

Facile mechanochemical synthesis of isoreticular metal-organic frameworks and comparative study of their potential for nitrobenzene sensing

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Experimental Section

Apparatus and Reagents

All starting materials, including terephthalic acid and 2-Bromoterephthalic acid, were purchased from commercial suppliers (Sigma-Aldrich, Merck) and used as received. The infrared spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500-4000 cm^{-1} using the KBr disk technique. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using an ECS 4010 CHN-O made in Costech, Italy. Melting points were obtained by a Bamstead Electrothermal type 9200 melting point apparatus and corrected. The ^1H NMR spectrum was recorded on a Bruker AC-300 MHz spectrometer at ambient temperature in d_6 -DMSO. X-ray powder diffraction (XRPD) measurements were performed using a Philips Xpert diffractometer with monochromated Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$).

Computational Details

Time-dependent density functional theory (TD-DFT) calculations were performed using GAMESS suite of program.¹ Frontier molecular orbitals were calculated for BDC, Cl-BDC, Br-BDC, I-BDC and nitrobenzene using TD-DFT calculations at the B3LYP/6-311g(d,p) basis set for all atoms except iodine, for which the LANL2DZdp-ECP (with polarization functions of d symmetry and diffuse functions of p symmetry) basis set was used. Frontier MOs were plotted at an isovalue of 0.02 au.

Fluorescence Measurements

The Fluorescence properties of the prepared IRMOF-1 and IRMOF-2-Xs materials were measured in the solid state and in different solvent emulsions recorded on a Perkin Elmer-LS55 Fluorescence Spectrometer at room temperature. Typically, after activation, 1 mg of MOF was grinded down, and then immersed in different organic solvent (2 ml) and after 24 h was made into emission.

Stern-Volmer Plots

According to the Stern-Volmer equation, $(I_0/I) = K_Q [A] + 1$,
Where here, I_0 is the initial fluorescence intensity of soaked MOF sample in toluene,
 I is the fluorescence intensity in the presence of nitrobenzene,
 $[A]$ is the molar concentration of nitrobenzene, and K_Q is the quenching constant (M^{-1}).
For the quenching constant extraction, emission intensity of all MOFs was recorded by suspending them into different concentrations of nitrobenzene solutions in toluene, upon the same manner described in Fluorescence measurement section.

Synthesis

The 2-chloro and 2-iodo-terephthalic acid were prepared from 2-aminoterephthalic acid by employing slightly modified literature procedures,^{2,3} while terephthalic acid and 2-bromo-terephthalic acid were provided from commercial suppliers.

Synthesis of 2-chloroterephthalic acid

2-aminoterephthalic acid (0.54 g, 3 mmol) and 30 mL of HCl (37%) were added to a 100 mL round-bottom flask and the mixture was stirred in an ice-acetone bath (ca. $-10\text{ }^{\circ}\text{C}$) for 10 min during which the color of the reaction mixture became white from pale yellow. An aqueous solution of sodium nitrite (0.414 g, 6 mmol) was then added drop wise, while the temperature kept at $-5\text{ }^{\circ}\text{C}$, over a period of 20 min during which time the solution became clear. After being stirred for an additional 30 min at $0\text{ }^{\circ}\text{C}$, a solution of CuCl (1.18 g, 12 mmol) in 10 mL of HCl (37%) was added and the resulting dark green solution was left stirring at RT for 4 h. Then the reaction mixture was warmed up to $100\text{ }^{\circ}\text{C}$ and stirred for an additional 2 h. After warming, a white solid starts to precipitate. The solid was filtered using Buchner funnel and rinsed with water for several times to give 0.36 g (60%) of 2-chloroterephthalic acid as a white-colored solid. (M.p. $299\text{--}300\text{ }^{\circ}\text{C}$), Anal. calcd for $\text{C}_8\text{H}_5\text{ClO}_4$: C, 47.90; H, 2.51, Found: C, 47.87; H, 2.49. $^1\text{H-NMR}$ (d_6 -DMSO) 13.59 (2H, bs), 7.96 (1H, d), 7.93 (1H, dd), 7.85 (1H, d). FT-IR (KBr pellet, cm^{-1}): 3424, 2869, 2816, 2653, 2549, 1692, 1419, 1297, 1210, 1051, 901, 761. MS (m/z): 200.1 (M^+ , base peak), 183.1, 164.1, 155.1, 136.1.

Synthesis of 2-iodoterephthalic acid

2-aminoterephthalic acid (0.54 g, 3 mmol) and 30 mL of HCl (37%) were added to a 100 mL round-bottom flask and the mixture was stirred in an ice-acetone bath (ca. $-10\text{ }^{\circ}\text{C}$) for 10 min during which the color of the reaction mixture became white from pale yellow. An aqueous solution of sodium nitrite (0.414 g, 6 mmol) was then added drop wise, while the temperature kept at $-5\text{ }^{\circ}\text{C}$, over a period of 20 min during which time the solution became clear. After being stirred for an additional 30 min at $0\text{ }^{\circ}\text{C}$, the diazonium salt was poured into a solution of KI (4.15 g, 25 mmol) in 50 mL of water and the resulting dark solution was left stirring at RT for 6 h. To the stirred solution was then added solid NaHSO_3 in portions till the dark color of the solution was discharged leaving behind a suspension of tan colored solid in the solvent mixture. The solid was filtered using Buchner funnel and rinsed with water for several times to give 0.61 g (70%) of 2-iodoterephthalic acid as a cream-colored solid. (M.p. $299\text{--}300\text{ }^{\circ}\text{C}$), Anal. calcd for $\text{C}_8\text{H}_5\text{IO}_4$: C, 32.90; H, 1.73, Found: C, 32.86; H, 1.72. $^1\text{H-NMR}$ (d_6 -DMSO) 13.52 (2H, bs), 8.41 (1H, d), 7.97 (1H, dd), 7.75 (1H, d). FT-IR (KBr pellet, cm^{-1}): 3427, 2966, 2816, 2646, 2530, 1692, 1410, 1294, 1257, 1132, 919, 778. MS (m/z): 292.2 (M^+ , base peak), 275.2, 247.2, 191.2, 165.2.

