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# Controlled Incorporation of Nanoparticles in Metal-Organic Framework Hybrid Thin Film

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## Section S1. General information

Commercial reagents were purchased from Sigma-Aldrich (ACS grade) and used as received unless otherwise noted. Powder X-ray diffraction (XRD) patterns were recorded with a Bruker AXS D8 Advance diffractometer using nickel-filtered Cu Kα radiation (λ= 1.5406 Å). Scanning electron microscope (SEM) images were taken by a JEOL JSM-7600 field-emission SEM with an accelerating voltage of 5 kV. Transmission electron microscope (TEM) images were taken by a JEOL JEM 2010F at an accelerating voltage of 200 kV. UV-visible spectra were recorded on a Shimadzu UV-2501 spectrophotometer. Photoluminescence spectra were obtained with a Shimadzu RF-5301 spectrofluorophotometer or with a DM150i monochromator equipped with a R928 photon counting photomultiplier tube (PMT), in conjunction with a 980 nm diode laser. The luminescence images were obtained on an Olympus BX51 microscope with the xenon lamp adapted to a diode laser. A standard spin coater (CEE Model 100, Brewer Science) is used to spin-coat different NPs in ZIF-8 film substrates.

## Section S2. Synthesis of and surface modification of NPs

### PVP-stabilized Au NPs[1]:

Au nanoparticles were prepared by a sodium citrate reduction method of $HAuCl_4$. In a typical procedure for the synthesis of 13 nm Au NPs, an aqueous solution of $HAuCl_4$ (0.01%, 150 ml) was brought to a vigorous boil with rapid stirring in a round bottom flask (250 ml) fitted with a reflux condenser. When the solution started to boil, an aqueous solution of trisodium citrate (1%, 4.5 ml) was added. The mixture was refluxed with stirring for another 20 min. The resulting deep red suspension and was then removed from the heat. After the Au NPs sol was cooled to room temperature, a solution of PVP (0.5 g, Mw = 55,000) in water (20 ml) was added dropwise to the Au NPs sol with stirring, and the mixture was further stirred at room temperature for 24 h. The PVP-stabilized Au NPs were collected by centrifugation at 14,000 rpm for 30 minutes, washed by methanol for three times, and final dispersed in methanol (absorbance at 520 nm, ~ 4).

### PVP-stabilized Pt NPs[2]:

2.9 nm PVP-stablized Pt NPs were prepared by refluxing a mixture of PVP (533 mg, Mw=29,000), methanol (180 ml), and aqueous solution of $H_2PtCl_6$ (6.0 mM, 20 ml) in a flask (500 ml) for 3 h under air. Methanol was removed by rotary evaporator. The NPs in the remaining solution were precipitated by acetone and then collected by centrifugation at 6,000 rpm for 5 min. The sample was cleaned with chloroform and hexane to remove excess free PVP. The PVP-stabilized Pt NPs were redispersed in methanol ($0.52 mg \cdot mL^{-1}$).

### 8 nm $Fe_3O_4$ NPs[3]:

8 nm $Fe_3O_4$ NPs were synthesized following the procedure of Hyeon et al. The as-synthesized NPs were precipitated with ethanol, collected by centrifugation at 6,000 rpm, and washed with several times with ethanol. $Fe_3O_4$ NPs were dipersed in 20 ml of chloroform (0.5 $mg\cdot ml^{-1}$). A solution of PVP (250 mg, Mw = 10,000) in chloroform (10 ml) was then added. After the mixture was stirred for 24 h, the PVP-stabilized NPs were precipitated with hexane and collected by centrifugation at 6,000 rpm for 5 min. The sample was cleaned with chloroform and hexane to remove the excess free PVP. Finally, the PVP-stabilized NPs were redispersed in methanol (0.25 $mg\cdot ml^{-1}$).

4 nm CdSe NPs:

4 nm oleic acid-capped CdSe NPs were synthesized using hot injection method. The as-synthesized NPs were precipitated with ethanol, collected by centrifugation at 6,000 rpm, and washed several times with ethanol. Oleic acid-capped CdSe NPs were modified with PVP using the same procedure used for 8 nm $Fe_3O_4$ NPs. The sample was cleaned with chloroform and hexane to remove the excess free PVP. Finally, the PVP-stabilized NPs were redispersed in methanol (0.25 $mg\cdot ml^{-1}$).

