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

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A series of halogen containing isoreticular metal-organic frameworks (IRMOFs) were synthesized *via* liquid-assisted grinding method. The luminescent property of these frameworks was described for
10 **nitrobenzene sensing. This investigation revealed the prominent roles of frontier molecular orbital energies of the linkers, substitution polarizability and structural parameters in the ability of IRMOFs to sense nitrobenzene.**

15 Recently, metal-organic frameworks (MOFs) have attracted increasing interest owing to their potential for a wide range of applications in many areas, including gas storage,[1] sensing[2] and catalysis.[3] An important feature of MOFs over other porous materials is the ability of tuning their topology, pore size and
20 functionality by judicious selection of the organic linkers and inorganic metal centers.[4] Due to these features, one may be able to engineer MOFs decorated with a variety of functionalities for specific applications. Over the past few years, a large number of MOFs have been examined for molecular detection and removal
25 of toxic chemicals, such as small aromatics,[5] polycyclic aromatic hydrocarbons (PAHs)[6] and nitroaromatic compounds (NACs).[7] Among the MOFs reported to date, topologically identical isoreticular metal-organic framework (IRMOF) series provide an opportunity for chemists to systematically study the effects of the
30 organic linker functionality on different properties including sensing.[8] Although this aspect of MOF chemistry is of high importance for better understanding the interaction between the framework and guest molecules, it has received a little attention from researchers until recently.[9] In this regard, Allendorf and his
35 co-workers studied the effects of linker polarizability on the adsorption properties of nitrogen and noble gases, by considering IRMOF-2-X series, where X is F, Cl, Br and I.[10] They have shown how increasing linker polarizability leads to an increase in gas uptake.

40 Herein, we report the mechanosynthesis of IRMOF-1 and IRMOF-2-X (X=Cl, Br and I) with a view aimed at understanding the influence of the presence of halogen atoms on nitrobenzene-MOF interactions. To the best of our knowledge, the mechanosynthesis of IRMOF-1 analogs has not
45 been reported to date, which may provide many more applications possible due to the ease of the method of preparation. Further, the solution state sensing properties of these

frameworks toward nitrobenzene were investigated and compared between the groups. Since neat grinding of $Zn(OAc)_2.(H_2O)_2$
50 and terephthalic acid derivatives did not result in a reaction, as evidenced by PXRD, we attempted liquid-assisted grinding (LAG)[11] method for synthesizing the corresponding frameworks.
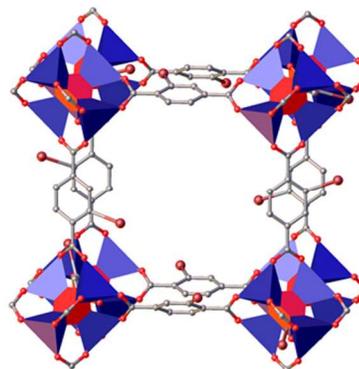

55 **Fig. 1** Representation of the structure of IRMOF-1 and IRMOF-2-X, where X is halogen atom, showing a cubic array of $Zn_4O(CO_2)_6$ units connected by terephthalate or *ortho*-halogenated terephthalate linkers.

