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Supporting Information

Iodine Decorated-UiO-67 MOF as a Fluorescent Sensor for Detection of Halogenated Aromatic Hydrocarbons

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Experimental Section

General Methods. The organic ligand 4,4′-biphenyldicarboxylic acid (BPDC) and the $ZrCl_4$ were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, and others). Fourier-transform infrared (FT-IR) spectra (4000−400 cm^{-1}) were collected in the solid state on a BOMEM- MB102 spectrometer using potassium bromide pellets. Powder X-ray diffraction (PXRD) experiments were performed on a Stöe StadiVari θ/θ powder X-ray diffractometer equipped with a graphite monochromator and CuKα at 50 kV, 50 mA. Thermogravimetric analysis (TGA) was carried out. under a continuous air flow and recorded on a SDT Q600 V20.9 Build 20 thermogravimetric analyzer with a heating rate of 20 °C per min (25-900˚C). NMR spectra were recorded on a Brüker DPX-300 spectrometer at 300 MHz for ^1H NMR and data for 1H NMR are collected in $CDCl_3$ as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration referenced to the appropriate solvent peak or 0 ppm for TMS. The dinitrogen (N_2) adsorption isotherm was measured at 77 K using a liquid-N_2 bath. SEM images were taken on Hitachi SU 3500. UiO-67 MOF was prepared following reported procedures.[1]

Linker Preparation

Preparation of 2,2'-diiodo-4,4'-biphenyldicarboxylate (1). To a vigorously stirred solution of dimethyl biphenyl-4,4'-dicarboxylale (46.9 g, 0.17 mol) and Ag_2SO_4 (159.5g, 0.51 mol) in H_2SO_4(98%, 570 mL) was added I_2 (103.2 g,0.41 mol) in one lot. With the flask stoppered, the mixture was heated at 80˚C for 36 h. The resulting purple reaction mixture was poured into diluted Na_2SO_3 solution (2 L) at 0˚C, and the yellow suspension was extracted with ethyl acetate. The combined organic extract was washed with water, dried over Na_2S0_4, and concentrated to give a white solid which was esterified in refluxing methanol (600 mL) for 24h, using cone. sulfuric acid (20 mL) as a catalyst, After removal of methanol (400 mL), subsequent work-up of the crude mixture by extraction with CH_2Cl_2,.washing with aqueous $NaHCO_3$, drying over anhydrous Na_2SO_4, and concentration under reduced pressure gave essentially pure **1**(80.0 g, 86%) as a white crystals: mp : 153˚C. ^1H NMR (300MHz, $CDCl_3$): δ 8.63 ppm (s, 2H), 8.10-8.12 (d, 2H), 7.25-7.27 (d, 2H) and 3.97 (s, 6H). FT-IR (KBr pellet, cm^{-1}): 1712, 1550, 1434, 1288, 1118, 964, 856, 709, 655, 509, 447.

Preparation of 2,2'-diiodo-4,4'-biphenyldicarboxylic acid (2). A mixture of 2,2′-diiodo-4,4′-biphenyldicarboxylate (0.26g, 0.5 mmol) in 2.8 mL of THF and 2.8 mL of an aqueous 1M KOH solution was heated to reflux for 16 h. After cooling to room temperature in air, the THF was removed under vacuum and the solution was acidified with aq. 1M HCl. The resulting precipitate was separated by filtration, washed with water, then methanol and air-dried. Yield: 0.2 g of yellow powder. ^1H NMR (300MHz, DMSO- d_6): δ 13.35 ppm (s, 1H), 8.43 (s, 2H), 8.012-8.039 (d, 2H) and 7.34-7.36 (d, 2H). FT-IR (KBr pellet, cm^{-1}): 3163, 2514, 1697, 1550, 1419, 1242, 118, 902, 848, 771, 686, 532, 447.

Single crystal diffraction studies. For crystal I_2BPDC ligand intensity data were collected using a STOE IPDS-2T diffractometer with graphite monochromated Mo Kα radiation (λ) 0.71073 (Å). Data were collected in an a series of ω scans in 1° oscillations and integrated using the Stöe X-AREA[S2] software package. A numerical absorption correction was applied using the X-RED2[S3] and X-SHAPE[S4] software's. All structures were solved by direct methods using SHELXS-97[S5] and refined with full-matrix least-squares on F^2 using the SHELXL-97 program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at ideal positions and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2Ueq. All refinements were performed using the X-STEP32 crystallographic software package.[S6] Structural illustrations have been drawn with ORTEP-3[S7] and MERCURY.[S8] Crystallographic data for compound 1 have been listed in Table S1.