Reference:

1. Frens, G. Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. *Nat. Phys. Sci.* **1973***, 241***,** 20-22.

2. Teranishi, T*et al*. Size control of monodispersed Pt nanoparticles and their 2D organization by electrophoretic deposition. *J. Phys. Chem. B* **1999***, 103***,** 3818-3827.

3. Park, J. *et al.* Ultra-large-scale syntheses of monodisperse nanocrystals. *Nat. Mater.* **2004**, *3*, 891-895.

## Section S3. Preparation of the NPs/ZIF-8 hybrid thin films

### Growth of ZIF-8thin film on glass or silicon slide

Glass slides and silicon wafers were cut into small pieces ($37\times15mm^2$) as substrate for growing ZIF-8 thin film. Before use, the substrates were ultrasounded in acetone and ethanol for 10min respectively, and then cleaned in a piranha solution at 120 ℃ for 60min, rinsed with distilled water, and dried under nitrogen flow.

500ml methanolic stock solution of $Zn(NO_3)_2$ (25mM) and 2-methylimidazole (mIm) (50 mM) were prepared, respectively. ZIF-8 thin film was obtained by immersing the cleaned substrates in a fresh mixture of 5 ml $Zn(NO_3)_2$ and 5ml mIm stock solution for 40 min at room temperature, then washed with methanol, and dried under nitrogen flow.

### Procedure for fabricating NPs/ZIF-8 hybrid thin films

A ZIF-8 layer with designed thickness was deposited on a glass substrate as describe above. 50ul Au NPs methanol dispersion was dispensed on the ZIF-8 film substrate, and keep the Au NPs methanol dispersion full coverage the ZIF-8 film. The wafer was spin-coated at 1500 rpm on a standard spin-coater for 30s. And then repeat the procedure. The sample was marked 1 cycle. And then, the substrate with 1 cycle Au/ZIF-8 were immersed in the fresh mixture of 5 ml $Zn(NO_3)_2$ and 5ml mIm stock solution for 40 min at room temperature, then washed with methanol, and dried under nitrogen flow. At last repeat the spin coating and film growth procedure.

