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A luminescent cationic metal–organic framework featuring $[\text{Cu}^{\text{I}}\text{pyrazolate}]_3$ units for volatile organic compound sensing†

Charlie E. Kivi and Datong Song*

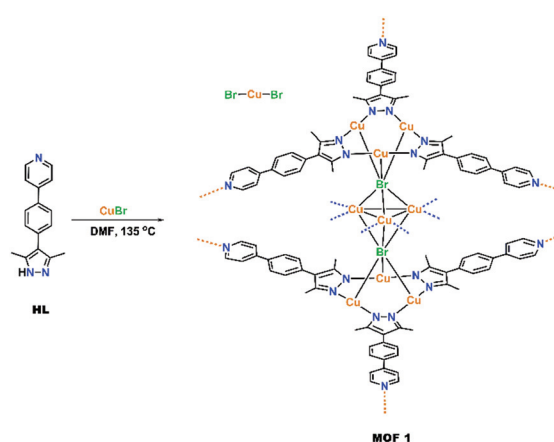
A new metal–organic framework (1) constructed from 4-(4-(3,5-dimethyl-1H-pyrazol-4-yl)phenyl)pyridine (HL) and CuBr shows potential as a luminescent sensor for volatile organic compounds.

Metal–organic frameworks (MOFs) have garnered a lot of recent attention due to their many applications.¹ Of particular interest to us is the ability of MOFs to perform as luminescent chemical sensors for volatile organic compounds (VOCs).^{2,3} While most current industrial VOC sensing is done *via* photo ionization detection (PID)^{4,5} or other solid state detection methods,⁶ sensing using supramolecular structures has been known for some time.⁷ Low energy, reliable VOC sensors with high sensitivity are desirable industrially to allow for the rapid detection of hazardous compounds (*e.g.*, solvent vapours). While there are many recent examples, most known luminescent MOF sensors for VOCs rely on ligand-based^{8,9} or lanthanide-based^{10,11} emissions.^{2,12,13} In contrast, luminescence involving the transition metal centres (*e.g.*, metal–ligand charge transfer)^{14,15} remains relatively underexplored in MOFs. Some known examples include Lin's Ru^{II} –bipyridine MOF¹⁶ and Mączka's Cr^{III} MOF.¹⁷

The trinuclear Cu^{I} –pyrazolate (Cu_3Pz_3) chromophore caught our attention due to its proven sensing ability in homogeneous solution¹⁸ and the active role of the Cu^{I} centres in luminescence.^{19–21} Simple luminescent Cu_3Pz_3 complexes consisting of prisms,^{21,22} cages^{23–25} and oligomers²⁶ are known. To date, there are only six reported MOF types that utilize the Cu_3Pz_3 building blocks,^{27–34} among which those with the pyridyl (Py) functional group on the ligand are most relevant to sensing.^{31–34} However, only thermochromism^{31,33} and a “chemopalette effect” (*i.e.*, doping the MOF with different coordinating solvents during synthesis)³⁴ were reported for the known Py-functionalized Cu_3Pz_3 -containing MOFs. All the

known Cu_3Pz_3 -containing MOFs have charge neutral skeletons with no reported role of the species in the pores impacting MOF luminescent behaviour.^{27–34} Herein we report an MOF synthesized from a new ligand, 4-(4-(3,5-dimethyl-1H-pyrazol-4-yl)phenyl)pyridine (**HL**), which features the Cu_3Pz_3 chromophore and a cationic skeleton with $[\text{Cu}^{\text{I}}\text{Br}_2]^-$ counterions in the pores. Preliminary experiments demonstrate the sensing ability of this material towards VOCs.

Yellow crystals of $[\text{Cu}_9\text{L}_6\text{Br}_2][\text{CuBr}_2]$ (**1**) can be obtained in moderate yields by heating CuBr and **HL** in dry, degassed DMF under an N_2 atmosphere at 135 °C for four days (Scheme 1). The cationic charge of the framework is balanced by $[\text{CuBr}_2]^-$ anions residing in the pores. Two building blocks can be found in the skeleton of **1**: (a) trigonal $[\text{Cu}_3\text{L}_3]$ units, similar to the known $[\text{Cu}_3\text{Pz}_3]$ compounds and (b) trigonal bipyramidal shaped $[\text{Cu}_3\text{Br}_2]^+$ clusters with the two bromides occupying the apical positions (Fig. 1a and b). The repeating unit of the cationic skeleton of **1** can then be described as a trigonal bipyramidal shaped $[\text{Cu}_3\text{L}_3\text{Br}_2]^+$ cluster sandwiched in between two staggered trigonal $[\text{Cu}_3\text{L}_3]$ layers, with each apical bromide of the $[\text{Cu}_3\text{L}_3\text{Br}_2]^+$ cluster interacting with all three Cu^{I} centres of one $[\text{Cu}_3\text{L}_3]$ unit (Fig. 1b and c). Each repeating unit in Fig. 1b



Scheme 1 Synthesis of MOF 1.