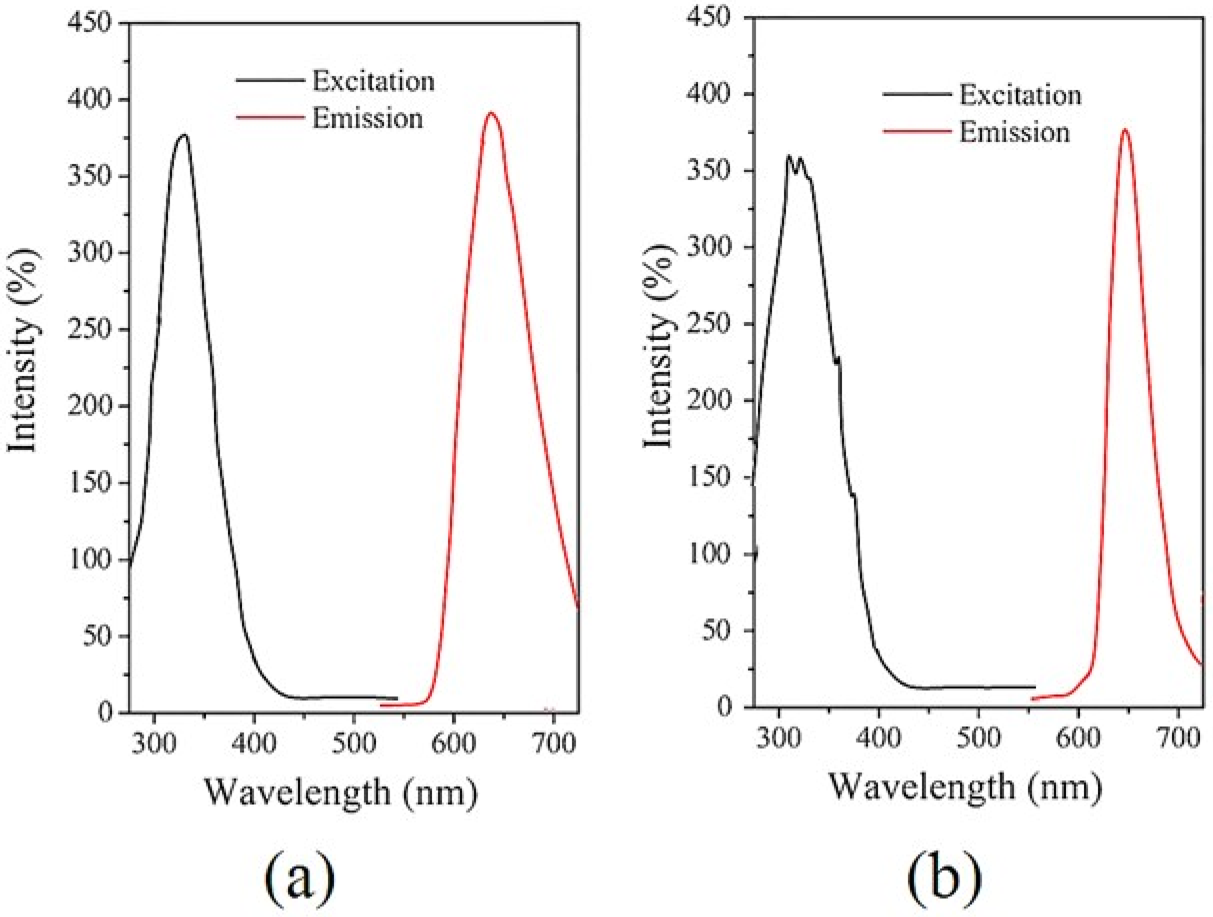
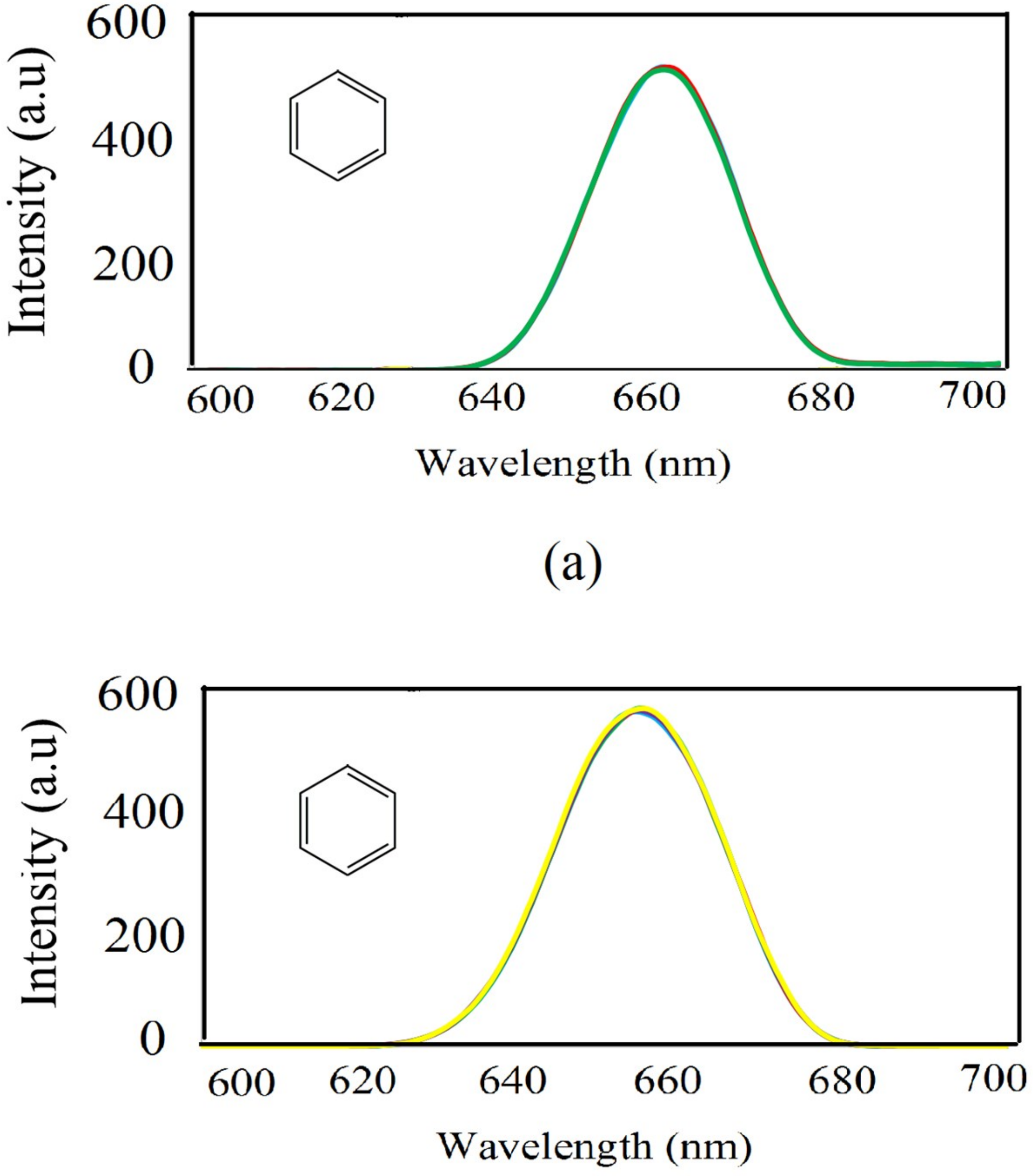


