

## Supporting information

### **Magnetic Ionic Crystals with Light Controllable Mobility and CO<sub>2</sub> Physisorption/desorption**

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## 1. Measurement and characterization

### 1.1 Materials.

1-vinyl-3-ethylimidazolium bromide was purchased from Shanghai Chengjie Chemical Co., Ltd. Azobenzene and hexahydrate ferric chloride were purchased from Chengdu Huaxia Chemical Reagent Co. Ltd. All compounds were used as received.

### 1.2 Characterization.

$^1\text{H}$  NMR spectra were recorded on AVANCE III HD 400 (Bruker) at 400 MHz. The chemical shift ( $\delta$ ) of the residual solvent was used as an internal reference:  $\delta = 2.50$  ppm (DMSO- $d_6$ ). Differential scanning calorimetry (DSC) data were collected on a TA Q2000 (TA Instruments, New Castle, DE) at a scanning rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  with a nitrogen flow of  $50\text{ mL}\cdot\text{min}^{-1}$  using aluminum pans as sample holder. FT-IR spectra were recorded on Spectrum Two, L1600300 FT-IR spectrometer. Raman spectra were recorded on Laser Confocal Raman Micro spectroscopy. Gas adsorption curves were recorded by Intelligent Weight Adsorption Instrument (IGA) at  $25\text{ }^\circ\text{C}$  (The sample was degassed at  $25\text{ }^\circ\text{C}$  for 2 hours before testing). XRD patterns were measured on a small angle X-ray scattering system (SAXSess  $\text{mc}^2$ ) before and after UV irradiation ( $365\text{ nm}$ ,  $200\text{ mW}\cdot\text{cm}^{-2}$ ) at room temperature. Magnetization curves were measured by superconducting quantum interference device (MPMS3) before and after UV irradiation ( $365\text{ nm}$ ,  $200\text{ mW}\cdot\text{cm}^{-2}$ ) at  $298\text{ K}$ . Polarizing microscope (Weitu XPL-30TF) was equipped with a WT-3000 hot stage to control temperatures. A portable light-emitting diode (LED) light source (Beijing Newbetter Optics Technology Co.) was utilized to provide photoirradiation with selective intensity and wavelength (UV:  $365\text{ nm}$ ).

### 1.3 Synthesis of $[\text{C}_2\text{VIM}][\text{FeCl}_3\text{Br}]$

$[\text{C}_2\text{VIM}]\text{Br}$  (2.03 g, 0.01 mol) and  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (1.62 g, 0.01 mol) were mixed in acetonitrile (20ml) and reacted in a three necked flask at room temperature for 24 hours to obtain a rufous liquid. The raw product was extracted and washed by water for

several times. A purified product was obtained after an evaporation of acetonitrile and dried at 45 °C for 48 hours to obtain brownish red solid MIL: [C<sub>2</sub>VIM][FeCl<sub>3</sub>Br], yielding 89%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ=9.80 (s, 1H, N-CH=N of rings), 8.27 (s, 1H, N-CH of rings), 8.01 (s, 1H, CH-N of rings), 7.33 (s, 1H, N-CH=), 6.01-5.37 (s, 1H, =CH<sub>2</sub>), 4.23 (t, 2H, N-CH<sub>2</sub>), 1.41 (t, 3H, -CH<sub>3</sub>).

#### 1.4 Preparation of Azo-MIL

*Trans*-Azo-MIL was obtained by mixing various mol ratio of [C<sub>2</sub>VIM][FeCl<sub>3</sub>Br] and azobenzene (Azo) in acetonitrile (10 ml). The mass ratio of Azo: [C<sub>2</sub>VIM][FeCl<sub>3</sub>Br] were 0:10, 1:9, 2:8, 4:6 and 6:4, respectively. The transparent mixtures were obtained and stirred at room temperature for 24 h. After evaporation of acetonitrile at room temperatures, the remained solvent was dried under vacuum at 25 °C for 48 h. During sample preparation, the weight loss ratio of Azo is limited in 1 wt%.