General procedure for mechanosynthesis and activation of IRMOF-1 and IRMOF-2-X series

IRMOF-1 and IRMOF-2-X compounds were synthesized by liquid-assisted grinding (LAG) of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (1.35 mmol) and corresponding X-BDC (0.5 mmol), where X=H, Cl, Br and I, with a small amount of *N,N*-dimethylformamide (DMF), for 30 minutes. Grinding and mixing were done with an agate mortar and pestle. The obtained powder was washed with small amount of DMF (3 times) in order to remove any unreacted starting material and then dried in air at room temperature. The products were characterized by different techniques such as powder X-ray diffraction (PXRD), IR spectroscopy and elemental analysis. The samples were activated by immersing them in anhydrous chloroform followed by heating at 90°C in vacuum for 24 h. The activation was also confirmed by PXRD and FT-IR spectroscopy.

IRMOF-1:

Neat grinding of terephthalic acid (0.083 g, 0.5 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.296 g, 1.35 mmol) did not result in any reaction, as evidenced by PXRD. Thus, liquid-assisted grinding (LAG) method was attempted for synthesizing the corresponding framework. IRMOF-1 was obtained from a LAG experiment, where terephthalic acid (0.083 g, 0.5 mmol) was ground together with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.296 g, 1.35 mmol) and 100 μL of *N,N*-dimethylformamide (DMF). As shown in Figure S1, the PXRD patterns give a good match to the simulated IRMOF-1. FT-IR (KBr pellet, cm^{-1}): 3418(br), 2933(w), 1601(vs), 1390(vs), 1100(m), 1016(m), 823(m), 748(s), 528(s). Anal. calcd for $\text{C}_{24}\text{H}_{12}\text{O}_{13}\text{Zn}_4$: C, 37.44; H, 1.57; N: 0, Found: C, 37.32; H, 1.51, N: 0.18.

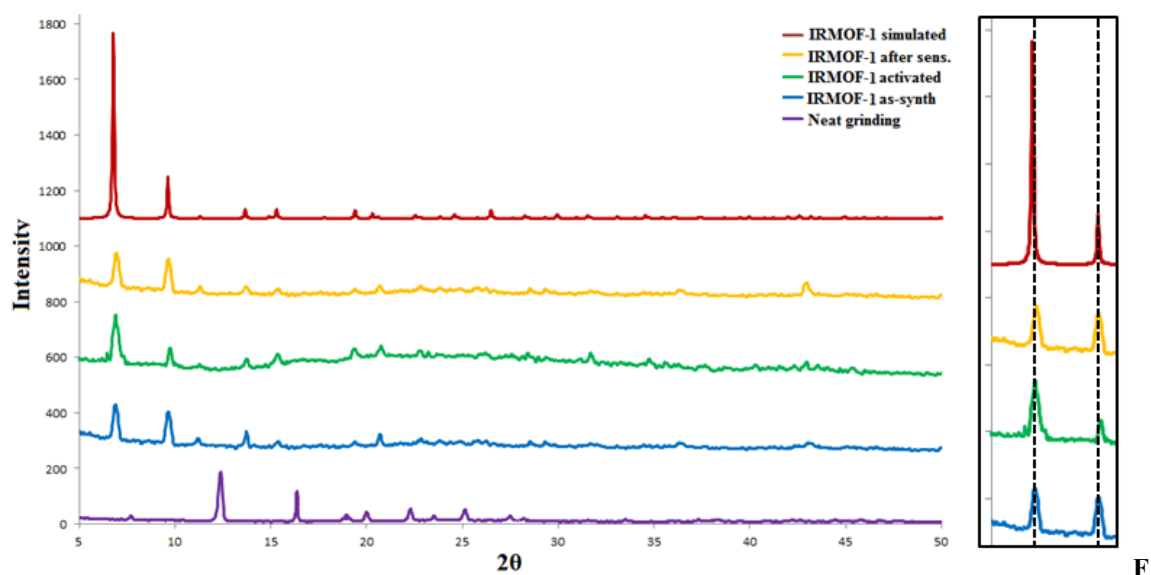


figure S1. PXRD patterns of neat grinding, as synthesized IRMOF-1 by LAG method, after activation, after sensing nitrobenzene and simulated from single crystal data of IRMOF-1. The right inset shows the matching between simulated and experimental XRD patterns for two high intense (2 0 0) and (2 2 0) peaks.

IRMOF-2-Cl:

Neat grinding of 2-chloroterephthalic acid (0.1 g, 0.5 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.296 g, 1.35 mmol) did not result in any reaction, as evidenced by PXRD. Thus, liquid-assisted grinding (LAG) method was attempted for synthesizing the corresponding framework. IRMOF-2-Cl was obtained from a LAG experiment, where 2-chloroterephthalic acid (0.1 g, 0.5 mmol) was ground together with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.296 g, 1.35 mmol) and 100 μL of *N,N*-dimethylformamide (DMF). As shown in Figure S2, the PXRD patterns give a good match to the simulated IRMOF-2. FT-IR (KBr pellet, cm^{-1}): 3409(br), 2938(w), 1590(vs), 1388(vs), 1155(m), 1048(m), 831(m), 769(s), 549(s). Anal. calcd for $\text{C}_{24}\text{H}_9\text{Cl}_3\text{O}_{13}\text{Zn}_4$: C, 33.01; H, 1.04; N: 0, Found: C, 32.88; H, 1.05, N: 0.21.