Figure S1. PL spectra of (a) UiO-67 and (b) UiO-67(I)$_2$ upon excitation of 320 nm.



(a)

(b)

Figure S2. PL spectra of (a) UiO-67 and (b) UiO-67(I)$_2$ upon addition of 10^{-4} solution of benzene in DMF.

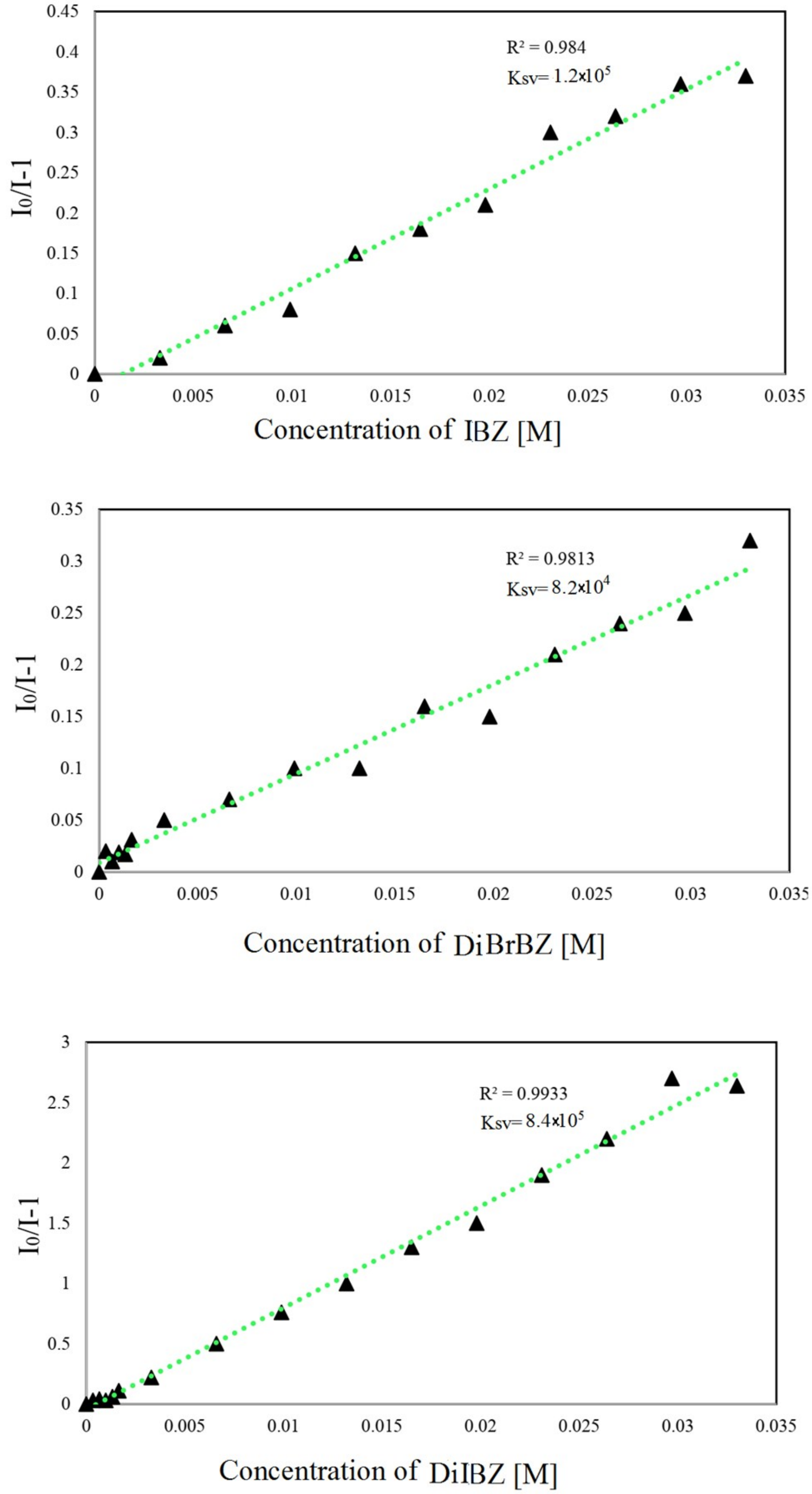


Figure S3. Stern-Velmer plot of UiO-67 with HAHs.