60 The IRMOF-1 and IRMOF-2-X (X=Cl, Br and I) were rapidly synthesized *via* LAG of $Zn(OAc)_2.(H_2O)_2$ and terephthalic acid derivatives with *N,N*-dimethylformamide (DMF) for 30 minutes. The 2-chloro and 2-iodo-terephthalic acid were prepared from 2-aminoterephthlic acid by employing
65 slightly modified literature procedures, while terephthalic acid and 2-bromo-terephthalic acid were provided from commercial suppliers. Detailed synthetic procedures and characterization of the synthesized frameworks are provided in the supporting information. Scheme 1 shows the general mechanosynthesis route
70 employed for the synthesis of IRMOF-1 and IRMOF-2-X series.
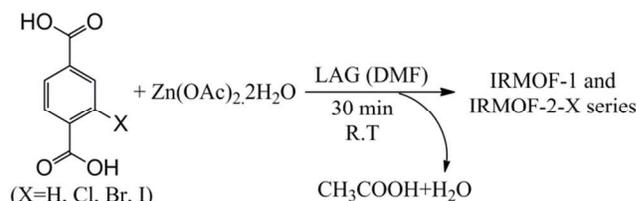
Scheme 1. Mechanochemical construction of IRMOF-1 and IRMOF-2-X (X=Cl, Br, I) series.
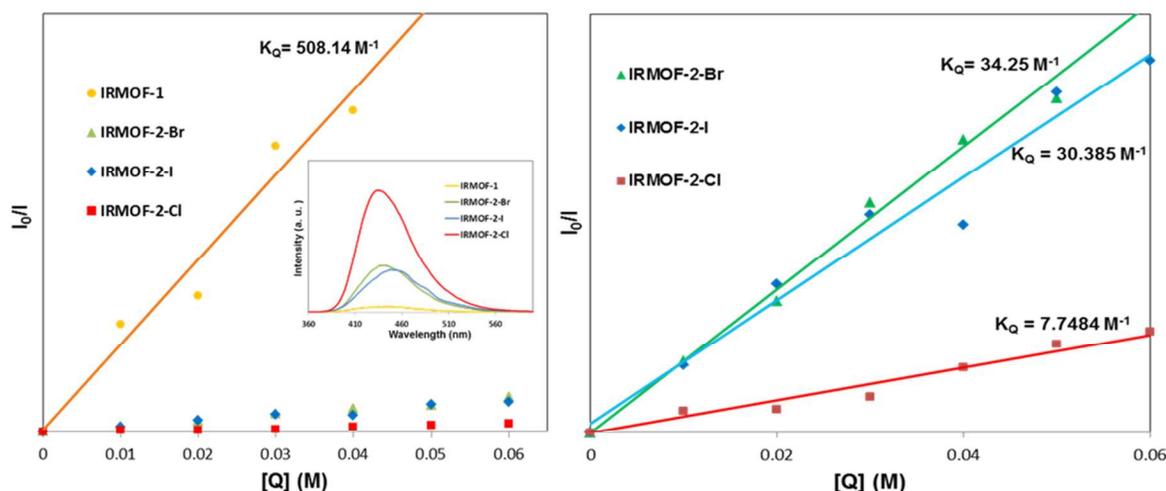
Fig. 2 Comparison of Stern–Volmer (SV) plots in the presence of 1 mg of different IRMOFs (left); and different halogenated IRMOF-2-Xs in different nitrobenzene concentrations ([Q]) in toluene (right). The inset: Comparison of various fluorescence emission spectra of IRMOFs dispersed in PhCH$_3$ at
5   0.04 M of nitrobenzene concentration.

The PXRD patterns of these frameworks match those simulated from the corresponding single-crystal X-ray data of IRMOF-1 and IRMOF-2 (Fig. S1-S4, see supporting information).[8, 11] SEM images of IRMOF-1 and all halogenated IRMOF-2-X prepared
10 via mechanochemical method have been represented in Fig. S5. As these images show, the texture of all substituted IRMOFs is relatively identical and other than a little alteration in the particle size, there is no remarkable difference between them. These frameworks share a common cubic topology where Zn$_4$O clusters
15 are bridged by terephthalate or *ortho*-halogenated terephthalate linkers (Fig. 1).[12] The thermogravimetric analyses of IRMOF-2-X series are also depicted in Figure S6.

To get insight into different properties of this chemical functionality may induce on sensing characteristics; the
20 fluorescence spectroscopy of the IRMOF-2-Xs was explored and compared with IRMOF-1. The initial sensing ability was investigated by immersing and subsequently suspending 1 milligram of the activated MOFs in various organic solvents containing toluene, nitrobenzene, chloroform and *N,N*-
25 dimethylformamide (DMF). Interestingly, among them, effective fluorescence quenching was observed for PhNO$_2$, that is a well-known toxic explosive contaminant (Fig. S7-S14).[13] Sensitive and selective detection of nitrobenzene using MOFs is in early stage that has been achieved in a few reports.[14] While emission
30 positions of the samples do not change significantly, more than 95% quenching efficiency is achieved for nitrobenzene. Comparing the emission spectra of all samples soaked in toluene, the observed quenching effect could be attributed into the nitro group existence. To further investigation of the functionalization
35 effect of IRMOF-1 and evaluate the sensing properties, the Stern–Volmer (SV) equation was constructed, by monitoring the samples including IRMOFs in PhCH$_3$ with gradually increased nitrobenzene concentration. By monitoring the concentration of nitrobenzene in the range of 0.01-0.06 M, the linear SV plots
40 were revealed that is ascribed to electron transfer mechanism and contradict the probable resonance energy transfer in fluorescence

quenching (Fig. 2). It is also worth mentioning that there is no overlap between the absorption band of PhNO$_2$ and the emission band of all IRMOFs that is firmly another reason confirming the
45 former quenching mechanism.[7] The absorption spectrum threshold of PhNO$_2$ lies till to the wavelength of 300 nm while the emission spectra of the whole mentioned MOFs in toluene begins after the wavelength of 350 nm.