#### 1.5 Calculation of permanent magnetic moment based on Curie constant

When atom, ion and molecule have unpaired electrons, the substance has a permanent magnetic moment. Atoms, ions, or molecules with permanent magnetic moments are arranged in the same direction as the external magnetic field under an external magnetic field, exhibiting paramagnetism. At the same time, their internal electron orbitals generate induced magnetic moments in the opposite direction of the magnetic field, exhibiting diamagnetism.

$$\chi_M = \chi_P + \chi_D \quad \#(1)$$

Where  $\chi_M$  is the molar magnetic susceptibility (m<sup>3</sup>·mol<sup>-1</sup>),  $\chi_P$  is the paramagnetic susceptibility and  $\chi_D$  is the diamagnetic susceptibility.

For paramagnetic substances, their magnetic susceptibility is inversely related to temperature, in accordance with Curie's law ( $|\chi_P| \gg |\chi_D| \rightarrow \chi_M \approx \chi_P$ ).

$$\chi_P = \frac{N_A \mu_m^2}{3kT} \quad \#(2)$$

Where  $N_A$  is Avogadro constant ( $6.023 \times 10^{23}$ ),  $\mu_m$  is the permanent magnetic moment ( $\text{erg} \cdot \text{G}^{-1}$ ) and  $k$  is the Boltzmann constant ( $1.380062 \times 10^{-16} \text{ erg} \cdot \text{K}^{-1}$ ).

$$\mu_m = \sqrt{n(n+2)}\mu_B \#(3)$$

Where  $n$  is the unpaired electron number and  $\mu_B$  is Bohr magneton ( $\mu_B = 9.273 \times 10^{-21} \text{ erg} \cdot \text{G}^{-1}$ ).

Also

$$\chi_M = \chi_g \cdot M \#(4)$$

Where  $\chi_g$  is the mass susceptibility ( $\text{cm}^3 \cdot \text{g}^{-1}$ ),  $M$  is the molar mass ( $\text{g} \cdot \text{mol}^{-1}$ ).

**Table S1.** The results of magnetic susceptibility and magnetic moment of 10Azo-MIL

UV irradiation time (min)	mass susceptibility $\chi_g$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	unpaired electron number $n$	permanent magnetic moment $\mu_m$
0	$2.854 \times 10^{-5}$	5 (4.95)	$5.87 \mu_B$
1	$2.960 \times 10^{-5}$	5 (5.05)	$5.97 \mu_B$
2	$3.035 \times 10^{-5}$	5 (5.13)	$6.05 \mu_B$
3	$3.058 \times 10^{-5}$	5 (5.15)	$6.07 \mu_B$
5	$3.062 \times 10^{-5}$	5 (5.16)	$6.08 \mu_B$

## 1.6 Calculation of the absorption ratio

The absorption ratio

$$\eta = \frac{\text{Absorbed mass}}{\text{Initial mass}} = \frac{M_2 - M_1}{M_1} \#(5)$$

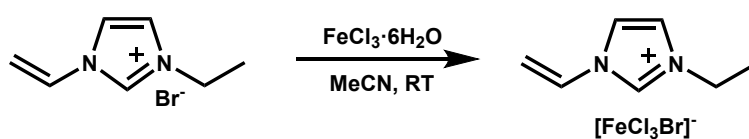
Where  $M_1$  is the *initial mass*,  $M_2$  is the final mass and  $\eta$  is the absorption ratio.

