

Supplementary Information

Experimental section.

Materials: γ -cyclodextrin (CD), toluene, dichloromethane, methanol and potassium hydroxide were purchased from Sigma-Aldrich and used as received.

Synthesis of γ -CD-MOF: Bare γ -CD-MOF was pre-synthesized according to previous report [S1]. In brief, 0.326 g of γ -CD was dissolved in 10 mL of potassium hydroxide aqueous solution (0.2 M). The solution was then filtered through a 0.45 μ m filter. Upon the slow evaporation of methanol into the γ -CD aqueous solution at room temperature (22 °C) for one week, as-formed γ -CD-MOF crystals were collected. After thorough rinse with methanol for two days, bare γ -CD-MOF was obtained.

Synthesis of γ -CD-MOF/ C_{60} : The γ -CD-MOF/ C_{60} composite was synthesized in a one-pot reaction. In a typical process, pre-synthesized γ -CD-MOFs were added into a vials containing a 2.8 mM of C_{60} solution in a mix solvent of toluene and dichloromethane (v/v = 1:1). The resulting mixture was incubated at 45 °C for 12 h. After thoroughly rinsing with dichloromethane, light brown γ -CD-MOF/ C_{60} composite was obtained.

Synthesis of DOX@ γ -CD-MOF/ C_{60} . In a typical process, as-prepared γ -CD-MOFs were immersed in a saturated DOX solution in methanol for 48 h. The free DOX was thoroughly removed by repeated rinse and soaking treatments. Thereafter, the DOX incorporated γ -CD-MOFs composites were coated with a C_{60} coating following the similar protocols mentioned above. Followed by thoroughly rinsing with dichloromethane, coffee-colour DOX@ γ -CD-MOF/ C_{60} composite was obtained.

Characterisation: The morphology of samples was analysed using a Philips XL-30 SEM. Dry samples were mounted on a silicon substrate followed by an Iridium coating. Powder X-ray diffraction of MOFs was measured at the powder diffraction using nickel-filtered Cu K α radiation. The diffraction pattern was collected in the 2 θ range of 3.5-60° in steps of 0.02° and a counting time of 2 s step⁻¹. Three-dimensional confocal imaging characterization was performed on Zeiss LSM780 confocal microscope. The samples were scanned from top surface downward to the median cross-section in 10 μ m of depth. The nitrogen sorption isotherms of MOF samples were obtained through Brunauer–Emmett–Teller (BET) on a Micromeritics ASAP2024. N₂ isotherm measurements were preceded at 77 K in a liquid nitrogen bath. BET surface area calculations for experimental samples were done using software provided within Quantachrome. The Raman spectra were collected on a Raman microprobe system (RENISHAW H13325 spectrophotometer) with the excitation line at 514.5 nm from an Ar ion laser and a line resolution of 4 cm⁻¹. This Raman instrument employs a holographic notch filter and a chargecoupled device (CCD) to gain high detecting sensitivity. The Raman band of a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer before performing the experiments. Thermogravimetric analyses (TGA) were performed using a TA Q500 thermal analysis system at a heating rate of 5 °C min⁻¹ in nitrogen. ¹H NMR spectra of MOF samples were recorded on a Bruker DRX-400 spectrometer with TMS as the internal standard and D₂O as the solvent. Fluorescence images of MOF samples were taken by an Olympus BX51M microscope equipped with a 473 & 488 nm BrightLine@longpass laser filter mounted in Olympus U-MF2 cube. The specimens (particles dispersed on slides) were imaged under the same instrumental conditions.