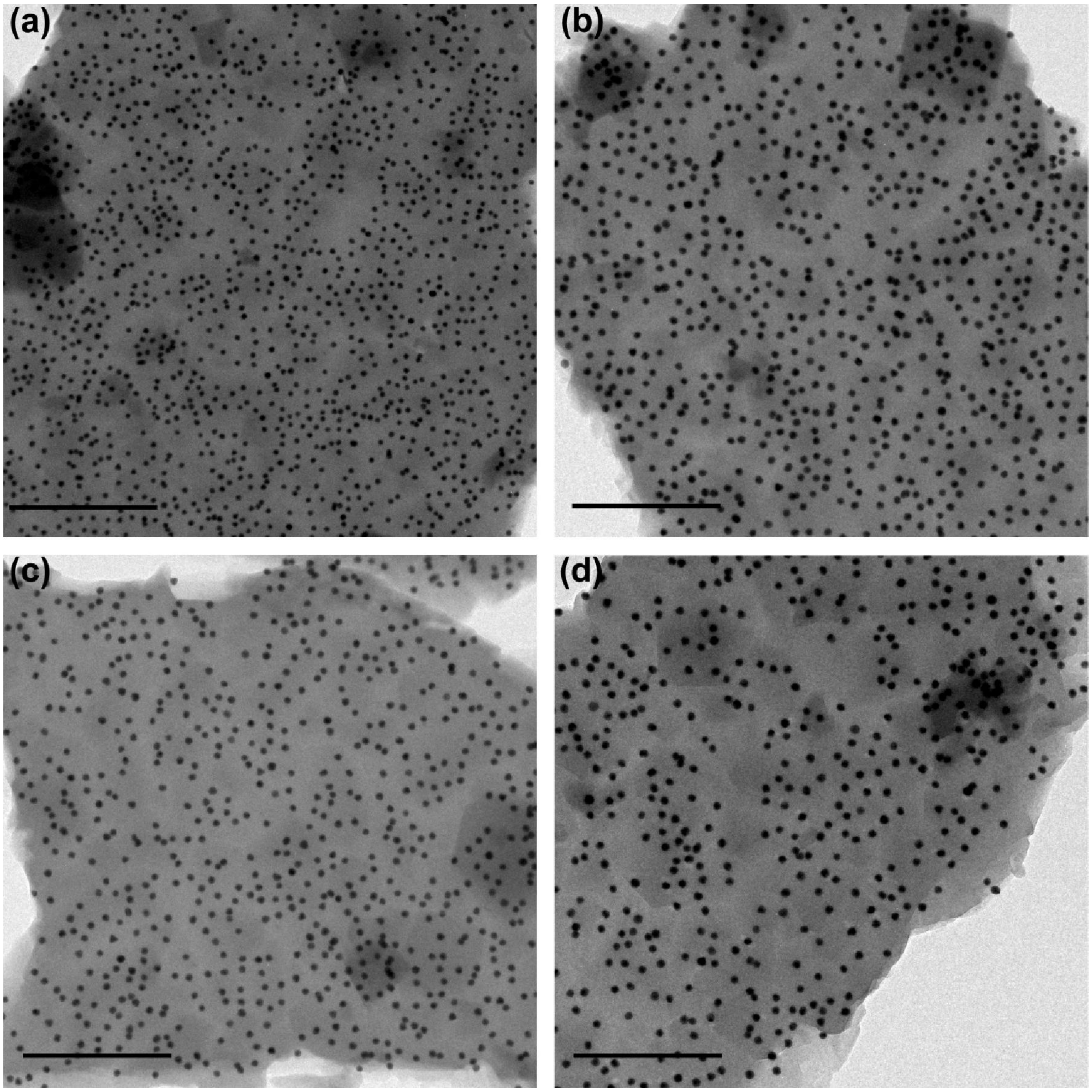


**Figure S1.** TEM images of Au/ZIF-8 hybrid thin film at different spinning coat rate, (a) 1500rpm, (b) 2000rpm, (c) 2500rpm and (d) 3000rpm.The scale bar is 500 nm.

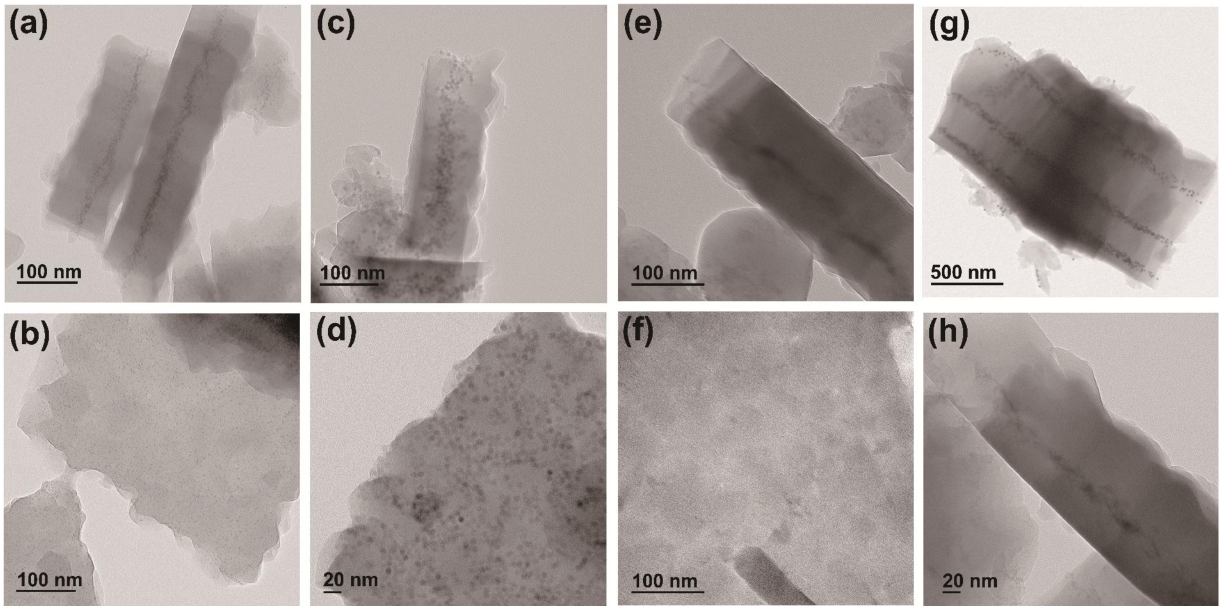


**Figure S2.** TEM image of NPs/ZIF-8 hybrid thin films containing different NPs. (a, b) Pt/ZIF-8, (c,d)$Fe_3O_4$/ZIF-8, (e,f) CdSe/ZIF-8, (g) Au/ZIF-8 hybrid thin films with controlled layer of ZIF-8 (1 layer, 2 layers, and 3 layers), and (h) CdTe/ZIF-8 hybrid thin films.

