some modifications.[2] Specifically, 0.734 g of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 50 mL methanol and 0.810 g of 2-methylimidazole and 0.400 g of 1-methylimidazole was dissolved in another 50 mL methanol. Then, the above two solutions were mixed, stirred for 15 sec, and allowed to stand at 25 °C for 30 min. Finally, the precipitate was centrifuged and washed with methanol and ethanol several times to obtain CB ZIF-8 crystals with a particle size of ~ 600 nm.

Preparation of monodisperse truncated rhombic dodecahedral (TRD) ZIF-8 nanoparticles. TC ZIF-8 particles were synthesized according to a previously reported method with some modifications.[3] Specifically, 0.300 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 5 mL H_2O, and 1.116 g of 2-methylimidazole was dissolved in 3 mL H_2O, respectively, to form solutions A and B. Add 2 mL of CTAB aqueous solution (0.44 mM) to solution B. Then, the A and B solutions were mixed, stirred for 15 sec, and allowed to stand at 25 °C for 2 h. The precipitate was centrifuged and washed with water and ethanol several times to obtain TC ZIF-8 crystals with a particle size of ~ 500 nm.

Surface modification of ZIF-8 nanoparticles with PVP. The synthesized polyhedral ZIF-8 particles were dispersed in an ethanol solution of PVP with a ratio of ZIF-8: PVP: ethanol = 1: 20: 750 and stirred at room temperature for 12 h. After this, ZIF-8 crystals were centrifuged and washed with excess ethanol for several

rounds before dispersed in a mixed solvent of water and ethanol (V_{water}: $V_{ethanol}$ = 1: 1) to prepare a ~20 wt% dispersion. The zeta potential of RD ZIF-8 particles changed from 9.36 mV to -9.19 mV, proving that the surface of RD ZIF-8 particles was coated by PVP.

Self-assembly of polyhedral ZIF-8 nanoparticles into monolayer colloidal crystals (MCCs). A piece of clean glass slide (1cm×1cm) was placed at the center of a 10 cm-diameter petri dish, and water was added to the petri dish until the water surface was flush with the upper surface of the glass slide and did not overflow. Then, 10 μL of the 20wt% ZIF-8 dispersion prepared above was dropped on the glass slide. After the free diffusion on the water surface was completed, a small amount of sodium lauryl sulfate aqueous solution (2 wt%) was added to the water surface at the edge of the diffuser to make it tightly arranged. Finally, a clean silicon wafer (1cm×1cm) was slowly inserted under the floating layer, and then carefully lifted and removed from the petri dish to deposit the layer on it. The silicon wafer was left to dry under normal pressure and temperature.

Preparation of polycrystalline (PC) ZIF-8 films. The PC ZIF-8 film was prepared according to a previously reported method [4]. Specifically, 10 mL $Zn(NO_3)_2$ methanol solution (25 mM) was mixed with 10 mL 2-methylimidazole methanol solution (50 mM). Then, a cleaned silicon wafer was insert vertically into the mixed solution and allowed to stand at room temperature for 30 min. After this, the silicon wafer was taken out, rinsed with excess methanol and dried in a nitrogen flow. This process was cycled 6 times to obtain a PC ZIF -8 film with a thickness of 530 nm.

Platinum sputtering. In the Leica EM ACE200 coating system, the samples were sputtered with platinum at 7×10^{-3} mbar for 45 s to form 3.6 nm-thick layer.

Characterizations. X-Ray diffraction (XRD) patterns were collected from a Rigaku D/Max 2200PC diffractometer with graphite monochromator and Cu Kα target (λ=0.15418 nm). Transmission electron microscope (TEM) and scanning electronic microscope (SEM) images were obtained using JEOL JEM-1011 and Hitachi SU8010, respectively. The reflectance spectra in the visible light range were acquired by an Ocean Optics USB2000 fiber optic spectrometer connected to a Leica

DM2700M optical microscope. The optical photographs were collected using Leica DFC450 color digital camera combined with Leica DM2700M optical microscope equipped with LED lights under a 10× objective lens.

Application of ZIF-8 MCC for organic vapor sensing. Before the vapor sensing experiment, the film samples were placed under vacuum (0.023 Pa) at 80°C for 12 h to remove residual solvent molecules entrapped in the MOF pores. After that, the samples were affixed at the bottom of a home-made transparent polystyrene flow chamber (1.4 cm × 4.8 cm× 1.4 cm), one end of which was blocked with a cotton ball. 50 μL of each solvent for testing was dripped onto the cotton ball and let the solvent volatilize in the chamber. Reflectance spectra in the visible region of the samples were collected before and after vapor exposure. Saturated vapor at 293 K was obtained by bubbling high-purity nitrogen through a vessel containing the corresponding solvent. n-heptane vapors with a series of concentrations were obtained by varying the ratio of the saturated n-heptane vapor and high-purity nitrogen using two mass flow controllers and mixing them in a stainless steel gas mixer at 293 K. Time-resolved reflectance spectra were measured at a frequency of 100 ms and used to record the time-dependent change in peak wavelength shifting.