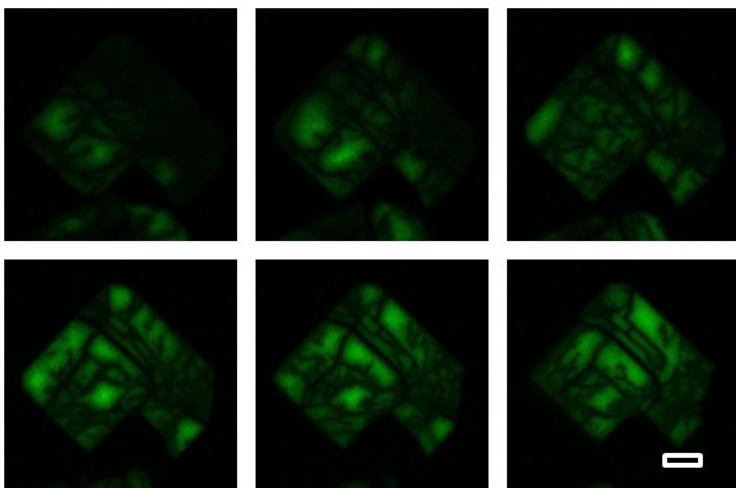


Fig. S1. Fluorescent confocal images of cross-sections of a γ -CD-MOF/ C_{60} crystal obtained by scanning the crystal from top surface downward to the median cross-section by 10 μm of depth. The scale bar is 200 μm .

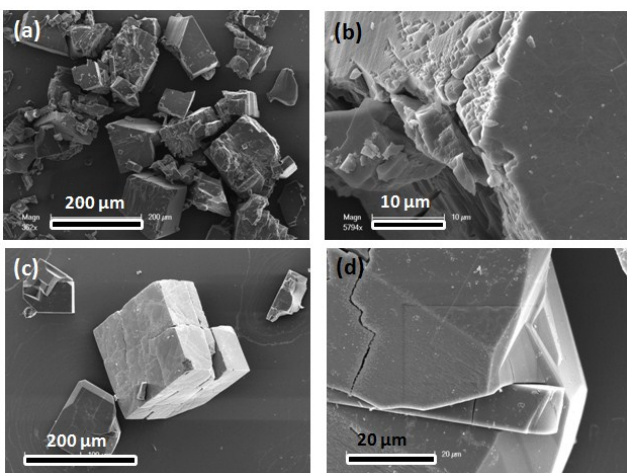


Fig. S2. SEM images of γ -CD-MOF before and after C_{60} incorporation.

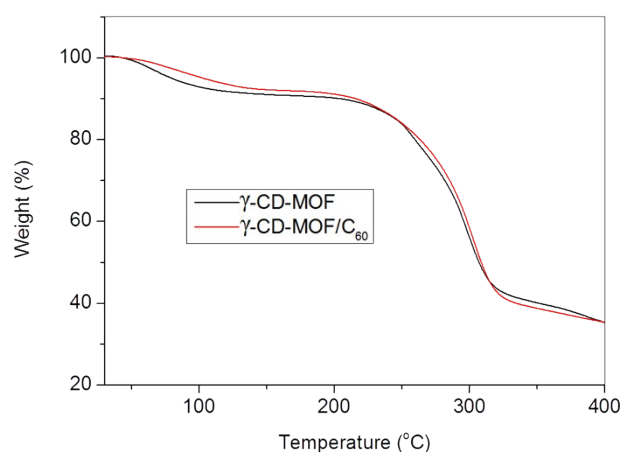


Fig. S3. TGA curve of γ -CD-MOF before and after C_{60} incorporation.

Simulation: Determined by a density function theory (DFT) method, the change in the hydrophobicity of γ -CD-MOF surface upon a C_{60} surface-coating was quantified through their water adsorption energies. Due to unmanageable atom number of γ -CD-MOF structure, the adsorption energy of a H_2O molecule with a γ -CD molecule, and a H_2O molecule with a γ -CD/ C_{60} complex was calculated, respectively. To construct the initial structure of a γ -CD/ C_{60} complex, we annealed the structure through empirical forcefield, followed by a validation of the structure through density function theory. DFT calculations were performed with the Vienna *Ab Initio* simulation package (VASP) [2]. The projector augmented wave (PAW) methods were used to describe the core and valence electrons [3]; The Perdew-Burke-Ernzerhof (PBE) was employed to describe the electron exchange and correlations [4]. The DFT-D2 method was employed for the long-range Van der Waals dispersion corrections. Brillouin zone was sampled by gamma centered k-point mesh [5].