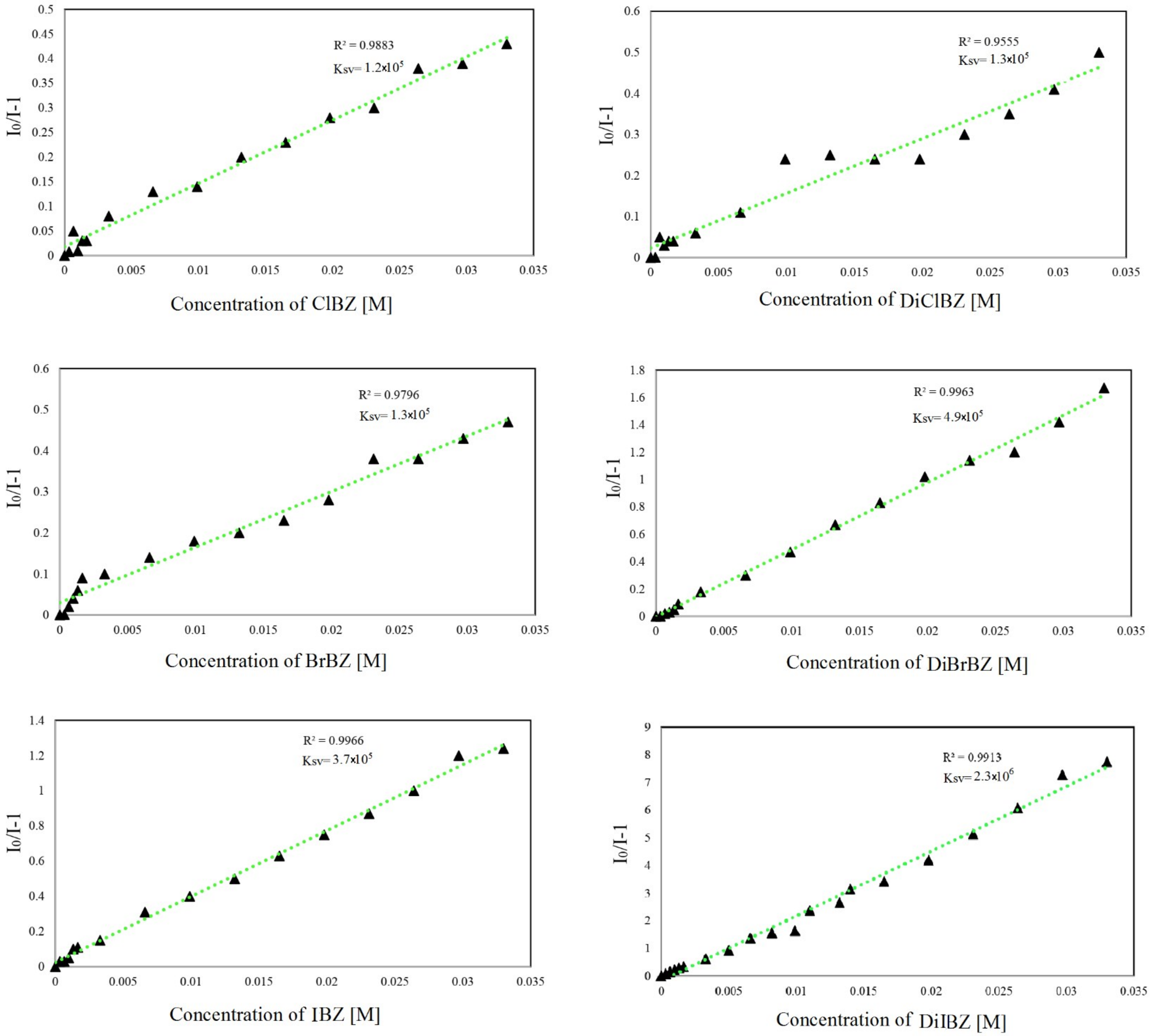


Figure S4. Stern-Velmer plot of UiO-67$(I)_2$ with HAHs.

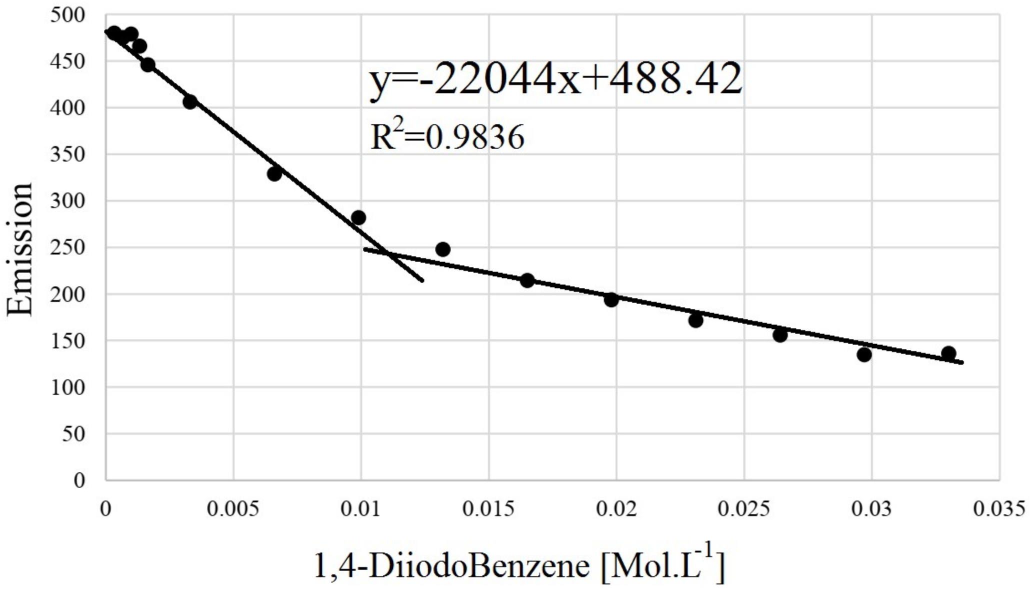


Figure S5. The LoD diagram of UiO-67 in the presence of 1,4-Diiodobenzene.