Gasoline octane number test. The standard 2,3,4-trimethylpentane (with an octane number of 100) and standard n-heptane (with an octane number of 0) are formulated into standard fuels of 0, 25, 50, 75 and 100 by volume percentage.

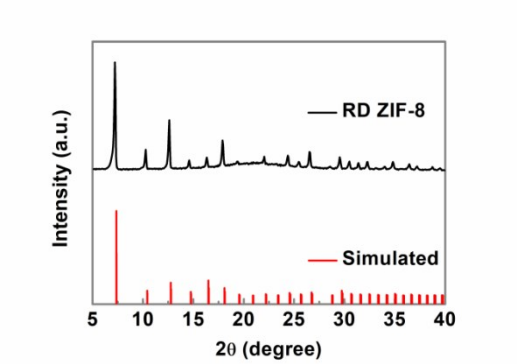

Figure S1 XRD patterns of synthesized RD ZIF-8 particles, as compared to simulated data.

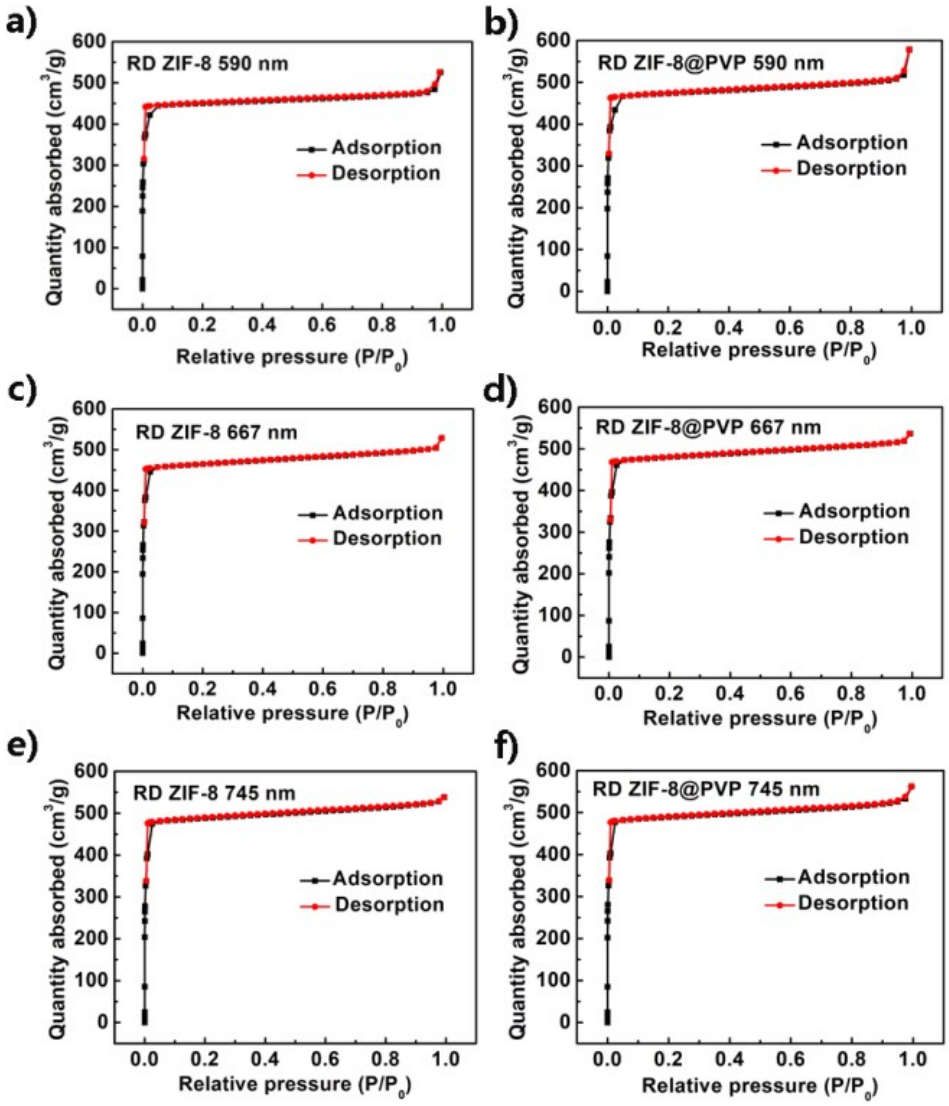

Figure S2 N_2 adsorption-desorption isotherms at 77 K of RD ZIF-8 with average particle sizes of 590, 667 and 745 nm before (a, c, e) and after PVP modification (b, d, f).