## 1.7 CO<sub>2</sub> adsorption and photodesorption experiments

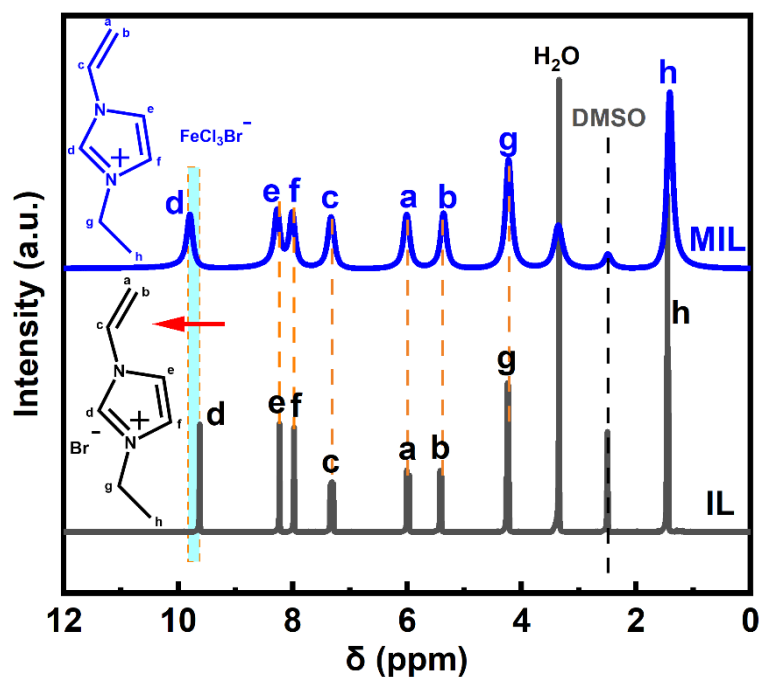
10Azo-MIL powder was placed in a quartz crucible. The sample was degassed at 25 °C for 2 h before testing. Firstly, CO<sub>2</sub> was added at the flow rate of 200  $\text{mbar} \cdot \text{min}^{-1}$  from 0 mbar until the mass weight of the sample was no longer increased. The increased

mass weight belonged to CO<sub>2</sub> physisorption. And then, UV light (365 nm, 200 mW·cm<sup>-2</sup>) was used to irradiate the sample to measure the releasement of CO<sub>2</sub>. UV light was on during the measurements to maintain liquid state. As long as the weight values of the sample were no longer decreased, the lost weight was ascribed to CO<sub>2</sub> desorption. Finally, the sample was degassed until the pressure near to 0 mbar for the preparation of the next cycle.

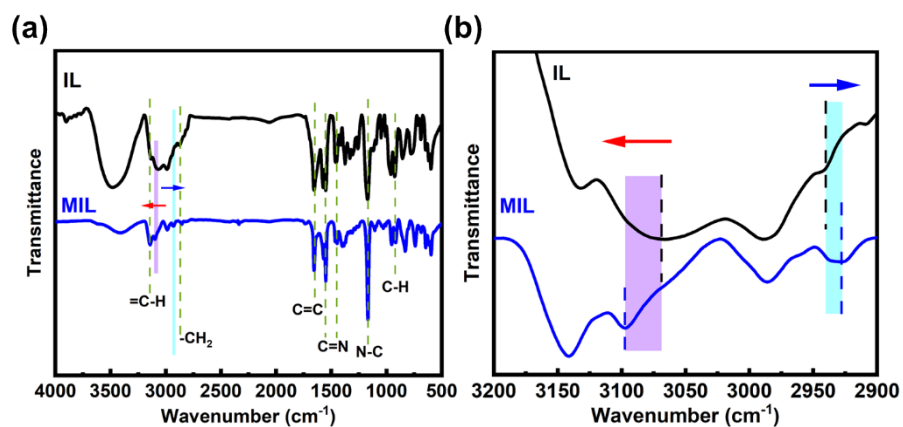
## 2. Figures



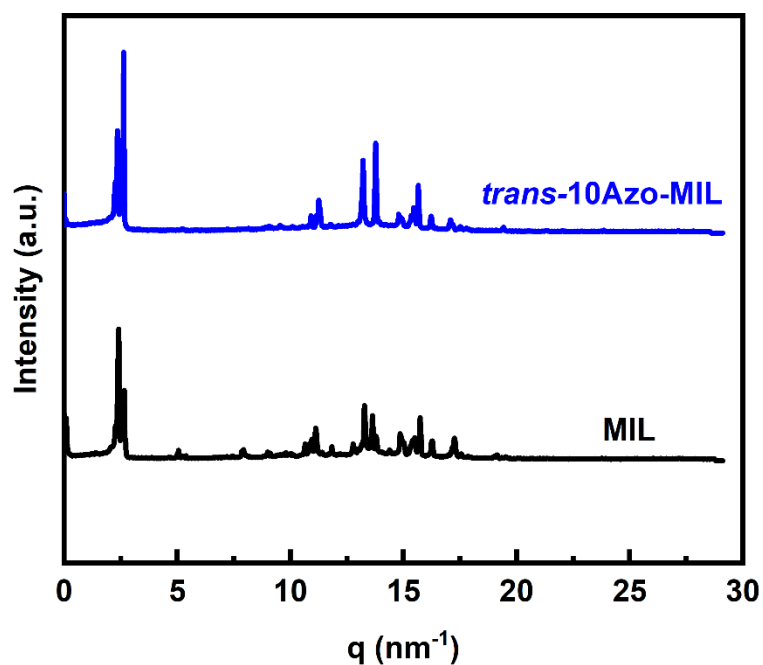
**Figure S1.** The synthesis step of the magnetic ionic liquid (MIL).