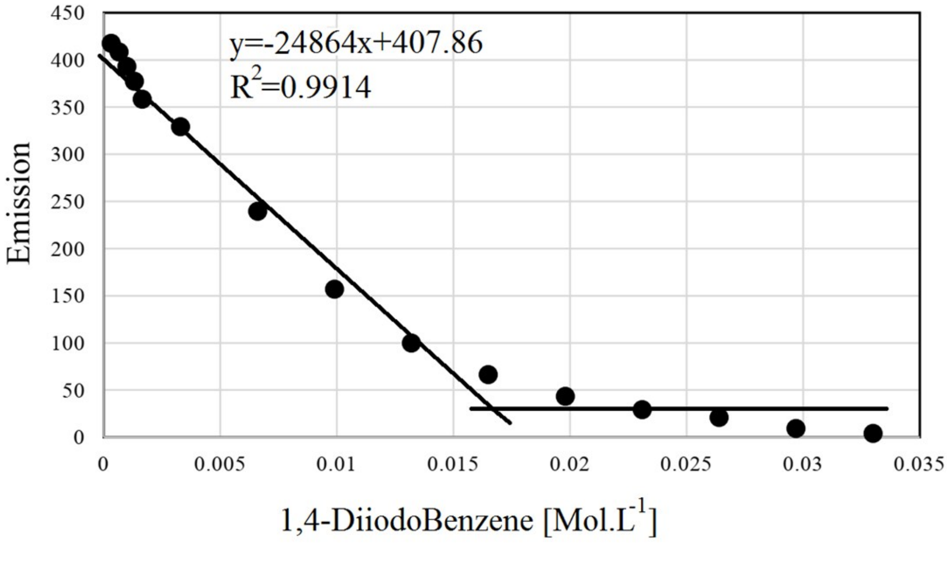


Figure S6. The LoD diagram of UiO-67$(I)_2$ in the presence of 1,4-Diiodobenzene.

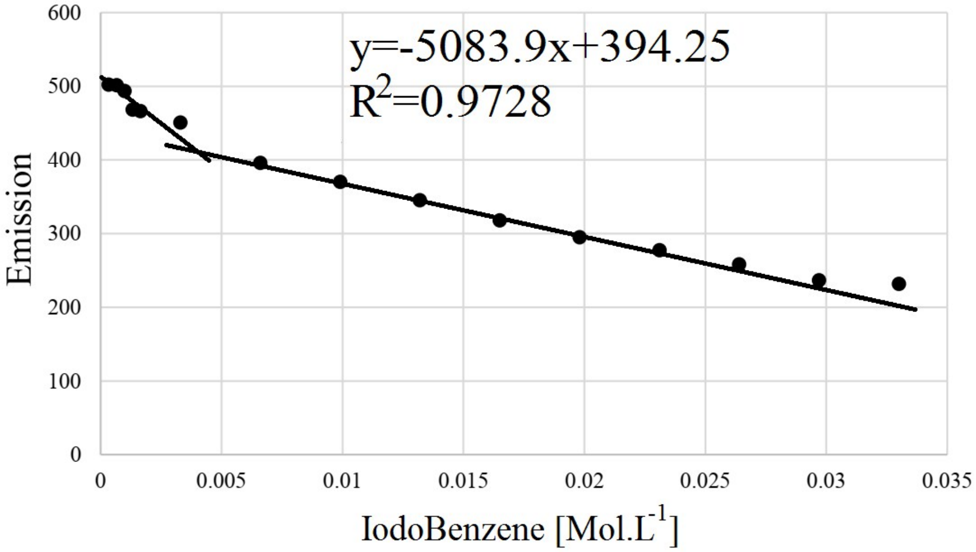


Figure S7. The LoD diagram of UiO-67(I)$_2$ in the presence of Iodobenzene.