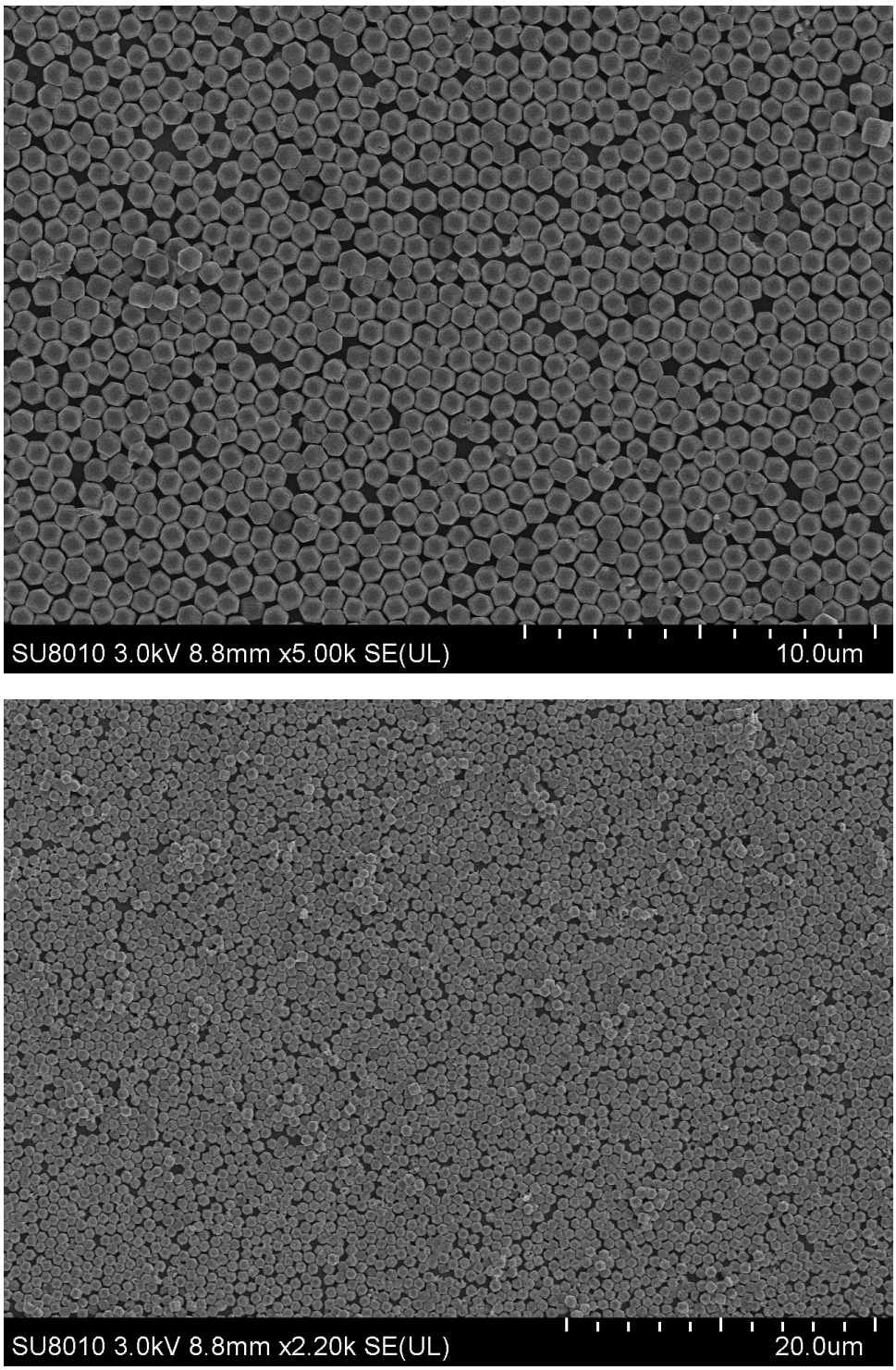

Figure S3 Low magnification SEM images of RD ZIF-8 MCCs (particle size: 667 ± 30 nm).

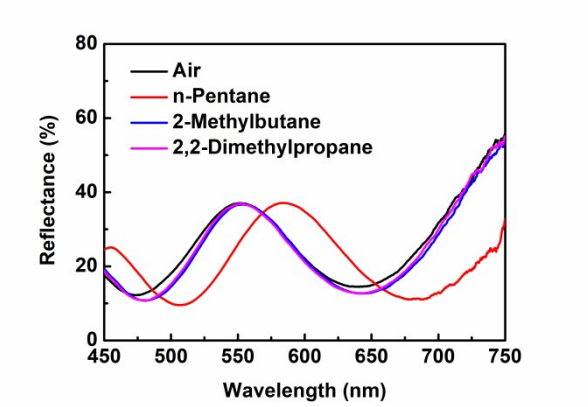

Figure S4 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of C5 alkane isomers.