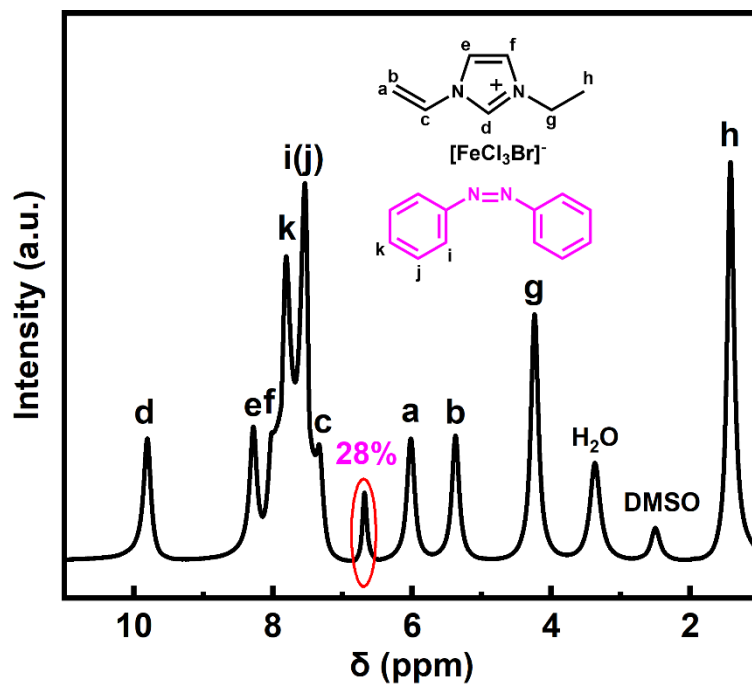
**Figure S2.** <sup>1</sup>H NMR spectra of IL and MIL in DMSO-*d*<sub>6</sub> at 25 °C.



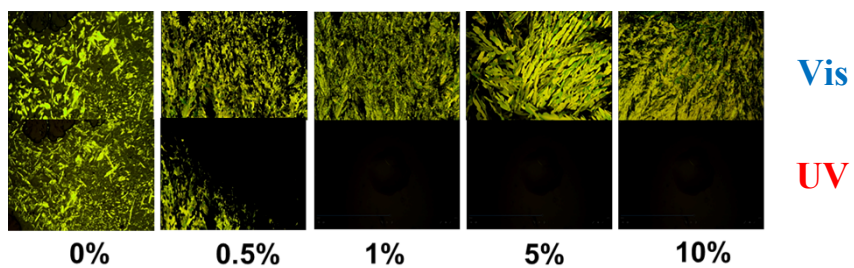
**Figure S3.** FT-IR spectra of IL and MIL from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> (a) and from 2900 cm<sup>-1</sup> to 3200 cm<sup>-1</sup> (b) at 25 °C.