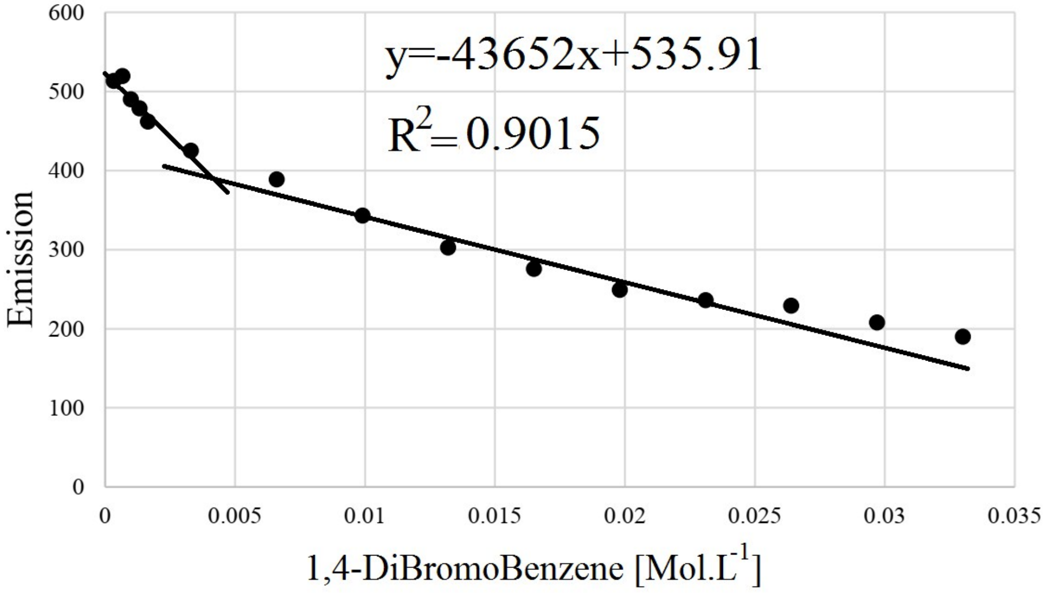


Figure S8. The LoD diagram of UiO-67(I)$_2$ in the presence of 1,4-Dibromobenzene.

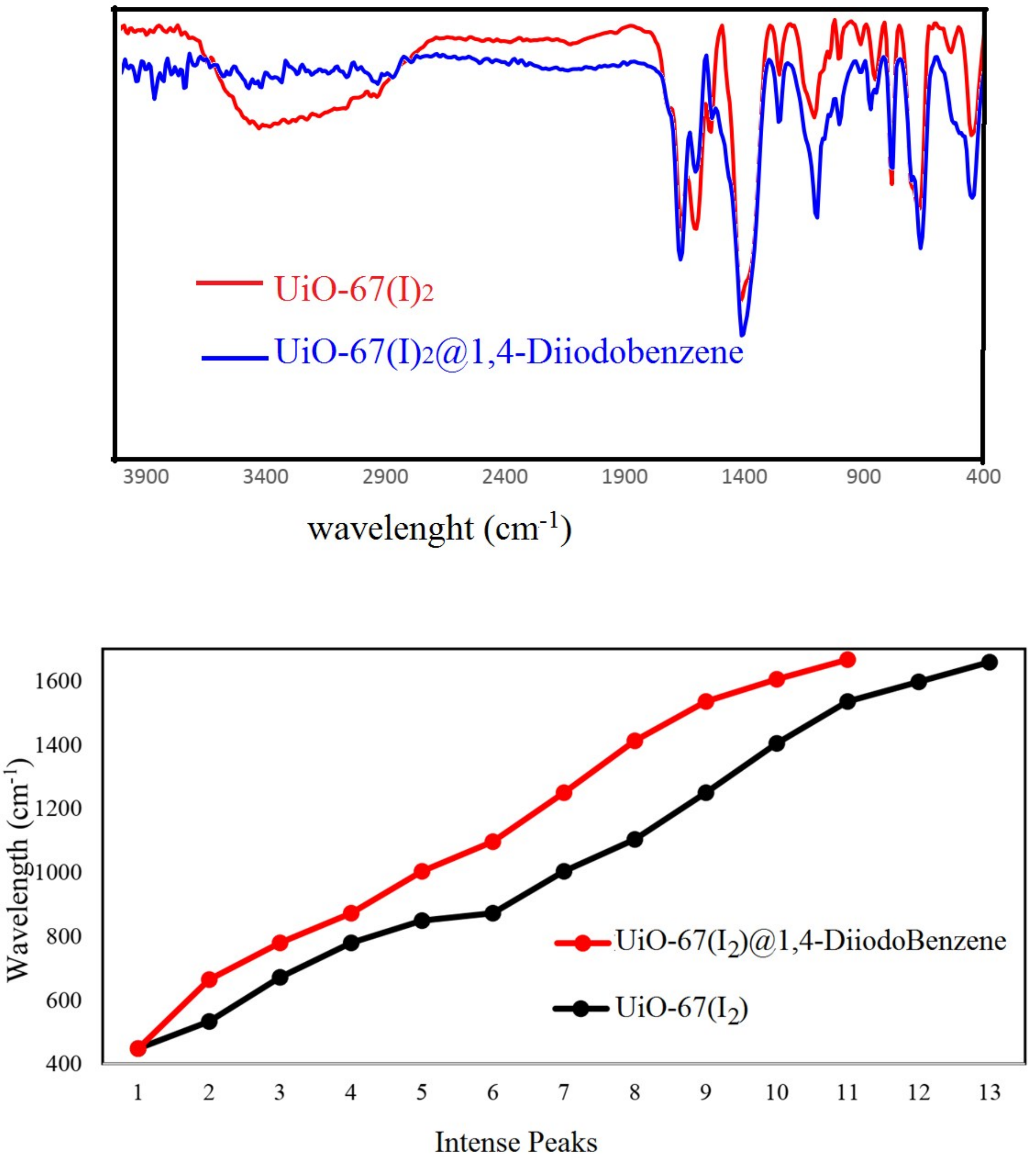


Figure S9. The FT-IR diagrams of UiO-67(I)$_2$ and UiO-67(I)$_2$@1,4-diiodobenzene.