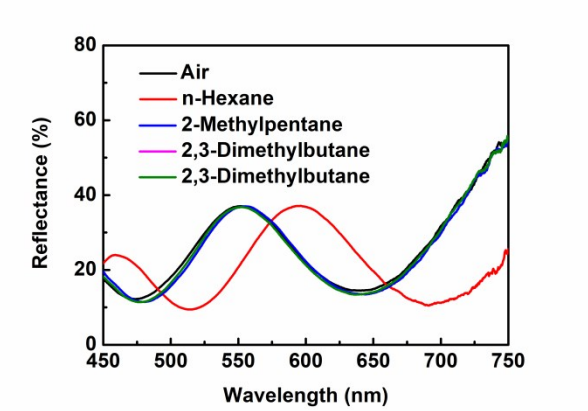

Figure S5 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of C6 alkane isomers.

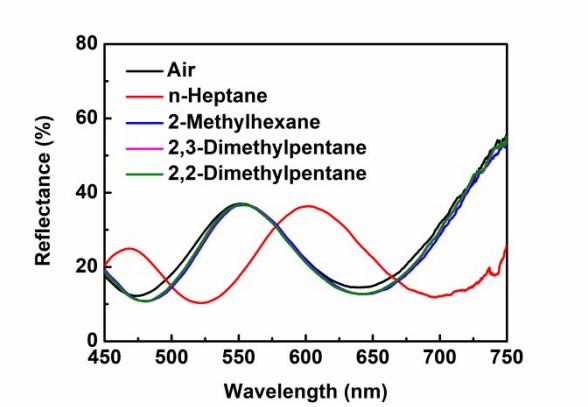

Figure S6 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of C7 alkane isomers.

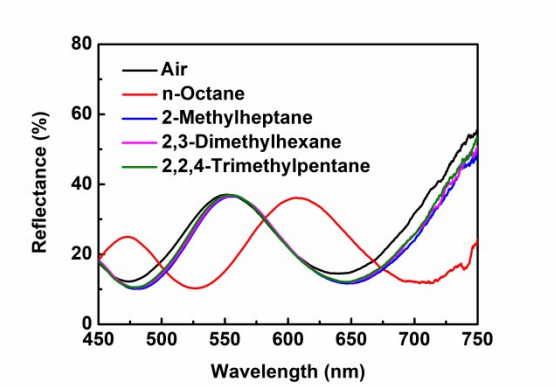

Figure S7 Reflectance spectra of RD ZIF-8 MCC before and after exposure vapors of C8 alkane isomers.

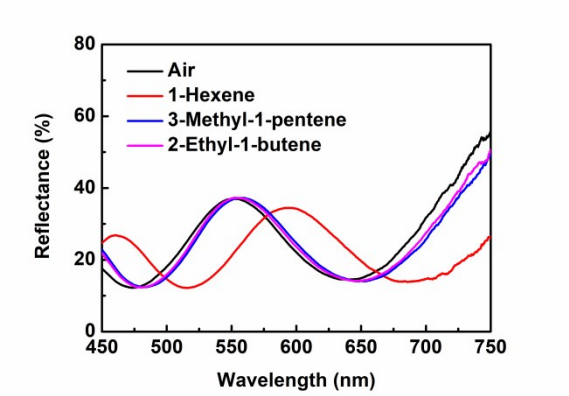

Figure S8 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of C6 alkene isomers.

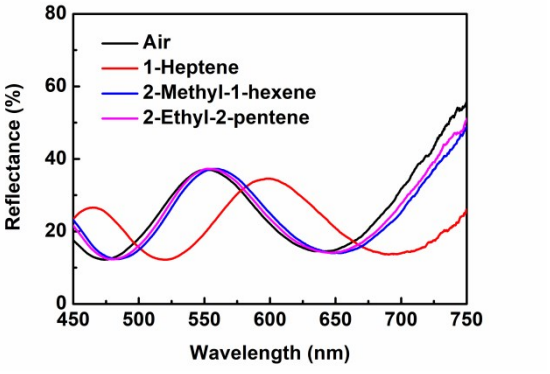

Figure S9 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of C7 alkene isomers.

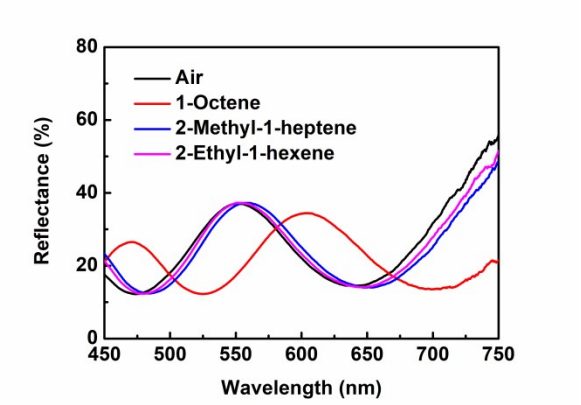

Figure S10 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of C8 alkene isomers.