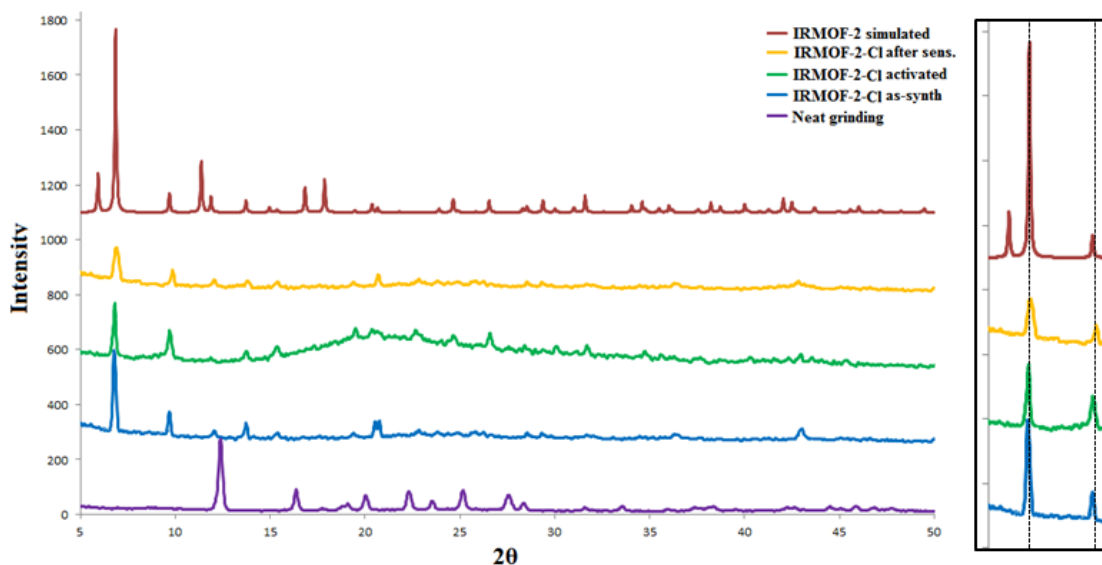


Figure S2. PXRD patterns of neat grinding, as synthesized IRMOF-2-Cl by LAG method, after activation, after sensing nitrobenzene and simulated from single crystal data of IRMOF-2. The right inset shows the matching between simulated and experimental XRD patterns for two high intense (2 0 0) and (2 2 0) peaks.

IRMOF-2-Br:

Neat grinding of 2-bromoterephthalic acid (0.122 g, 0.5 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.296 g, 1.35 mmol) did not result in any reaction, as evidenced by PXRD. Thus, liquid-assisted grinding (LAG) method was attempted for synthesizing the corresponding framework. IRMOF-2-Br was obtained from a LAG experiment, where 2-bromoterephthalic acid (0.122 g, 0.5 mmol) was ground together with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.296 g, 1.35 mmol) and 100 μL of *N,N*-dimethylformamide (DMF). As shown in Figure S3, the PXRD patterns give a good match to the simulated IRMOF-2. FT-IR (KBr pellet, cm^{-1}): 3414(br), 2933(w), 1605(vs), 1390(vs), 1109(m), 1037(m), 829(m), 769(s), 542(s). Anal. calcd for $\text{C}_{24}\text{H}_9\text{Br}_3\text{O}_{13}\text{Zn}_4$: C, 28.64; H, 0.90; N: 0, Found: C, 28.54; H, 0.81, N: 0.12.

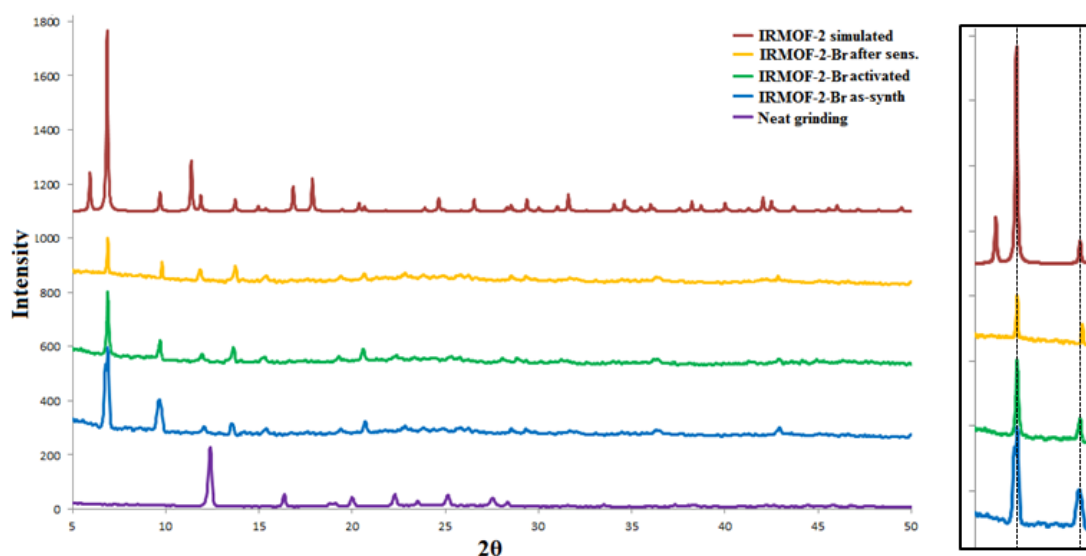


Figure S3. PXRD patterns of neat grinding, as synthesized IRMOF-2-Br by LAG method, after activation, after sensing nitrobenzene and simulated from single crystal data of IRMOF-2. The right inset shows the matching between simulated and experimental XRD patterns for two high intense (2 0 0) and (2 2 0) peaks.