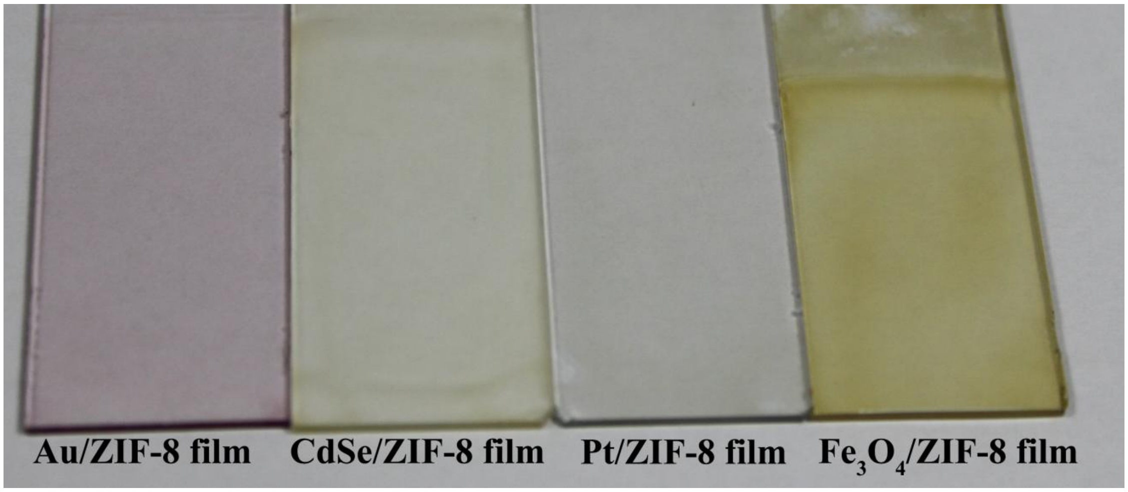


**Figure S3**. The photo of NPs/ZIF-8 hybrid thin films(from left to right is Au/ZIF-8, CdSe/ZIF-8,Pt/ZIF-8 and $Fe_3O_4$/ZIF-8 hybrid thin films).