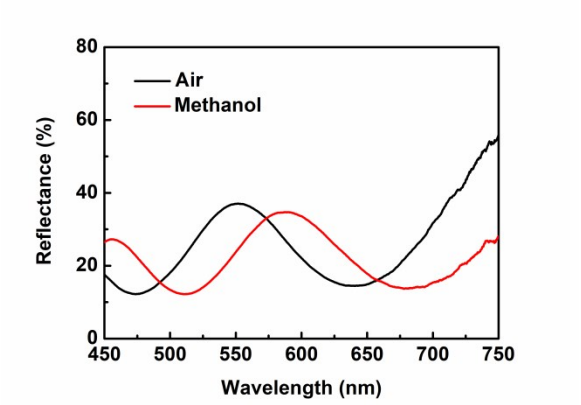

Figure S11 Reflectance spectra of RD ZIF-8 MCC before and after exposure to methanol vapor.

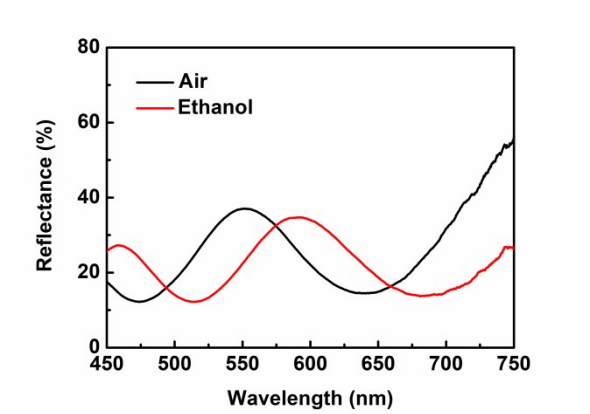

Figure S12 Reflectance spectra of RD ZIF-8 MCC before and after exposure to ethanol vapor.

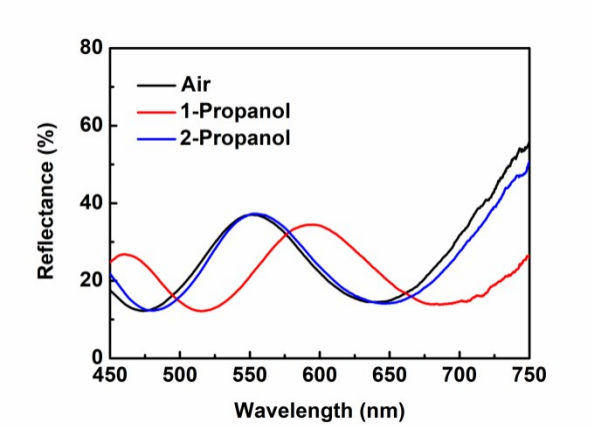

Figure S13 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of 1-propanol and 2-propanol vapor.

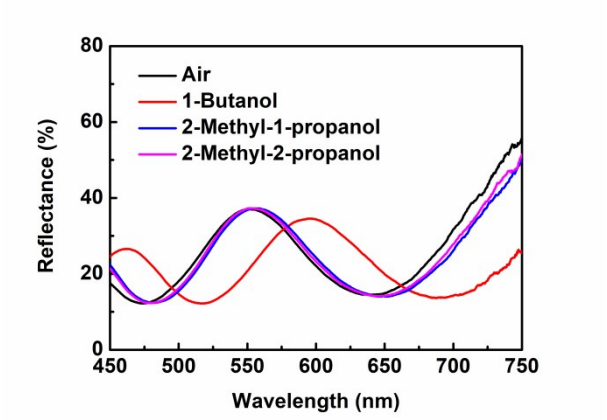

Figure S14 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of 1-butanol, 2-methyl-1-propanol and 2-methy-2-propanol.

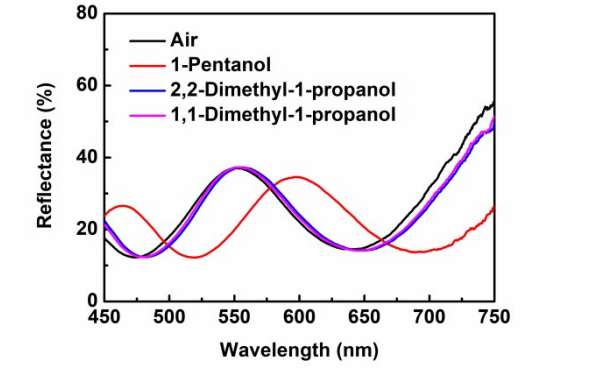

Figure S15 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of 1-pentanol, 2,2-dimethyl-1-propanol and 1,1-dimethyl-1-propanol.

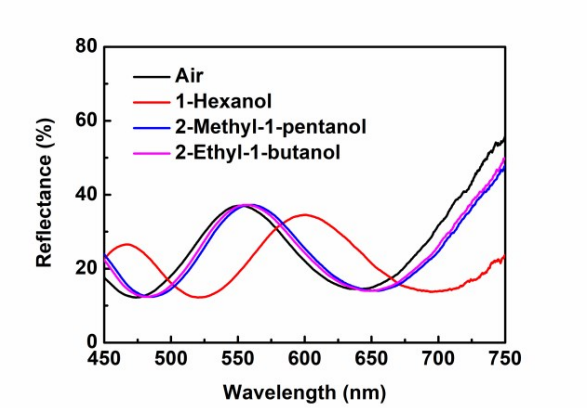

Figure S16 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of 1-hexanol, 2-methyl-1-pentanol and 2-ethyl-1-butanol.