IRMOF-2-I:

Neat grinding of 2-iodoterephthalic acid (0.146 g, 0.5 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.296 g, 1.35 mmol) did not result in any reaction, as evidenced by PXRD. Thus, liquid-assisted grinding (LAG) method was attempted for synthesizing the corresponding framework. IRMOF-2-I was obtained from a LAG experiment, where 2-iodoterephthalic acid (0.146 g, 0.5 mmol) was ground together with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.296 g, 1.35 mmol) and 100 μL of *N,N*-dimethylformamide (DMF). As shown in Figure S4, the PXRD patterns give a good match to the simulated IRMOF-2. FT-IR (KBr pellet, cm^{-1}): 3410(br), 2929(w), 1600(vs), 1387(vs), 1107(m), 1030(m), 826(m), 766(s), 537(s). Anal. calcd for $\text{C}_{24}\text{H}_9\text{I}_3\text{O}_{13}\text{Zn}_4$: C, 25.12; H, 0.79; N: 0, Found: C, 25.10; H, 0.80, N: < 0.1.

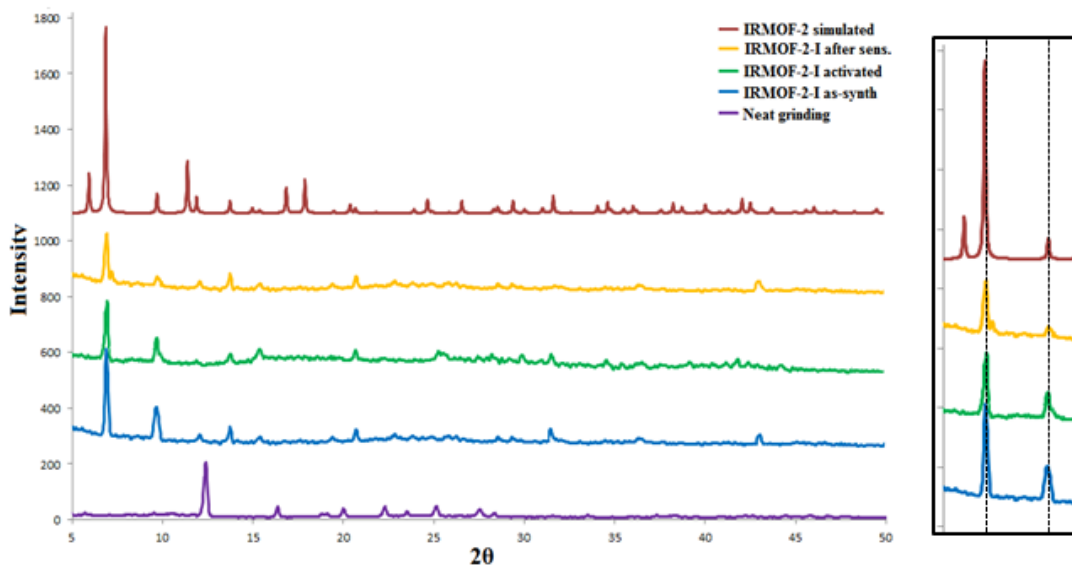


Figure S4. PXRD patterns of neat grinding, as synthesized IRMOF-2-I by LAG method, after activation, after sensing nitrobenzene and simulated from single crystal data of IRMOF-2. The right inset shows the matching between simulated and experimental XRD patterns for two high intense (2 0 0) and (2 2 0) peaks.

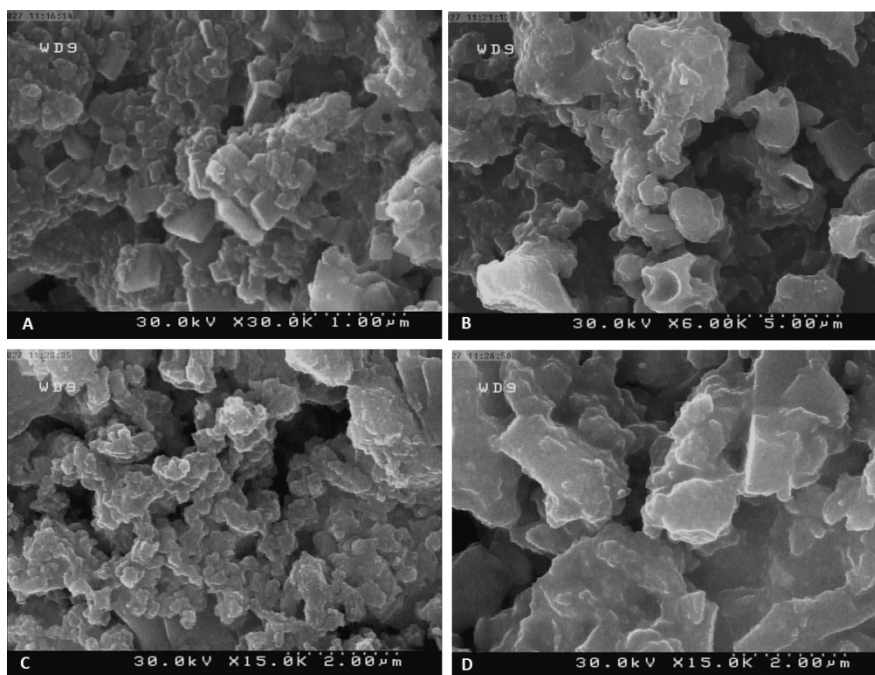


Figure S5. Represented SEM images for (a) IRMOF-1, (b) IRMOF-2-Cl, (c) IRMOF-2-Br and (d) IRMOF-2-I prepared via mechanochemical method.