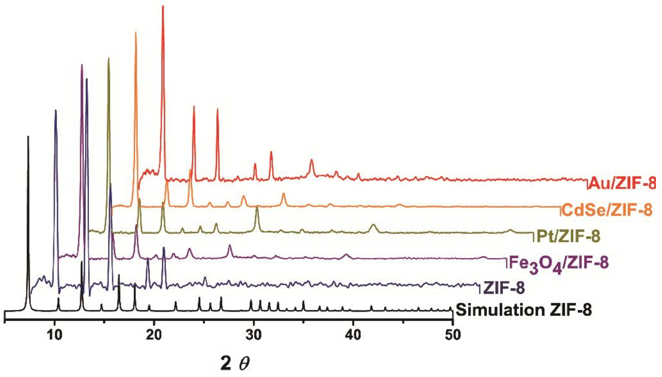


**Figure S4.**XRD spectra of NPs/ZIF-8 hybrid thin films.

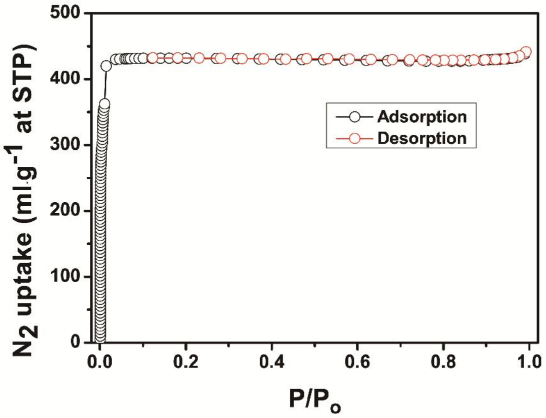
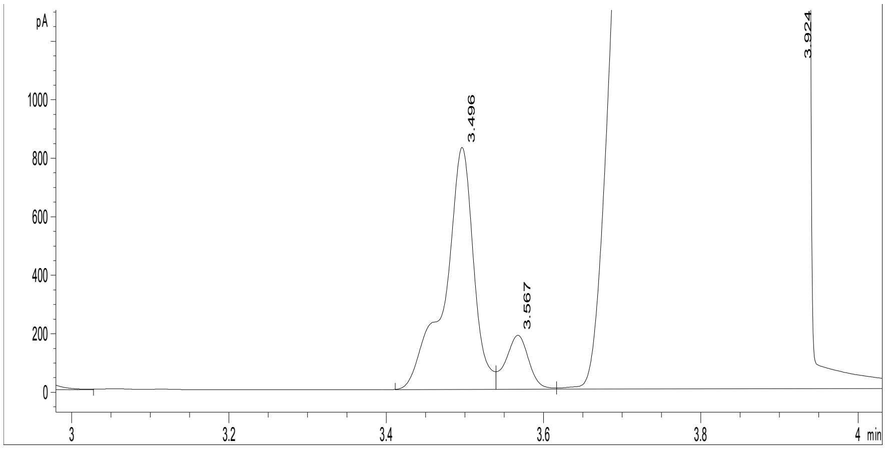


**Figure S5.**The nitrogen adsorption-desorption isotherm at 77 K of ZIF-8.

## Section S4. Catalytic hydrogenation of olefins

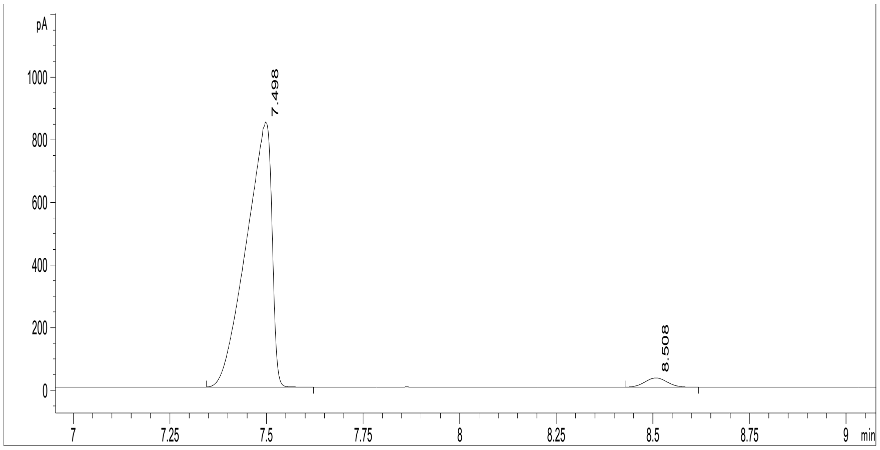
Hydrogenation of olefins (n-hexene>99%, and cis-cyclooctene>95%,) was carried out in ethyl acetate solution in a static hydrogen atmosphere (1 bar). In a typical experiment, the catalyst Pt/ZIF-8 hybrid thin film was loaded in a reactor and residual air in the reactor was expelled by purging with hydrogenfor several times. Ethyl acetate (10 ml) andolefin (0.01 ml) were added in the reactor. After that, the reactor was purged with hydrogen one more time and the reaction was allowed to proceed at 1 atm of hydrogen and room temperature for 24 hours under 700rpm stirring. After the reaction, products and reactants were analyzed using a gas chromatography (Agilent, 6890N) equipped with a HP-5 column (Agilent) and FID. It is worth noting that the commercial chemical of 95% cis-cyclooctene (Aldrich, Cat No. 125482) contains ~3.6% cyclooctane as detected by the gas chromatography analysis.