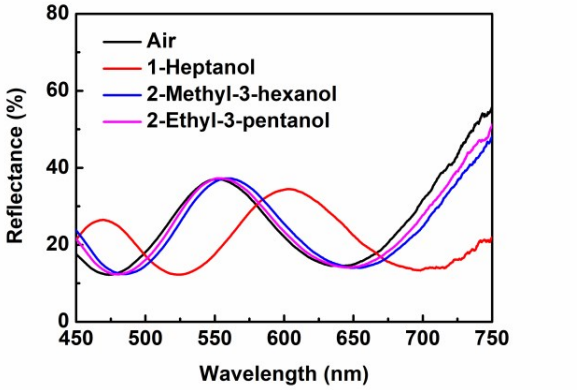

Figure S17 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of 1-heptanol, 2-methyl-3-hexanol and 2-ethyl-3-pentanol.

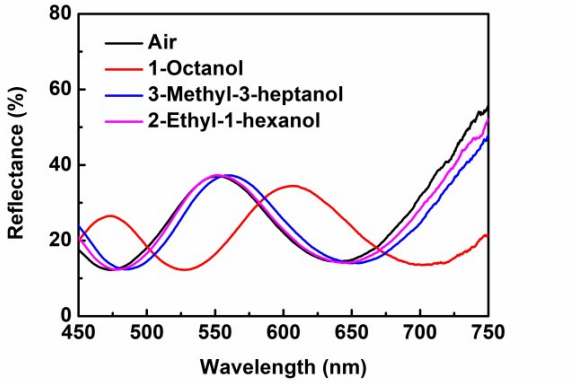

Figure S18 Reflectance spectra of RD ZIF-8 MCC before and after exposure to vapors of 1-octanol, 3-methyl-3-heptanol and 2-ethyl-1-hexanol.

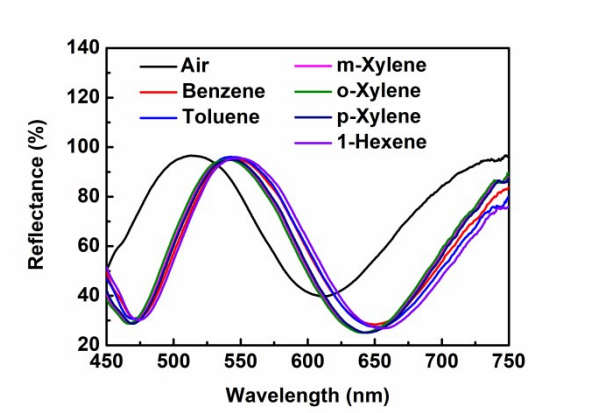

Figure S19 Reflectance spectra of PC ZIF-8 films before and after exposure to vapors of 1-hexene and BTEX.

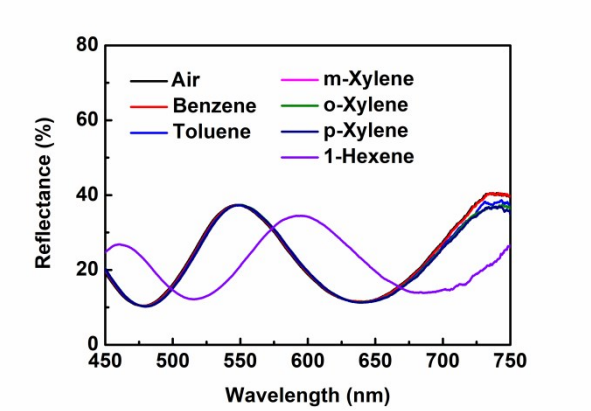

Figure S20 Reflectance spectra of RD ZIF-8 MCCs before and after exposure to vapors of 1-hexene and BTEX.

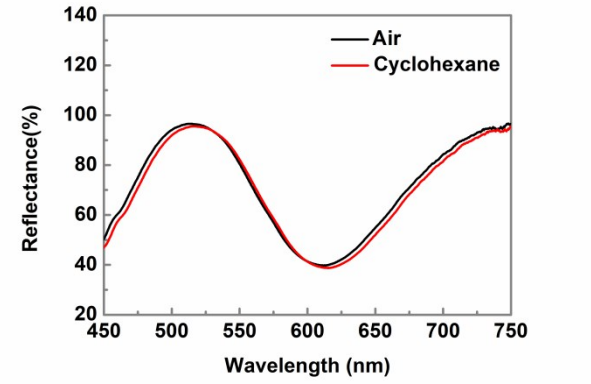

Figure S21 Reflectance spectra of PC ZIF-8 films before and after exposure to cyclohexane vapor.

