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Tetraarylpyrrolo[3,2-*b*]pyrroles as versatile and responsive fluorescent linkers in Metal-Organic Frameworks

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The first examples of crystalline coordination polymers containing the tetraarylpyrrolo[3,2-*b*]pyrrole (TPP) fluorophore are presented. We have prepared three new TPP ligands **L1**, **H2L2** and **H2L3**, containing nitrile, carboxylate and mixed imidazole-carboxylate donor functionality, respectively. The ligands themselves each show significant fluorescence in the solution phase, with the nitrile species exhibiting solvatofluorochromism and the two carboxylate-containing compounds exhibiting concentration-dependent emission colour suggesting aggregation processes in solution. Three 3-dimensional polymeric structures are then presented. The compound *poly*-[Ag**L1**2]SbF6·3THF·2H2O **1** is an eightfold-interpenetrated diamondoid material, while *poly*-[Zn4O(**L2**)3]·20DMA·10H2O **2** is a porous Metal-Organic Framework with **pcu** topology, and both **1** and **2** show notable luminescence in the solid state. Complex **2** readily undergoes guest exchange accompanied by a reversible switching in emission colour with no change in chemical structure. While complex *poly*-[Cd**L3**]·2.5DMA·3.5H2O **3** is non-emissive, it displays a twofold interpenetrated **pts** topology with hexagonal symmetry and an extremely long hexagonal pitch of 100.3 Å, and shows an impressive 22 wt% CO2 uptake capacity at 278 K and 1 bar.

Introduction

The impetus to understand the fascinating properties of Metal-Organic Frameworks (MOFs) has driven the field to new heights in recent years, with new properties and potential applications being constantly unearthed.1 While much attention has been paid to the outstanding ability of these materials to adsorb, separate and store small gas molecules, equally exciting is their ability to adsorb and exchange larger guest molecules from the solution phase.2 Brilliantly harnessed by Fujita in the development of the ‘crystalline sponge’ method for structure determinations,3 these properties are particularly desirable for chemical sensors.4 While substantial work has recently appeared in ‘turn-off’ fluorescent sensing using MOFs, particularly for strongly absorbing or quenching analytes,5 sensing mechanisms which operate independently of absolute emission intensity are still rare. Such processes, when also taking advantage of the spatial confinement of guest molecules in nanopores and their potential to influence luminescence,6 may represent a great opportunity for fluorescent sensing utilizing weaker analyte-fluorophore interactions.

Recently, the Gryko group have reported a fascinating new class of fluorophores with a pyrrolo[3,2-*b*]pyrrole core.7 Conceptually related to the more familiar diketopyrrolo[4,3-*c*]pyrrole dyes,8 tetraarylpyrrolo[3,2-*b*]pyrrole (TPP) fluorophores display exceptional solvatochromism and two-photon cross sections, and benefit from a modular and widely applicable synthesis which has already engendered a range of fascinating outcomes.9 As well as exhibiting modulation of emission properties in response to aggregation phenomena,10 TPP fluorophores exhibit good stability in the presence of metal ions, making them excellent candidates for ligand-based fluorescence applications in MOF chemistry. Here, we present the synthesis of three new divergent TPP-containing ligands, the synthesis and structural chemistry of the first three examples of crystallographically-characterised coordination polymers containing TPP fluorophores, and a study into their guest exchange, gas uptake and fluorescence properties.



**Scheme 1** General synthetic procedure and structure of ligands **L1**, **H2L2** and **H2L3**. Reagents and conditions: (i) 2,3-butanedione, TsOH, HOAc, 90 °C

Results and Discussion

Synthesis and Spectroscopic Behavior of L1, H2L2 and H2L3

With a preference for *d*10 metal ions to avoid quenching the ligand-based fluorescence of the TPP fluorophores, several different approaches to attaching coordinating functionality to the TPP fluorophore can be envisaged. For coordination to soft metal ions, e.g. Ag(I), a nitrile donor species **L1** was devised. For harder 3*d* metal ions, such as Zn(II), a dicarboxylate species **H2L2** was prepared. Finally, a mixed-ligand donor species **H2L3** was prepared, containing both carboxylate and imidazole donor groups. The combination of N-heterocycles and carboxylic acids has been shown previously to give access to a range of structural types and properties not necessarily available from pure carboxylate functionality,11 and tend towards mixed-ligand mononuclear nodes rather than carboxylate cluster nodes. The ligands **L1**, **H2L2** and **H2L3** (Scheme 1) were each prepared in moderate yields in a single step following the procedure outlined by Gryko *et al*.,7 and all characterisation data were consistent with the expected structures. The yields (12 – 37%) are comparable with those reported by Gryko, and are representative of the complex multi-component nature of the coupling reaction.