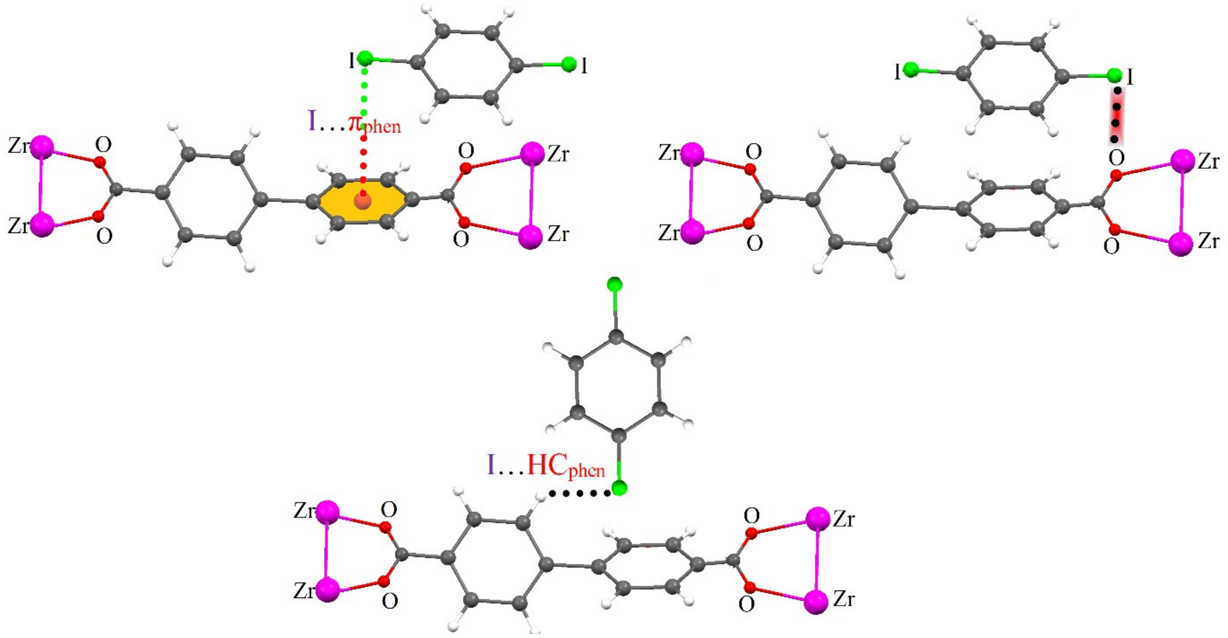


Figure S10. The possible intermolecular interactions in UiO-67.

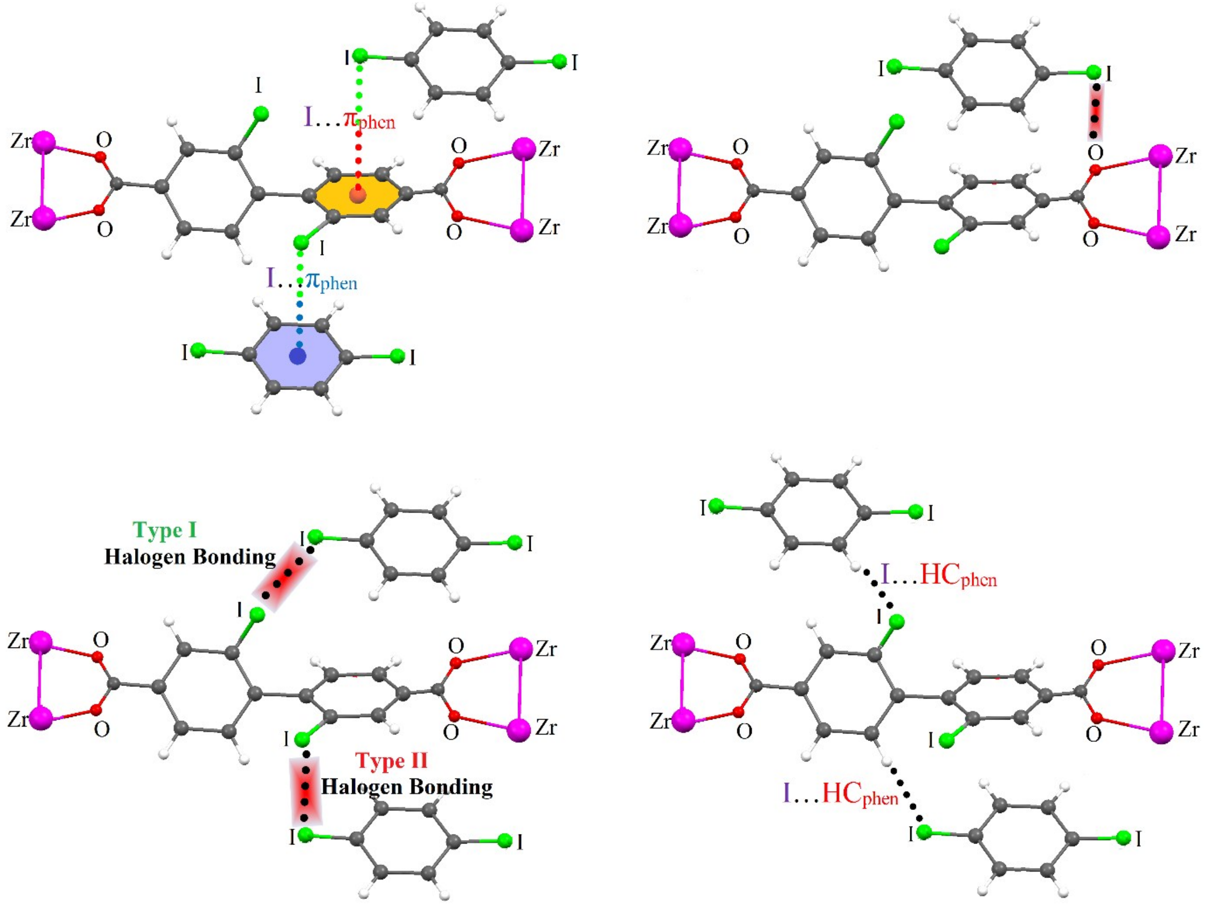


Figure S11. The possible intermolecular interactions in UiO-67(I)$_2$.