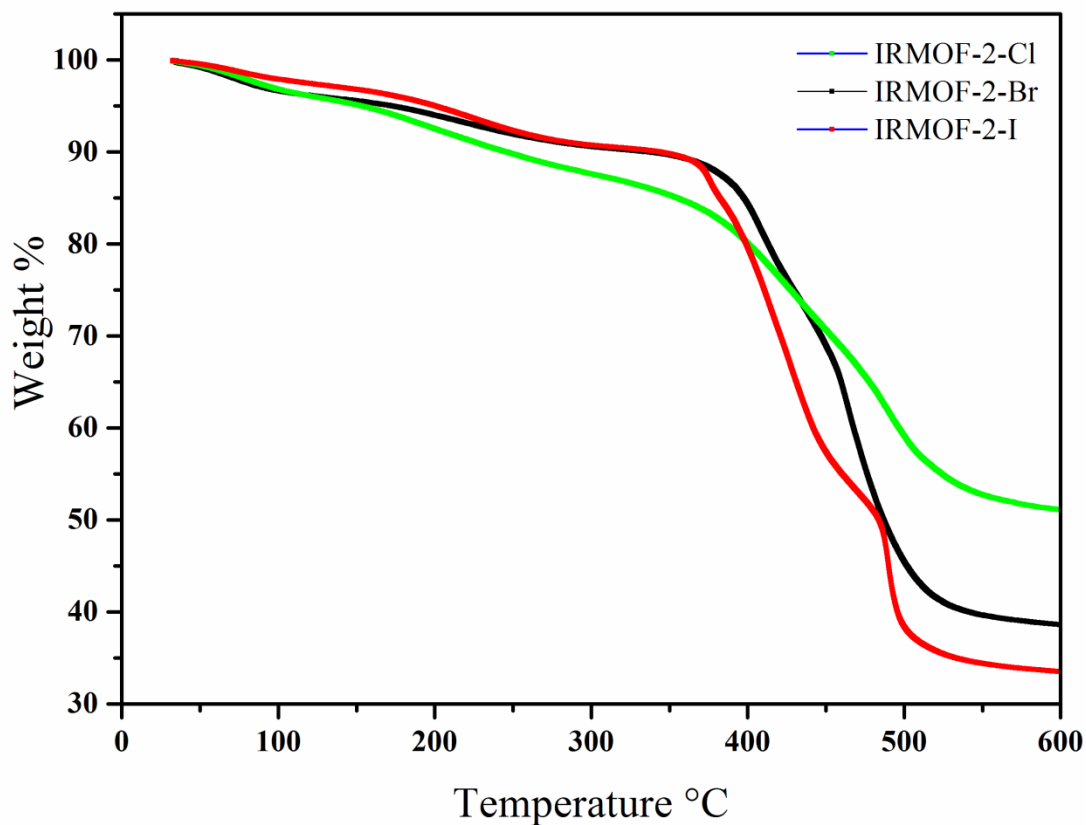


Figure S6. Thermogravimetric analysis of IRMOF-2-Cl (green line), IRMOF-2-Br (Black line) and IRMOF-2-I (red line)

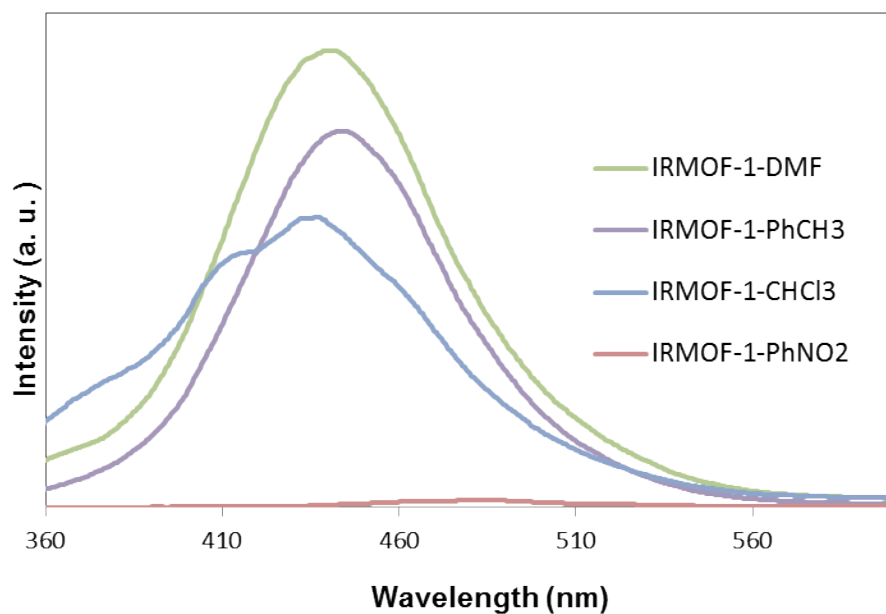


Figure S7. Fluorescence emission spectra of IRMOF-1 dispersed in different solvents, excited at 325 nm.

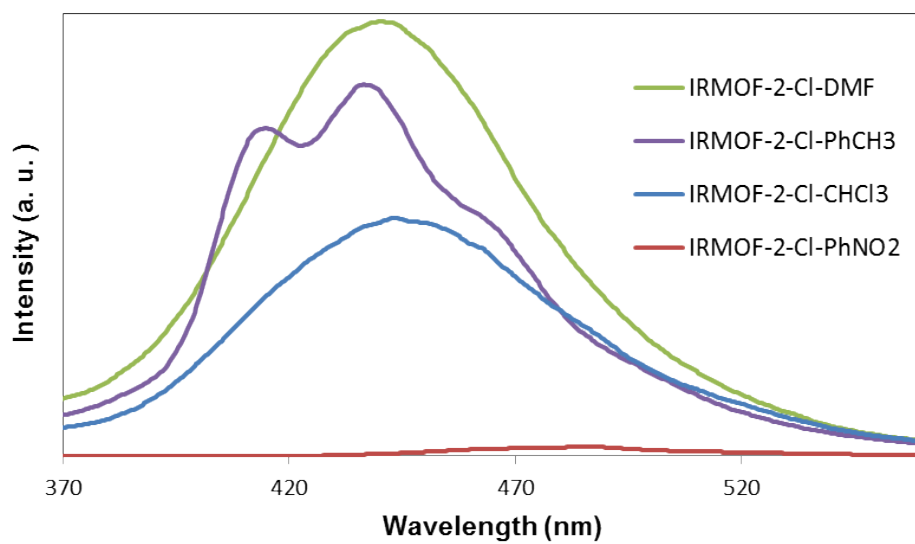


Figure S8. Fluorescence emission spectra of IRMOF-2-Cl dispersed in different solvents, excited at 340 nm.