In all three cases, single crystals of the ligands could be prepared by recrystallisation from an appropriate solvent (PhMe, N,N-dimethylacetamide, and DMSO, for **L1**, **H2L2**and **H2L3**, respectively). As each of these procedures gave highly solvated structures, these crystallisations were not carried out on preparative scales; the as-synthesised materials exhibited suitable purity for further use. The structures of **L1**, **H2L2** and **H2L3** are shown in Figure 1. Each of the three solvates conformed to the geometries expected, with the four phenyl rings twisted out of the plane of the central pyrrolopyrrole fragment, with the N-substituents aligned at *ca*. 60° and the C-substituents at *ca*. 30° relative to the central core. While the intermolecular interactions in each structure tend to consist of the expected motifs (especially the carboxylic acid groups, which form hydrogen bonding interactions with the lattice solvent molecules), it is noteworthy that the pyrrolopyrrole units in each structure do not participate in homotopic face-to-face π-π interactions, and instead favor weak and offset edge-to-face type interactions with the phenyl rings of adjacent molecules. Most likely this a consequence of the steric hinderance from the four non-coplanar phenyl substituents, and also the electron rich quadrupolar nature of the central π system. This observation is in contrast to the behavior of many aromatic fluorophores which tend to strongly aggregate through *H-* or *J*-aggregate-type π-π interactions.12

The photophysical properties of the three ligands were also examined. As shown in Figure 2, all three compounds possess absorption bands bordering the visible region and green or blue/green emission (Table 1). While the very low solubilities of **H2L2** and **H2L3** effectively prohibited measurements in any common spectroscopic solvents besides DMSO, **L1** exhibited good solubility in a range of solvents, and absorption and emission spectra could be measured in solvents of varying polarities, revealing the anticipated solvatochromism (Supporting Information, Figure S9). While we did not observe any significant concentration dependence to the absorption or emission behaviour of **L1** in any solvent, both **H2L2** and **H2L3**



**Figure 1** Structure of **L1**, **H2L2** and **H2L3**, (A, B and C, respectively),with heteroatom labelling scheme. Lattice solvent molecules, and hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

display concentration-dependent absorption and emission profiles (Supporting Information, Figures S13 and S14). Comparisons can be drawn to the recent report by Tang *et al.*, who reported aggregation-induced emission for a series of N-carboxyphenyl TPP analogues, which showed the degree to which TPP emission can be modulated by solution aggregation processes.10 For **H2L2** and **H2L3**,both the pure high-concentration (> 5 µM and > 7 µM, respectively) and low-concentration (< 0.9 µM and < 1.7 µM, respectively) forms exhibited prominent photoluminescence, but with a bathochromic shift in both absorption and emission maxima at the higher concentration. Nonetheless, all three compounds exhibited moderate to high photoluminescence quantum yields (Table 1), consistent with the intense luminescence which has been previously reported for TPP compounds.7



**Figure 2** Absorption (black) and emission (red, λex = 366 nm) for compounds **L1** (top), **H2L2**(middle) and **H2L3** (bottom). In the latter two cases, the photophysical properties of the high-concentration forms are shown as solid lines, and the low-concentration forms are shown as dashed lines. Plots showing the stepwise conversion from the high to low concentration forms is given as Supporting Information, Figures S13 and S14.

**Table 1** Summary of photophysical parameters for **L1**, **H2L2**and **H2L3**

|  |  |  |  |
| --- | --- | --- | --- |
| Compound (solvent) | λmax /nm (ε /103 L·mol‑1·cm-1) | λem /nm | ΦPL (± 10%) |
| L1 (CHCl3) | 407 (44 ± 2) | 459 | 0.55 |
| H2L2 (DMSO, > 5 µM) | 396 (47 ± 1) | 481 | - (a) |
| H2L2 (DMSO, < 0.9 µM) | 369 (43 ± 6) | 431 | 0.45 |
| H2L3 (DMSO, > 7 µM) | 393 (48 ± 2) | 479 | - (a) |
| H2L3 (DMSO, < 1.7 µM) | 366 (34 ± 1) | 429 | 0.47 |

(a) ΦPL measurement unreliable at this concentration

Synthesis and Structure of *poly*-[AgL12]SbF6·3THF·2H2O 1

Having prepared and characterised the ligands **L1**, **H2L2** and **H2L3,** a study into their coordination chemistry was undertaken. Reaction of **L1** with AgSbF6 in THF yielded X-ray quality single crystals after two days. The diffraction data for complex **1** were solved and refined in the orthorhombic space group *Ccca*, with the asymmetric unit containing half of one molecule of **L1**, a silver ion occupying a crystallographic special position, and fragments of two SbF6- anions. As shown in Figure 3, the silver ion is coordinated by four equivalent nitrile nitrogen atoms (N1) in a regular tetrahedral geometry (τ4 = 0.81),13 with Ag-N distance 2.260(4) Å. The **L1** ligand bridges two silver ions, giving an Ag-Ag distance of 22.3866(4) Å. The ligand adopts a slightly twisted conformation, with interplanar angles of 24.5 and 52.3° between the central pyrrolopyrrole unit and the cyanophenyl and tert-butylphenyl rings, respectively.