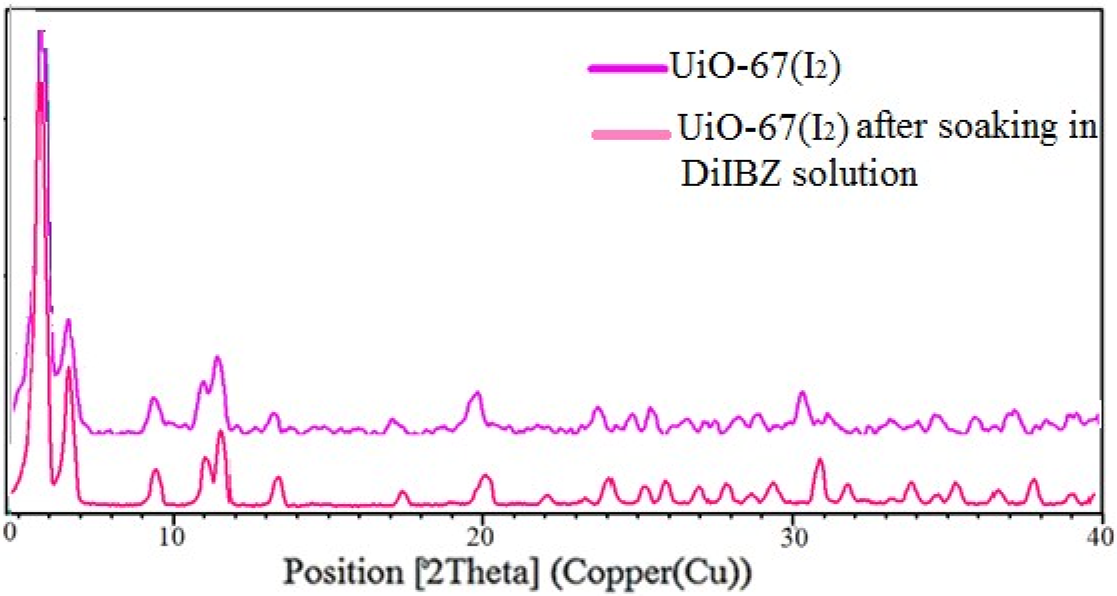


Figure S12. The PXRD data of UiO-67(I)2 after soaking in DMF solution of 1,4-diiodobenzene for 24h.

Table S1. Crystal data and structural refinement for copper complex of 2,2´-diiodo,1,1´-biphenyl,4,4´-biphenyldicarboxylic acid (I_2BPDC) ligand

	I_2BPDC ligand
formula	$C_{16}H_{12}I_2O_4$
fw	522.06
λ/Å	0.71073
T/K	298(2)
crystal.system	Monoclinic
space group	$I2/a$
a/Å	15.8426(17)
b/Å	7.9016(6)
c/Å	13.7208(14)
β/°	90.146(9)
V/Å^3	1717.6(3)
ρ_{calc}g/cm^3	2.019
Z	4
μ/mm^{-1}	3.675
F(000)	984
2θ/°	54.00
R(int)	0.0416
GOOF	1.005
$R_1^a(I > 2\sigma(I))$	0.0420
$wR_2^b(I > 2\sigma(I))$	0.1067
CCDC No.	1957756

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)2]^{½}$.

REFERENCES:

[S1] Wang, J.; Hanan, G. A Facile Route to Sterically Hindered and Non-Hindered 4′-Aryl-2,2′:6′,2″-Terpyridines. *Synlett* **2005**, *8*, 1251–1254.

[S2] Stoe, C. X–AREA: Program for the Acquisition and Analysis of Data, Version 1.30. *Stoe Cie GmbH Darmatadt, Ger.* **2005**.

[S3] X–RED: Program for Data Reduction and Absorption Correction, vesion 1.28b: Stoe & Cie GmbH: Darmstadt, Germany, 2005. *No Title*.

[S4] X–SHAPE: Program for crystal optimization for numerical absorption correction, vesion 2.05: Stoe & Cie GmbH: Darmstadt, Germany, 2004. No TitleX–SHAPE: Program for Crystal Optimization for Numerical Absorption Correction, Vesion 2.05: Stoe & Cie GmbH: Darmstadt, Germany, 2004.

[S5] Sheldrick, G. M. SHELX-97, Program for the Solution and Refinement of Crystal Structures. *Univ. Göttingen, Ger.* **1997**.

[S6] Stoe, C. X-STEP32, Version 1.07 b, Crystallographic Package. *Stoe Cie GmbH, Darmstadt, Ger.* **2000**.

[S7] Farrugia, L. J.; IUCr. *WinGX* and *ORTEP for Windows* : An Update. *J. Appl. Crystallogr.* **2012**, *45* (4), 849–854.

[S8] Mercury 3.10.1 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2017−2018. Mercury 3.10.1 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2017−2018No Title.