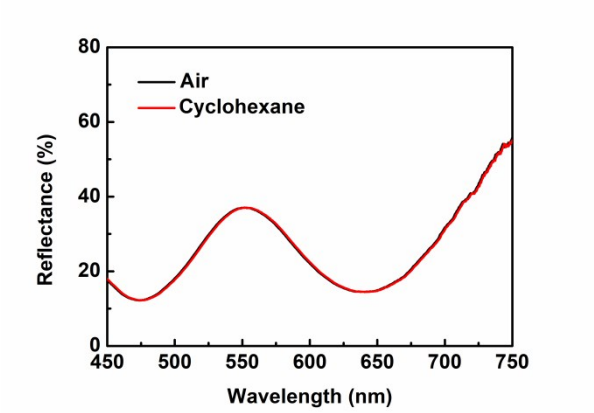

Figure S22 Reflectance spectra of RD ZIF-8 MCCs before and after exposure to cyclohexane vapor.

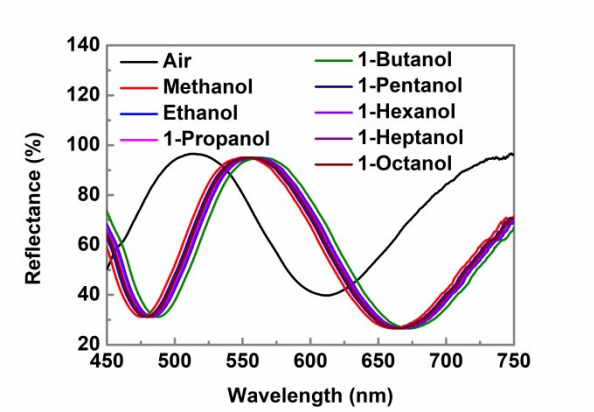

Figure S23 Reflectance spectra of PC ZIF-8 films before and after exposure to vapors of C1-C8 linear alcohols.

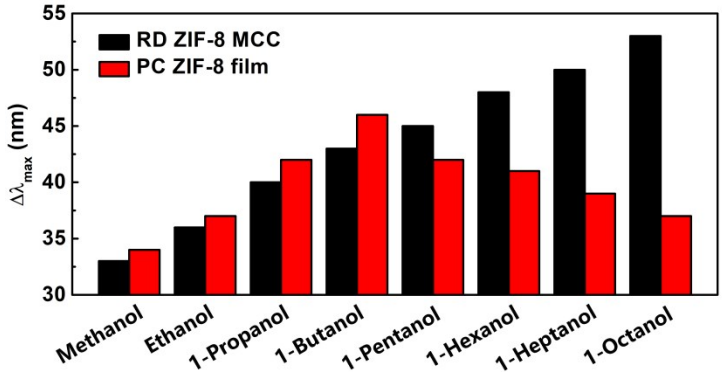

Figure S24 Reflectance peak shifts of RD ZIF-8 MCCs and PC ZIF-8 films exposed to vapors of C1-C8 linear alcohols.

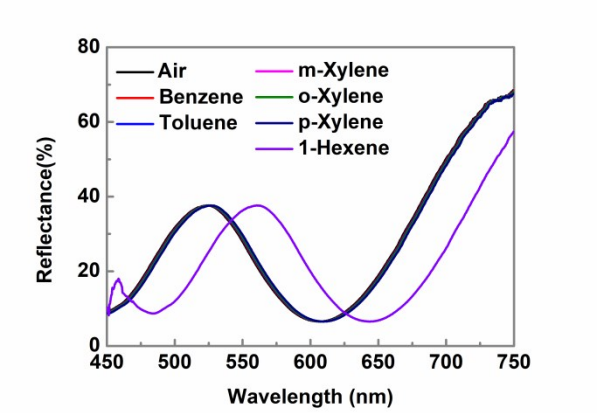

Figure S25 Reflectance spectra of TC ZIF-8 MCCs before and after exposure to vapors of 1-hexene and BTEX.

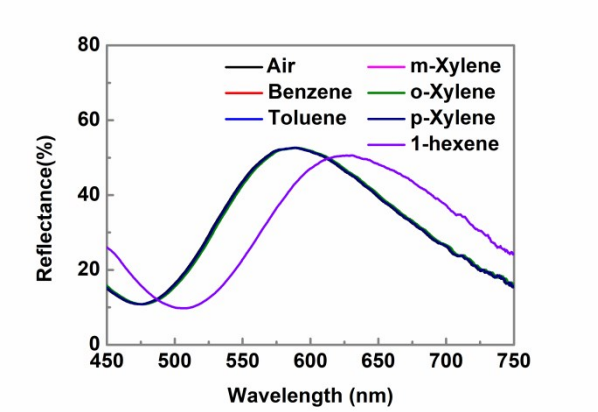

Figure S26 Reflectance spectra of TRD ZIF-8 MCCs before and after exposure to vapors of 1-hexene and BTEX.