**Figure S4.** XRD patterns of MIL and *trans*-10Azo-MIL at 25 °C.

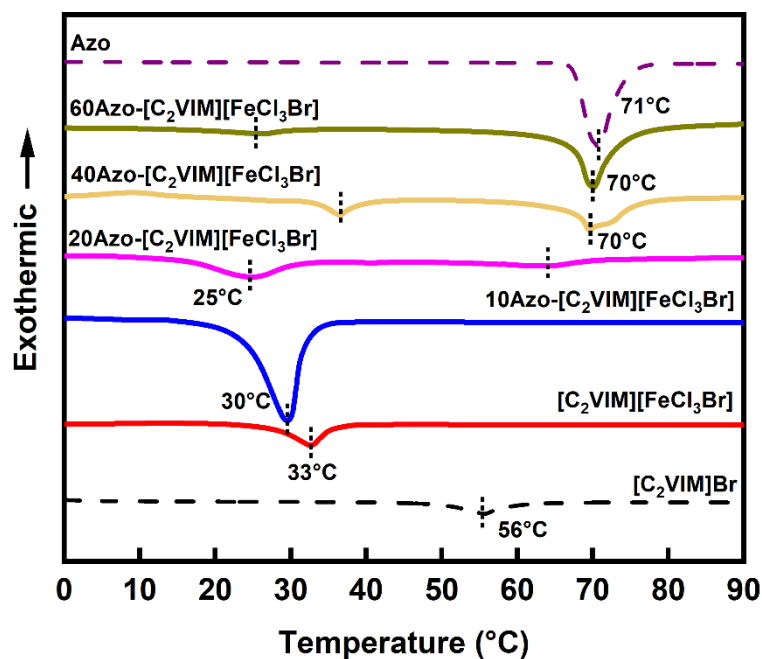


**Figure S5.**  $^1\text{H}$  NMR spectra of *cis*-10Azo-MIL in  $\text{DMSO-}d_6$  at  $25\text{ }^\circ\text{C}$ .

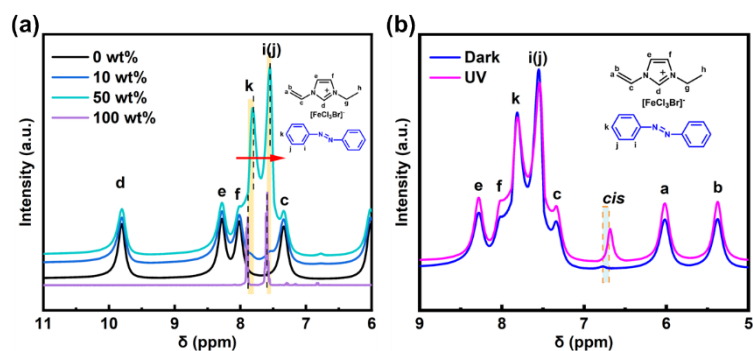


**Figure S6.** POM texture for various mixtures of Azo-MIL under UV and Vis light irradiation at  $25\text{ }^\circ\text{C}$ .