Davenport Chemical Research Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6.

E-mail: dsong@chem.utoronto.ca

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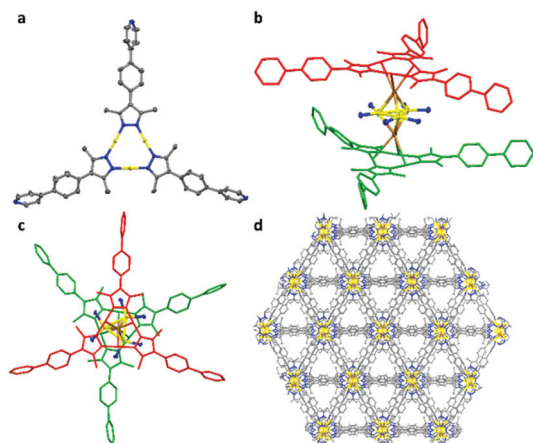


Fig. 1 Crystal structure of **1**. (a) The $[\text{Cu}_3\text{L}_3]$ building block; (b) the 'sandwich' repeating unit with the top and bottom $[\text{Cu}_3\text{L}_3]$ units colour coded in red and green, respectively; (c) top view of the 'sandwich' repeating unit (down the $a + c$ direction). (d) Channels down the $a + c$ direction. Note: in (b) and (c) the L^- ligands bound to the $[\text{Cu}_3\text{Br}_2]^+$ cluster are truncated down to the pyridine nitrogen donors for clarity; hydrogen atoms, $[\text{CuBr}_2]^-$ counterions, and channel solvents are omitted for clarity. Colour key: C in grey, Br in brown, N in blue, and, Cu in yellow.

is linked to six adjacent units through the coordination of the pyridine nitrogen donor from one unit (shown in blue in Fig. 1b) to the Cu^{I} centre in the middle of the other unit, resulting in the formation of a 3D framework (see the ESI† for further descriptions). There are trigonal prismatic channels along the $a + c$ direction of the crystal lattice, where the disordered counterions and solvent molecules reside (Fig. 1d).

MOF **1** shows broadband excitation and emission spectra in the solid state with excitation and emission maxima at 469 and 560 nm, respectively (Fig. S7†) and a quantum yield of 8.6%. Treatment of **1** with water vapour to eliminate any residual channel organic solvents results in a decrease of quantum yield to 1.8%. The water-treated sample is used as the baseline for VOC sensing experiments. Representatives of each common solvent type were compared (Fig. 2). Ethyl acetate, benzene and pentane all show notable *turn-on* behaviour with a greater than 60% increase of luminescence intensity *versus*

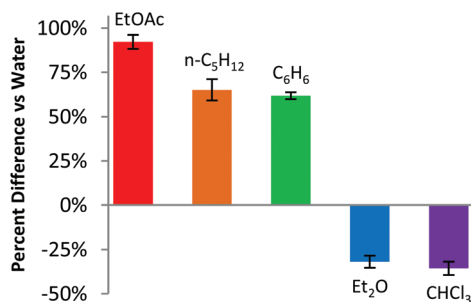


Fig. 2 Abridged VOC sensing results.† An excitation wavelength of 469 nm was used and the luminescence response was measured at the emission maximum (Table S2†) for each solvent treated sample.

the water baseline indicating that the MOF may be a potential sensor for esters, alkanes and aromatics. Acetone shows a slight increase (20%), while acetonitrile, tetrahydrofuran (THF)† and methanol all have negligible impact on luminescence intensity (Fig. S19†). Diethyl ether and chloroform both cause notable *turn-off* with a luminescence intensity decrease of more than 25%. Notably, ethyl acetate vapour causes the most significant luminescence intensity enhancement and the quantum yield of the ethyl acetate-treated MOF is 24.3%. Such a high quantum yield allows us to measure the luminescence lifetime accurately. Multiple lifetimes were observed (Tables S4 and S5†) with the longest being 2.6 μs , which is comparable to other MOFs containing Cu_3Pz_3 units and is indicative of metal-based phosphorescence.^{32–34} Lastly, some solvchromism is observed but the overall effect is minimal, *i.e.*, all luminescent maxima are within the range of 555 to 585 nm (Table S2†).