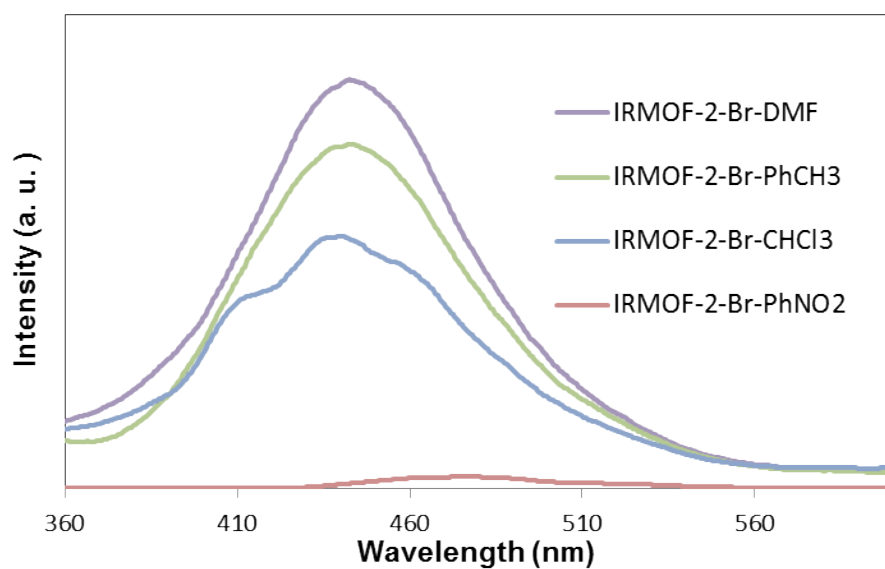


Figure S9. Fluorescence emission spectra of IRMOF-2-Br dispersed in in different solvents, excited at 320 nm.

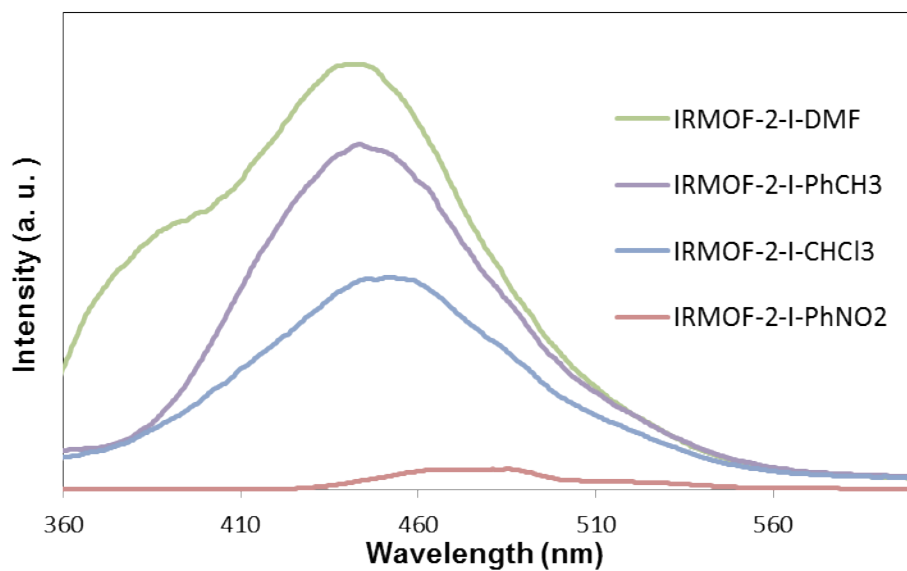


Figure S10. Fluorescence emission spectra of IRMOF-2-I dispersed in different solvents, excited at 325 nm.

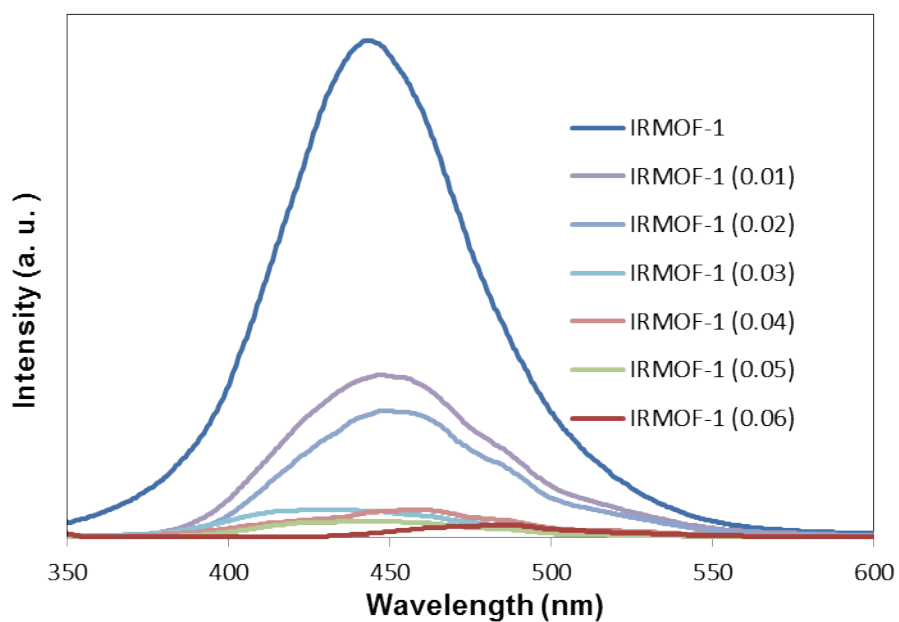


Figure S11. Fluorescence emission spectra of IRMOF-1 dispersed in PhCH₃ at different nitrobenzene concentrations represented in parentheses, excited at 325 nm.