Hexene

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 3.496 | 2123.6 | 824.8 | 0.037 | 1.422 | 1.466**Hexene** |
| 2 | 3.567 | 374.2 | 184.2 | 0.0307 | 0.251 | 1.045**Hexane** |
| 3 | 3.924 | 146633.8 | | 16075.40.1134 | 98.209 | 10.907**EA** |

Conversion: 14.98%



| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 7.498 | 3894.7 | 846.1 | 0.0667 | 2.752 | 3.045**cis-cyclooctene** |
| 2 | 8.508 | 120.3 | 29.6 | 0.0633 | 0.085 | 0.97**cyclooctane** |

Conversion: 0

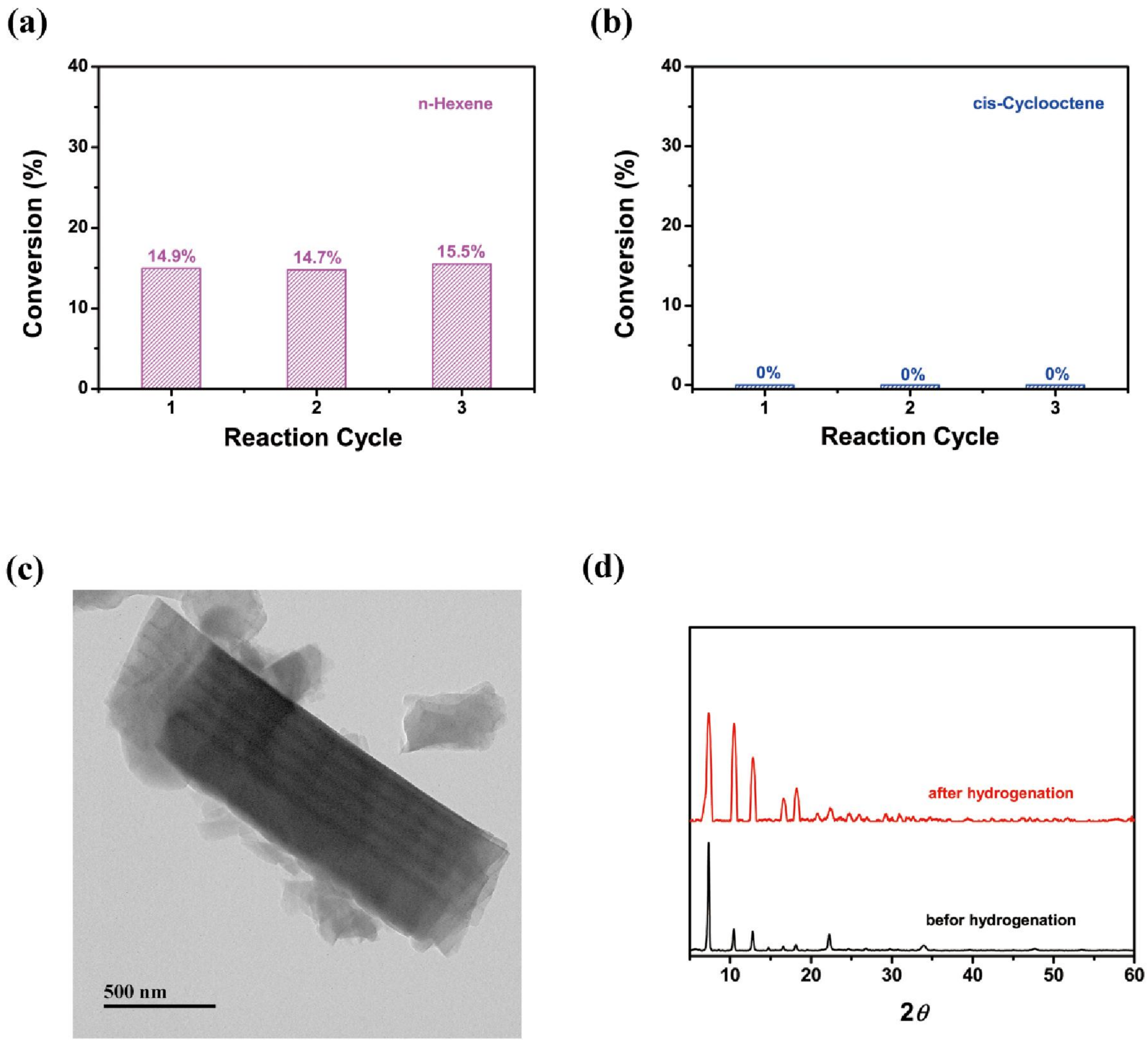


**Figure S6.**(a, b) The consecutive three runs of Pt/ZIF-8 hybrid thin film as catalyst in n-Hexene and cis-Cylcooctene, (c)TEM image and (d) XRD spectraof Pt/ZIF-8 hybrid thin film after hydrogenation of olefin.