In order to probe whether the key luminescent changes are the results of MOF structural changes or surface effects, a structure–activity study was conducted. Since ethyl acetate yielded the highest luminescent enhancement, the structures of MOF samples treated with ethyl acetate and water vapour were examined *via* PXRD experiments. Treatment of as-synthesized **1** with water vapour shows a significant alteration of the PXRD pattern indicative of a structural change. The subsequent treatment with ethyl acetate vapour results in the restoration of the PXRD pattern of as-synthesized **1**. Sequential exposures of as-synthesized **1** to water and ethyl acetate vapours yield reversible structural changes as evidenced by the cycling of PXRD patterns (Fig. S10†). All other solvents (except for ether) cause a similar structural change as ethyl acetate (Fig. S11–S18†).

Based on the studies of similar compounds in the literature,³² the luminescence of **1** likely originates from the metal-to-metal charge transfer ³[MMCT], metal-to-ligand charge transfer ³[MLCT], and halide-to-ligand charge transfer ³[XLCT] excited states. The ³[MMCT] excited state is likely the main contributor, evidenced by the broad and featureless emission spectrum of **1**. All three types of excited states are well-known contributors for related luminescent $\text{Cu}(\text{I})$ complexes.^{15,20,32,35} Coordinating solvents (such as water, acetonitrile, alcohols, and THF) are known to quench the luminescence of $\text{Cu}(\text{I})$ compounds *via* exciplex formation.^{36,37} Presumably, the more substantial *turn-on* caused by water-immiscible solvents (*i.e.*, EtOAc, pentane, benzene) is due to their non-coordinating nature and ability to displace the quencher water from the pores. Conversely, although the water-miscible solvents (*i.e.*, acetonitrile, THF, acetone, and methanol) may also displace water molecules in the pore as shown by the PXRD experiments, which should cause luminescence enhancement, these solvents can quench luminescence *via* exciplex formation due to their coordinating nature. Therefore, most of these solvents cause no significant luminescence intensity change overall. Only the less coordinating acetone gives a 25% *turn-on* compared to water-treated **1**.

Since chloroform is able to displace water and halocarbons are well known to quench the transition metal-based luminescence,



science through electron transfer,³⁸ the interactions between chloroform and the luminescent sites within the pores likely account for the observed luminescence intensity decrease. On the other hand, ether causes no structural change to the water-treated **1** (Fig. S18†), implying that the luminescence quenching caused by ether is a surface effect.

In summary, we have prepared a new luminescent Cu(I)-pyrazolate MOF **1**, featuring a [Cu₃Pz₃] triangle and Cu(I) cluster building units and a cationic skeleton. The exposure of water-treated **1** to the vapours of water-immiscible VOCs causes luminescence signal modulations, which can potentially be used for the detection of these VOCs. Preliminary studies show that most VOCs cause structural changes to the water-treated **1**, except for ether. Further investigations into the origin of the luminescence signal modulation and isoreti-cular MOFs of the functionalized **HL** ligand for selective VOC sensing are being carried out in our laboratory.

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Notes and references

† In order to test the role of residual water in the solvent, the performance of the MOF was examined with wet (reagent grade THF from a commercial bottle) versus dry (distilled over sodium/benzophenone ketyl and stored over 3 Å molecular sieves in a glovebox) THF was compared (Fig. S20†). No significant difference was observed.

§ Full figure available in ESI (Fig. S19†).