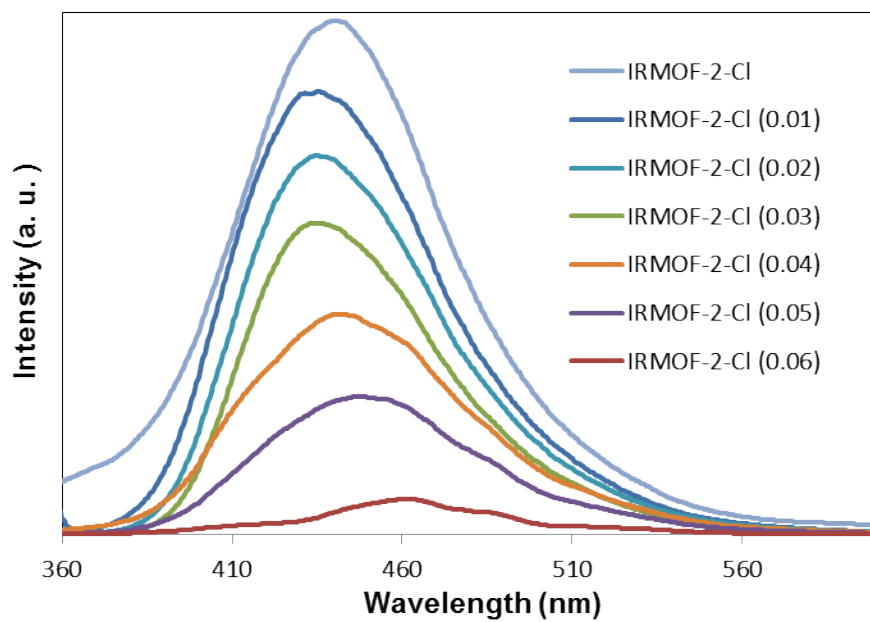


Figure S12. Fluorescence emission spectra of IRMOF-2-Cl dispersed in PhCH₃ at different nitrobenzene concentrations represented in parentheses, excited at 340 nm.

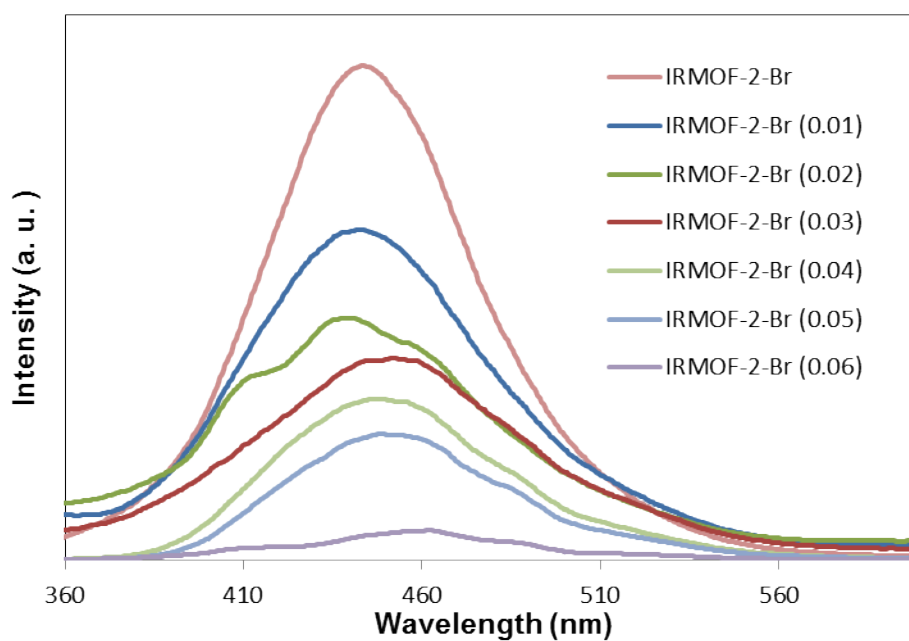


Figure S13. Fluorescence emission spectra of IRMOF-2-Br dispersed in PhCH₃ at different nitrobenzene concentrations represented in parentheses, excited at 320 nm.

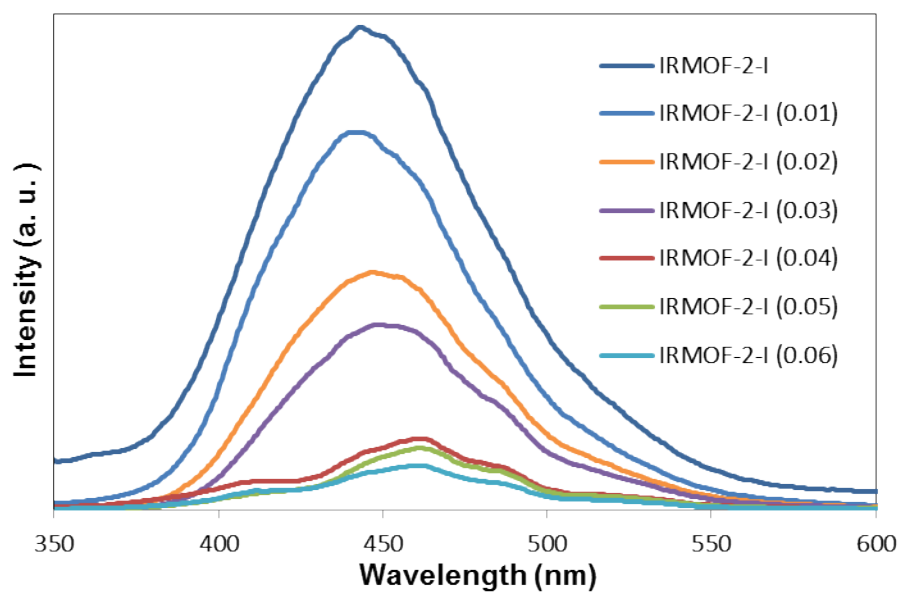


Figure S14. Fluorescence emission spectra of IRMOF-2-I dispersed in PhCH₃ at different nitrobenzene concentrations represented in parentheses, excited at 325 nm.