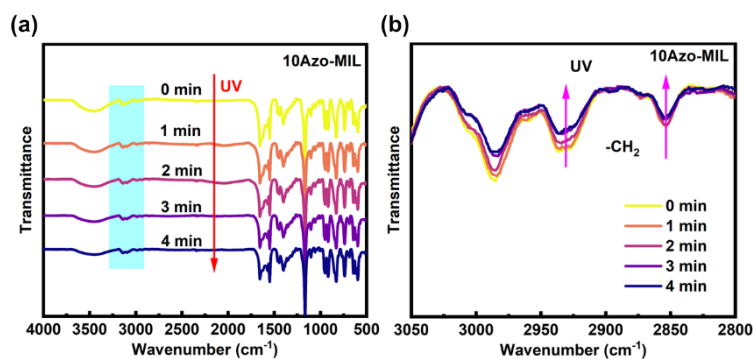




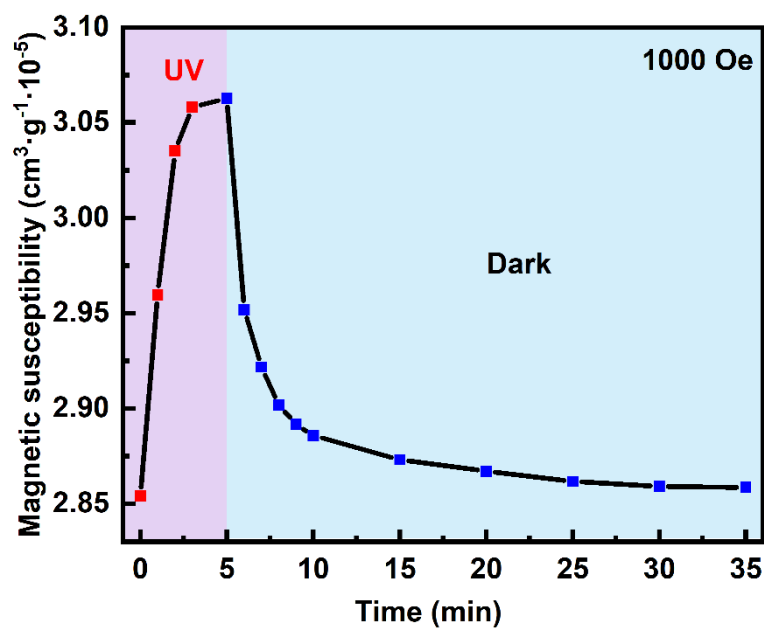
**Figure S7.** DSC curves of *trans*-Azo-MIL upon the second heating process at a rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .



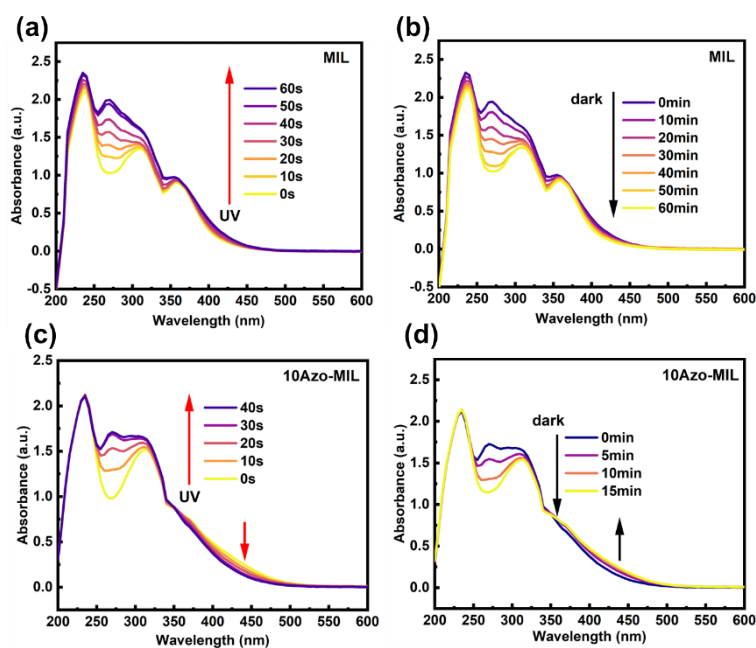
**Figure S8.**  $^1\text{H}$  NMR spectra of *trans*-Azo, MIL, *trans*-10Azo-MIL and *trans*-50Azo-MIL at  $25\text{ }^{\circ}\text{C}$  (a);  $^1\text{H}$  NMR spectra of *trans*-50Azo-MIL and *cis*-50Azo-MIL at  $25\text{ }^{\circ}\text{C}$  (b).



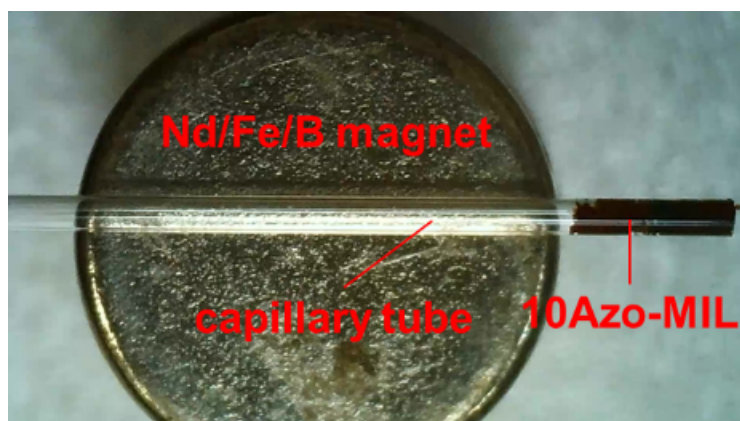
**Figure S9.** FT-IR spectra for 10Azo-MIL under UV irradiation from  $500\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  (a) and from  $2800\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  at  $25\text{ }^{\circ}\text{C}$  (b).