Through density function theory, the adsorption energy between the cyclodextrin and water is around -42.27 kJ/mol. While after the C_{60} coated on the cyclodextrin surface, the

adsorption energy dramatically dropped to -13.09 kJ/mol. The adsorption energy was calculated in the ground state where no thermal energies were taken into consideration. Meanwhile, from TIP4P water model, the bulk vaporization enthalpy of water is 44 kJ/mol, which is comparable with water adsorption enthalpy of cyclodextrin, indicating an adsorbed phase with strong water interactions.

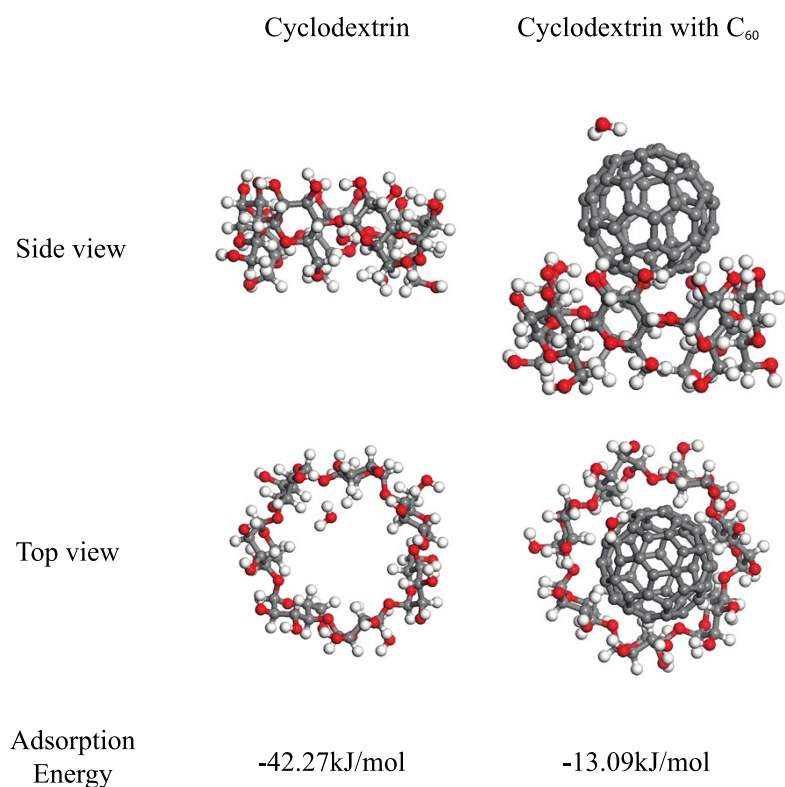


Fig. S4. Adsorption energy for the first water molecule (zero loading) in each of the structure studied.

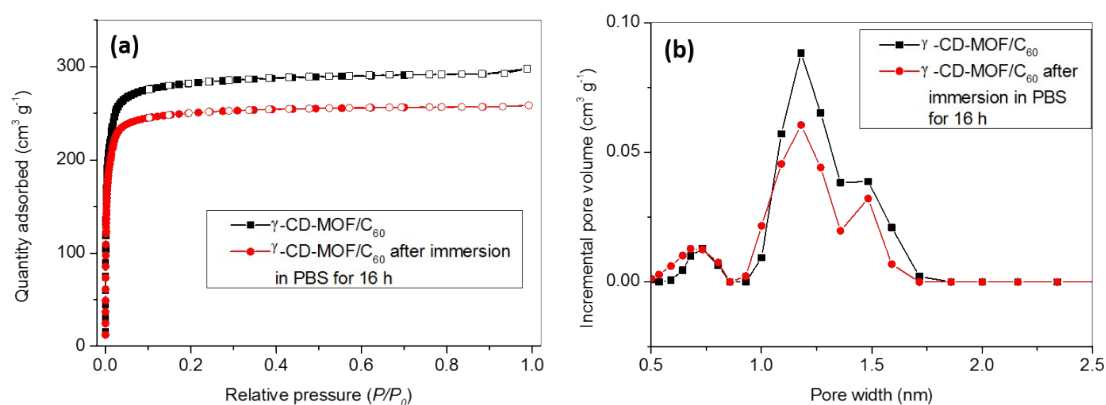


Fig. S5. N₂ adsorption isotherms (a) and pore size distribution (b) of γ-CD-MOF/C₆₀ composite before and after exposing flowing PBS solution for 16 h.