## Section S5. Sensor performances of Au/ZIF-8hybrid thin films

The vapor testing was carried out in a polystyrene cuvette (10 ×10 ×45 $mm^3$). After the cotton ball with 50 µl of solvents were added into the cuvette, a 5-cycle Au/ZIF-8 thin film grown on a glass substrate (37.5 ×15 $mm^2$) was fixed to a stopper and then placed in the cuvette carefully without contacting the solvents. The interference peak of ZIF-8 thin film was monitored via UV-vis Absorbance spectra at room temperature.

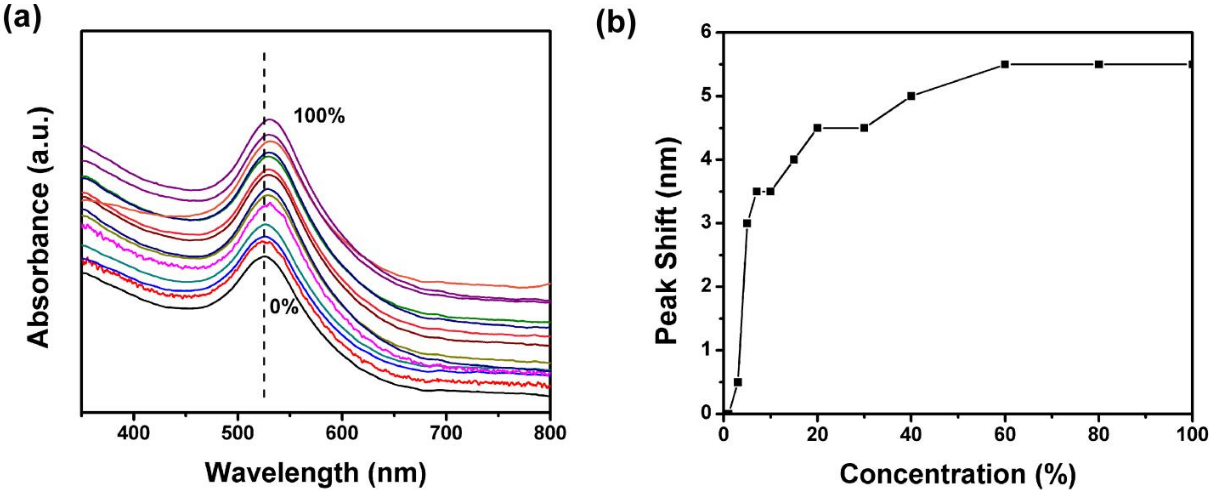


**Figure S7.**(a) UV-vis Absorbance spectra of 5-cycle Au/ZIF-8 hybrid thin films grown on glass substrate on exposure to vapors of ethanol and water,(b) Interference peak (originally at 520 nm) shift versus ethanol concentration in ethanol/water solutions. The concentration is expressed as a volume percentage.

Au/ZIF-8 hybrid thin film as the sensor does display some chemical selectivity in responding to a range of vapors and gases, which is confirmed by the UV-vis spectra. It's well known that the ZIF-8 is hydrophobic material. Therefore, the sensor is unresponsive to water vapor, while ethanol is readily detected. In the UV-vis spectra, the absorbance peak of the Au NPs at 520nm. After exposure to the mixed vapourof ethanol/water with various ethanol contents, and the sensor gives rise to response and the absorbance peak red-shifts by up to 5.5 nm, with the sensor response saturating at ca. 60% ethanol (Figure S6).

**Photoluminescence quenching of CdSe/ZIF-8 hybrid thin film**

PVP-modified CdSe NPs (as control) were dispersed in 2.5 ml methanol and placed in a quartz cuvette. Suspensions were excited at 350 nm and the intensity of emission at 567 nm was recorded.

CdSe/ZIF-8 hybrid thin film were placed in a quartz cuvette and were excited at 350 nm and the intensity of emission at 550 nm was recorded before and after adding cotton ball immersed with 10 µl 2-mercaptoethanol or cyclohexanethiol.