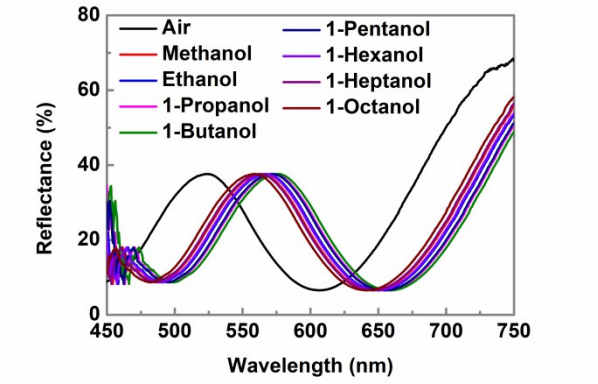

Figure S27 Reflectance spectra of TC ZIF-8 MCCs before and after exposure to vapors of C1-C8 linear alcohols.

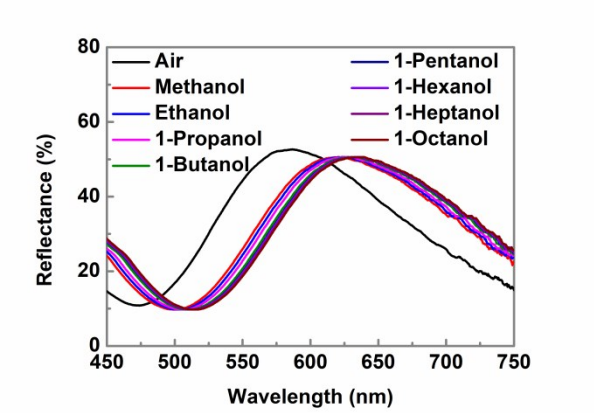

Figure S28 Reflectance spectra of TRD ZIF-8 MCCs before and after exposure to vapors of C1-C8 linear alcohols.

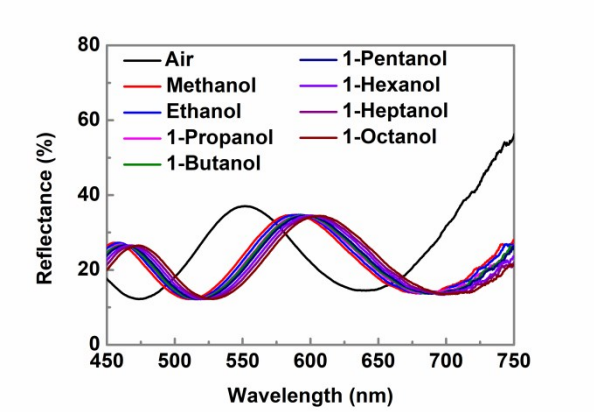

Figure S29 Reflectance spectra of RD ZIF-8 MCCs before and after exposure to vapors of C1-C8 linear alcohols.

Table S1 BET surface area and porosity of synthesized RD ZIF-8 particles before and after PVP modification.

Sample		Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
RD ZIF-8 590 nm	before	1889	0.686
	after	1987	0.719
RD ZIF-8 667 nm	before	1970	0.708
	after	2049	0.748
RD ZIF-8 745 nm	before	1982	0.727
	after	2081	0.736

Table S2 Kinetic diameters (d) of structural isomers of C5-C8 alkanes, C6-C8 alkenes and C1-C8 alcohols.

C5-C8 alkanes								
Carbon number	Molecules	*d* (Å)	Molecules	*d* (Å)	Molecules	*d* (Å)	Molecules	*d* (Å)
5	n-Pentane	4.5	2-Mbut	5.7	2,2-DMPro	6.1	-	-
6	n-Hexane	4.5	2-MPen	5.8	2,3-DMBut	6.0	2,2-DMBut	6.3
7	n-Heptane	4.7	2-MHex	5.9	2,3-DMPen	6.0	2,2-DMPen	6.4
8	n-Octane	4.8	2-MHep	6.0	2,4-DMHex	6.1	2,2,4-TMPen	6.4
C6-C8 alkenes								
6	1-Hexene	4.7	3-M-1-Pen	5.7	2-E-1-But	5.8	1-Hexene	4.7
7	1-Heptene	4.8	2-M-1-Hex	5.8	3-E-2-Pen	6.7	1-Heptene	4.8
8	1-Octene	4.8	2-M-1-Pen	5.9	2-E-1-Hex	6.8	1-Octene	4.8
C1-C8 alcohols								
1	Methanol	3.9	-	-	-	-	-	-
2	Ethanol	4.5	-	-	-	-	-	-
3	1-Propanol	4.6	2-Propanol	4.6	-	-	-	-
4	1-Butanol	4.6	2-M-1-Pro	5.9	2-M-2-Pro	6.0	-	-
5	1-Pentanol	4.7	2,2-DM-1-Pro	6.1	1,1-DM-1-Pro	6.4	-	-
6	1-Hexanol	4.7	2-M-1-Pen	5.9	2-E-1-But	6.8	-	-
7	1-Heptanol	4.7	2-M-3-Hex	5.9	3-E-3-Pen	7.2	-	-
8	1-Octanol	4.8	3-M-3-Hep	5.9	2-E-1-Hex	7.3	-	-

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