- 1 T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, 2013, **113**, 734–777.
- 2 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840 and references therein.
- 3 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125.
- 4 P. C. Hsi (Rae Systems, Inc.), WO 1994027141A1, 1994; P. C. Hsi (Rae Systems, Inc.), US Pat, 5393979, 1995; P. C. Hsi (Rae Systems, Inc.), US Pat, 5561344A, 1996.
- 5 J. D. Coy, P. L. Bigelow, R. M. Buchan, J. D. Tessari and J. O. Parnell, *AIHAJ*, 2000, **61**, 268–274.
- 6 *Solid state gas sensing*, ed. E. Comini, G. Faglia, and G. Sberveglieri, Springer, New York, N.Y., 2009.
- 7 L. You, D. Zha and E. V. Anslyn, *Chem. Rev.*, 2015, **115**, 7840–7892.
- 8 M. M. Wanderley, C. Wang, C.-D. Wu and W. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 9050–9053.
- 9 M. Zhang, G. Feng, Z. Song, Y.-P. Zhou, H.-Y. Chao, D. Yuan, T. T. Y. Tan, Z. Guo, Z. Hu, B. Z. Tang, B. Liu and D. Zhao, *J. Am. Chem. Soc.*, 2014, **136**, 7241–7244.
- 10 Y. Li, S. Zhang and D. Song, *Angew. Chem., Int. Ed.*, 2013, **52**, 710–713.
- 11 C. Zhan, S. Ou, C. Zou, M. Zhao and C.-D. Wu, *Anal. Chem.*, 2014, **86**, 6648–6653.
- 12 D. Zhao, Y. Cui, Y. Yang and G. Qian, *CrystEngComm*, 2016, **18**, 3746–3759.
- 13 L. Zhang, Z. Kang, X. Xin and D. Sun, *CrystEngComm*, 2016, **18**, 193–206.
- 14 V. W.-W. Yam, V. K.-M. Au and S. Y.-L. Leung, *Chem. Rev.*, 2015, **115**, 7589–7728.
- 15 A. Vogler and H. Kunkely, in *Transition Metal and Rare Earth Compounds*, ed. H. Yersin, Springer, Berlin, Heidelberg, 2001, pp. 143–182.
- 16 C. A. Kent, D. Liu, T. J. Meyer and W. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 3991–3994.
- 17 M. Mączka, B. Bondzior, P. Dereń, A. Sieradzki, J. Trzmiel, A. Pietraszko and J. Hanuza, *Dalton Trans.*, 2015, **44**, 6871–6879.
- 18 H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjairami, M. A. Rawashdeh-Omary and M. A. Omary, *J. Am. Chem. Soc.*, 2005, **127**, 7489–7501.
- 19 M. A. Omary, M. A. Rawashdeh-Omary, M. W. A. Gonser, O. Elbjairami, T. Grimes, T. R. Cundari, H. V. K. Diyabalanage, C. S. P. Gamage and H. V. R. Dias, *Inorg. Chem.*, 2005, **44**, 8200–8210.
- 20 B. Hu, G. Gahungu and J. Zhang, *J. Phys. Chem. A*, 2007, **111**, 4965–4973.
- 21 G.-F. Gao, M. Li, S.-Z. Zhan, Z. Lv, G. Chen and D. Li, *Chem. – Eur. J.*, 2011, **17**, 4113–4117.
- 22 M. Veronelli, S. Dechert, S. Demeshko and F. Meyer, *Inorg. Chem.*, 2015, **54**, 6917–6927.
- 23 P.-C. Duan, Z.-Y. Wang, J.-H. Chen, G. Yang and R. G. Raptis, *Dalton Trans.*, 2013, **42**, 14951–14954.
- 24 M. Grzywa, B. Bredenkötter, D. Denysenko, S. Spirkel, W. Nitek and D. Volkmer, *Z. Anorg. Allg. Chem.*, 2013, **639**, 1461–1471.
- 25 T. Jozak, Y. Sun, Y. Schmitt, S. Lebedkin, M. Kappes, M. Gerhards and W. R. Thiel, *Chem. – Eur. J.*, 2011, **17**, 3384–3389.
- 26 J.-H. Wang, M. Li, J. Zheng, X.-C. Huang and D. Li, *Chem. Commun.*, 2014, **50**, 9115–9118.
- 27 J. He, Y.-G. Yin, T. Wu, D. Li and X.-C. Huang, *Chem. Commun.*, 2006, 2845–2847.
- 28 J.-P. Zhang and S. Kitagawa, *J. Am. Chem. Soc.*, 2008, **130**, 907–917.
- 29 Z. Wei, D. Yuan, X. Zhao, D. Sun and H.-C. Zhou, *Sci. China: Chem.*, 2013, **56**, 418–422.
- 30 J.-H. Wang, M. Li and D. Li, *Chem. – Eur. J.*, 2014, **20**, 12004–12008.
- 31 J.-X. Zhang, J. He, Y.-G. Yin, M.-H. Hu, D. Li and X.-C. Huang, *Inorg. Chem.*, 2008, **47**, 3471–3473.
- 32 L. Hou, W.-J. Shi, Y.-Y. Wang, H.-H. Wang, L. Cui, P.-X. Chen and Q.-Z. Shi, *Inorg. Chem.*, 2011, **50**, 261–270.



- 33 S.-Z. Zhan, M. Li, X.-P. Zhou, J.-H. Wang, J.-R. Yang and D. Li, *Chem. Commun.*, 2011, **47**, 12441–12443.
- 34 S.-Z. Zhan, M. Li, S. W. Ng and D. Li, *Chem. – Eur. J.*, 2013, **19**, 10217–10225.
- 35 P. C. Ford, E. Cariaty and J. Bourassa, *Chem. Rev.*, 1999, **99**, 3625–3648.
- 36 D. R. McMillin, J. R. Kirchhoff and K. V. Goodwin, *Coord. Chem. Rev.*, 1985, **64**, 83–92.
- 37 J. V. Lockard, S. Kabehie, J. I. Zink, G. Smolentsev, A. Soldatov and L. X. Chen, *J. Phys. Chem. B*, 2010, **114**, 14521–14527.
- 38 H.-K. Yip, H.-M. Lin, K.-K. Cheung, C.-M. Che and Y. Wang, *Inorg. Chem.*, 1994, **33**, 1644–1651.