Interestingly, the value of K$_Q$ for IRMOF-1 was calculated to be
50 508.14 M^{-1}, which is about more than 10 times larger than K$_Q$ for the halogenated IRMOFs (Fig. 2). As shown in Fig. 2, within the range of K$_Q$ values obtained for IRMOF-2-Cl, IRMOF-2-Br and IRMOF-2-I (7.75, 34.25, 30.35 M^{-1}, respectively, the order of quenching efficiency discerns to be IRMOF-2-Br> IRMOF-2-I>
55 IRMOF-2-Cl, that is opposite to the order of electron-affinity induced by halogen atoms, except for a little relocation exist between IRMOF-2-Br and IRMOF-2-I. On the other hand, according to the valuable reports by Allendorf and co-workers,[10] in the cases of weakly interacting substrates (gases including N$_2$,
60 Ar, Kr, and Xe), the gas uptake potential of a series of halogenated IRMOF frameworks, is in agreement with the polarizability induced by substitution.[11, 15] Since the electron transfer quenching strongly deduced of inductive effect, the order of the observed fluorescence quenching of these series of
65 halogenated IRMOFs can be firmly ascribed to the electron deficiency of the nitro group in the analyte, and electron donating character as well as polarizability of the fluorophore in this series of halogenated IRMOFs. Recently, it has been explained that the luminescence of IRMOF-1 is attributed to ligand-to-ligand charge
70 transfer, namely intraligand $\pi^* \rightarrow \pi$.[16] Thus, to better understand the fluorescence behavior, the frontier molecular orbitals of nitrobenzene and X-BDC (X=H, Cl, Br and I) were calculated using time-dependent DFT (TD-DFT) calculations at the B3LYP/6-311g (d,p) level for all atoms except iodine, for which
75 the LANL2DZdp-ECP basis set was used. It is obvious that the LUMOs of the X-BDC lies at higher energies than the LUMO of nitrobenzene, and thus electron transfer occurs from the X-BDC

ligand of IRMOFs to the low-lying π*-type orbital of nitrobenzene, which leads to fluorescence quenching. In terms of LUMO level energies, BDC and nitrobenzene show the largest energy offset and hence favorable electron transfer compared to others, which confirms results obtained here (Fig. 3). The order of the calculated LUMO energies is also in good agreement with the order of the quenching efficiency (IRMOF-1>IRMOF-2-Br>IRMOF-2-I>IRMOF-2-Cl). Interestingly, the difference between LUMO energies of the Br-BDC quencher and $PhNO_2$ analyte is 0.220 eV and it is more than the value obtained for the couple of I-BDC/$PhNO_2$ (0.207 eV). Therefore, the discrepancy observed in K_Qs of the IRMOF-2-Br and IRMOF-2-I could be logically explained by the difference between their LUMO energies and the analyte, Which is an Important factor in luminescence quenching phenomena.[14b, 16b, 17]

This result confirms the electron transfer quenching mechanism deduced from molecular orbital energies, not only introduces IRMOF-1 as an efficient and selective fluorescence quenching agent for nitrobenzene detection, but also indicates that the key rule of the heavy atom effect as an important reason for significant difference between IRMOF-1 and those including halogenated linkers.[18] In addition, substitution of the organic linker give rise to considerable decrease in surface area of the resultant IRMOF,[10a] leading to restricted diffusion which subsequently reduces the framework potential for adsorption of the guest molecules and eventually affects its interactions for quenching process. Ultimately, comparing the results of adsorption ability described by Allendorf and co-workers, and luminescence potential disclosed here manifests prominent role of electronic configuration factors, in quenching, more than structural parameters in adsorption process.

In summary, a series of IRMOFs containing halogen substitution were synthesized for the first time, via a fast and facile mechanochemical method. The patterns of PXRD for IRMOF-1 and halogenated analogous remain intact after activation with $CHCl_3$. Subsequently, the luminescent property of the prepared MOFs was explored and described their potential for nitrobenzene sensing. Our investigation revealed the prominent role of frontier molecular orbital energies of the MOF linkers, induced substitution polarizability in combination with structural parameters affect the sensing potential of the metal-organic framework. We also displayed the talent of IRMOF-1 as a highly sensitive and selective quenching agent for nitrobenzene detection.
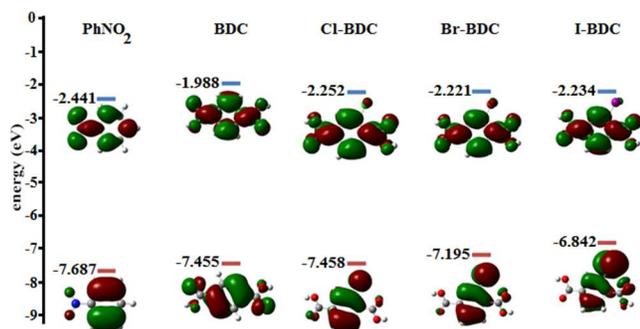

Fig. 3 HOMO and LUMO of nitrobenzene and X-BDC (X=H, Cl, Br and I).

Experimental

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 Zn(OAc)$_2$.2H$_2$O (1.35 mmol) and corresponding X-BDC (0.5mmol), 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 (see Supporting Information for detailed synthetic procedure and characterization data).

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† Electronic Supplementary Information (ESI) available: [Experimental, computational and fluorescence measurements details, PXRD patterns, TGA, SEM images and nitrobenzene sensing graphs]. See DOI: 10.1039/b000000x/
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