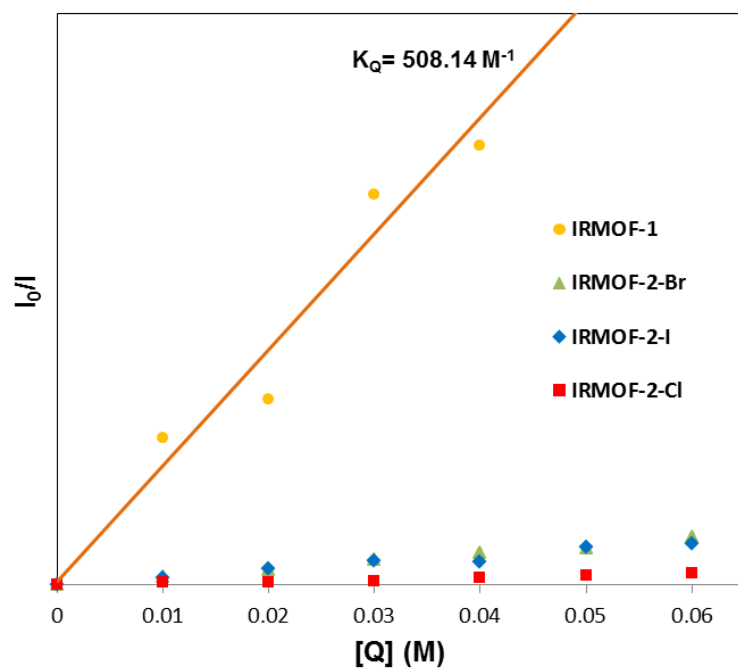


Figure S15. Comparison of Stern–Volmer (SV) plots in the presence of 1 mg of different IRMOFs in different nitrobenzene concentrations ($[Q]$) in toluene.

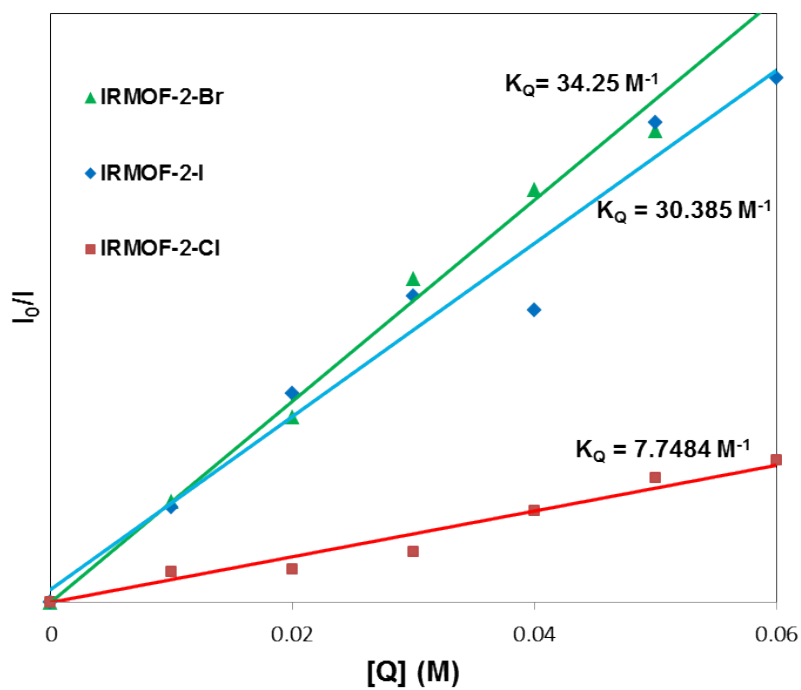


Figure S16. Comparison of Stern–Volmer (SV) plots in the presence of 1 mg of different halogenated IRMOF-2s in different nitrobenzene concentrations ($[Q]$) in toluene.

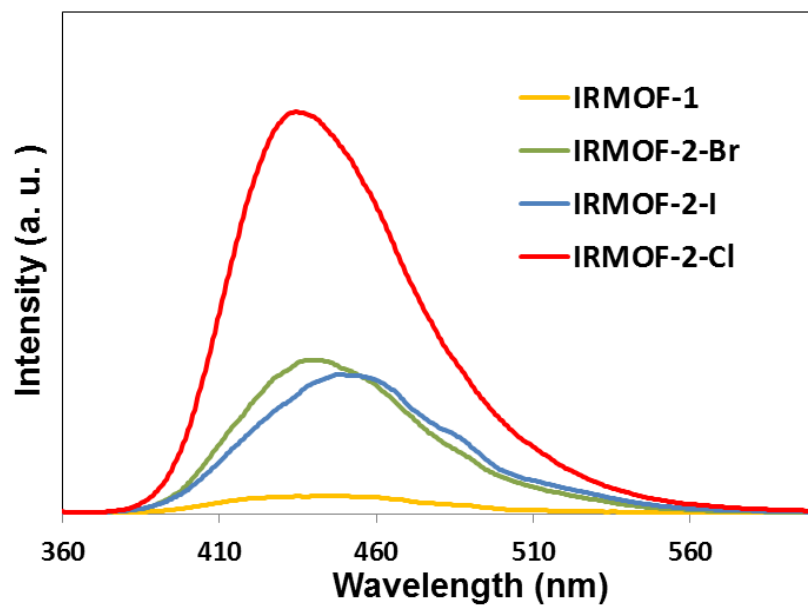


Figure S17. Comparison of different fluorescence emission spectra of IRMOFs dispersed in PhCH₃ at 0.04 M of nitrobenzene concentration.

References

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- 3) Kommareddy, A.; Bowsher, M. S.; Botha, K.; Gunna, M. R.; Vinod, T. K. *Tetrahedron Lett.* 2008, 49, 4378–4382.