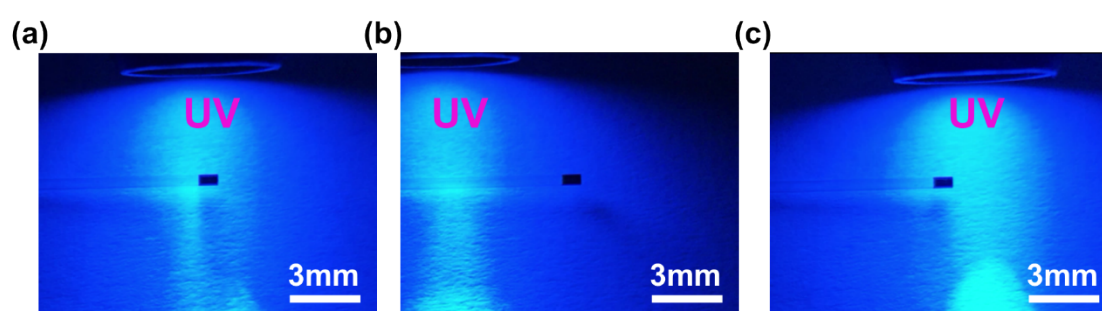
**Figure S10.** Changes of magnetic susceptibility of 10Azo-MIL after UV irradiation and in the dark under 1000 Oe at 298 K.



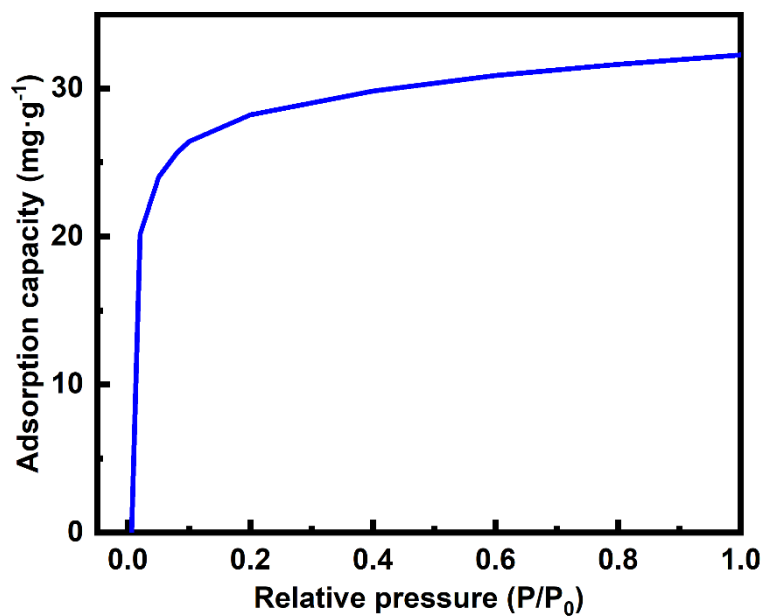
**Figure S11.** UV-Vis absorption spectra of MIL and 10Azo-MIL in acetonitrile before and after UV irradiation at 25 °C.



**Figure S12.** No-response of *trans*-10Azo-MIL in a magnetic field at 25 °C.



**Figure S13.** No-movements of *cis*-10Azo-MIL along moving UV light at 25 °C.



**Figure S14.** The CO<sub>2</sub> physisorption isotherm of *trans*-10Azo-MIL at 25 °C ( $P_0$  is standard atmospheric pressure).

### **3. Videos (S<sub>1</sub>-S<sub>4</sub>)**

**Video S1.** [Photoinduced phase transition of 10Azo-MIL.](#)

**Video S2.** [Separation of 20Azo-MIL.](#)

**Video S3.** [Horizontal movement of 10Azo-MIL.](#)

**Video S4.** [Vertical movement of 10Azo-MIL.](#)