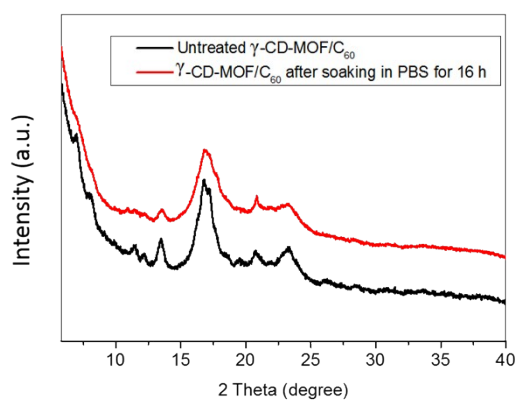


Fig. S6. Powder XRD patterns of γ-CD-MOF/C₆₀ composite before and after exposing flowing PBS solution for 16 h.

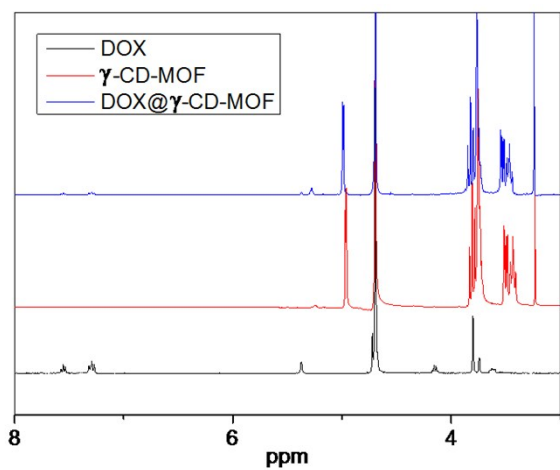


Fig. S7. ^1H NMR spectra of pure DOX, γ -CD-MOF, and DOX@ γ -CD-MOF.

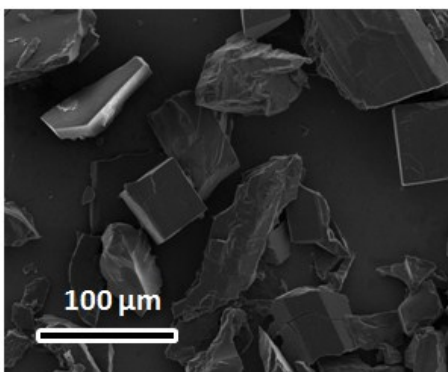


Fig. S8. SEM image of DOX@ γ -CD-MOF/ C_{60} composite.

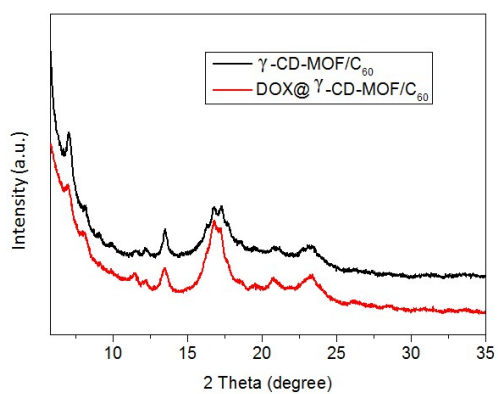


Fig. S9. Powder XRD patterns of γ -CD-MOF/ C_{60} before and after trapped with DOX.

Reference:

- [S1] Y. Furukawa, T. Ishiwata, K. Sugikawa, K. Kokado, K. Sada. *Angew. Chem. Int. Ed.* 2012, 51: 10566.
- [S2] G. Kresse, J. Furthmüller, *Phys Rev B* 1996, 54: 11169-86.
- [S3] P. E. Blöchl, *Phys Rev B* 1994, 50: 17953-79.
- [S4] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys Rev Lett* 1996, 77: 3865-8.
- [S5] S. Grimme, *J Comput Chem* 2006, 27: 1787-99.