Expansion through crystallographic symmetry reveals a three-dimensional polymeric structure for **1**, with tetrahedral silver ions acting as four-connected nodes in a (6,4) **dia** network. The large bridging distance imparted by the **L1** ligand leads to very large inter-nodal distances in each six-membered loop, with diagonal (node-node) distances all in the range 38 – 47 Å.

Unsurprisingly, these large windows lead to interpenetration; specifically, an eightfold interpenetration mode. Despite the high density of the material, no significant face-to-face π-π interactions are present within the structure. Instead, the primary crystal packing interactions between interpenetrated networks are based on C-H···π interactions between the **L1** molecules, of which two types are present, both with C-H donors from the tert-butylphenyl groups. The anions reside within square channels parallel to the *a* axis (Figure 3c), and are localized within two part-occupancy positions. The remainder of the channel volume is occupied by solvent molecules; elemental analysis gives a formula of *poly*-[Ag**L1**]SbF6·3THF·2H2O, corroborated by TGA (15 wt% volatiles, calculated 14 wt%, Supporting Information Figure S6).

Complex **1** retains the photoluminescence properties of the free **L1**; excitation at 366 nm gave an emission band with maximum at 528 nm (Supporting Information, Figure S15), a significant bathochromic shift compared to the free ligand in solution. This can most likely be ascribed to a combination of the high density of fluorophores brought about by crystal packing influences, and the influence of the AgI ions on the electronics of the **L1** ground and excited states, particularly involving the nitrile acceptor. The influence of AgI coordination



**Figure 3** (A) Structure of complex **1** with heteroatom labelling scheme; (B) Extended structure of **1**; a single diamondoid net; (C) The complete structure of **1** showing SbF6- columns parallel to the c axis. All hydrogen atoms are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) –x, 1-y, 1-z; (ii) 1-x, 3/2-y, +z; (iii) +x, 3/2-y, 3/2-z; (iv) 1-x, +y, 3/2-z.

to **L1** is also evident from infrared spectroscopy, with a shift of 12 cm-1 in the nitrile stretching frequency upon coordination. Although **1** contains continuous anion/solvent channels, we were unable to effect any solvent or anion exchange in this material, with all attempts at soaking the material in other solvents or anion mixtures leading to destruction of the material. As such, we turned our attention tothe carboxylate derivatives **H2L2** and **H2L3**, which would be expected to generate more resilient framework materials.

Synthesis and Structure of *poly*-[Zn4O(L2)3]·20DMA·10H2O 2

As a rigid linear aromatic dicarboxylate, the deprotonated ligand **L2** could be expected to coordinate to ZnII ions to give a **pcu**-type network containing basic zinc acetate nodes.12 Indeed, on reaction with zinc nitrate hexahydrate in a DMA/EtOH mixture, with 1,4-diazabicyclo[2.2.2]octane (DABCO) included as a base, yellow block crystals were isolated within 6 hours. Despite exhibiting intrinsically poor diffraction characteristics, a single-crystal X-ray diffraction dataset could be obtained of sufficient resolution to provide a structural model of *poly*-[Zn4O(**L2**)3] **2**. The diffraction data for **2** were solved and refined in the monoclinic space group *P*-1, and revealed [Zn4O(COO)6] nodes bridged into a three-dimensional, twofold-interpenetrated **pcu** framework by **L2** units, shown in Figure 4.



**Figure 4** (A) Representative structure of a ligand and metal environment in complex **2** with labelling scheme for unique heteroatoms; (B) Extended structure of complex **2** showing the connectivity of a single **pcu** cage**;** (C) Topological representation of the offset twofold interpenetration present in complex **2.** All hydrogen atoms and ligand disorder are omitted for clarity.

The asymmetric unit contains one unique Zn4O core, and three crystallographically independent **L2** groups. The **L2** units provide bridging distances of 22.5696(8), 22.7345(8) and 22.7582(8) Å, the lengths of the three unit cell edges, between the oxo cores of each Zn4O node. Similarly to the structure of **1**, in **2** each of the four aryl rings attached to each unique **L2** central core adopt a non-coplanar conformation generally reminiscent of that observed in the structure of the free ligand. Due to the low density of the material, geometric constraints and the uniformly π-electron-rich central core, remarkably few defined **L2···L2** interactions are present within the structure of **2.** These are essentially limited to weak C-H···π interactions between the phenyl groups and pyrrole centers. This feature is a continuation of the surprisingly modest crystal packing forces observed in the structure of the free ligand, and continues to distinguish the structure of **2** from other coordination polymer structures containing large conjugated organic fluorophores. While its derivatives show similar emission characteristics, the 1,8-naphthalimide fluorophore, for example, dominates the extended structure of its coordination polymers through π-π interactions.14 Despite the interpenetration in **2**, significant solvent-accessible volume remains, accounting for *ca.* 63% of the unit cell. The irregular shape of the TPP units and steric bulk of the *t*-butyl groups may hinder the occurrence of further interpenetration, which would typically be expected for a void volume of this magnitude.

Synthesis and Structure of *poly*-[CdL3]·2.5DMA·3.5H2O 3

With the formation of basic zinc acetate-type nodes in the structure of **2**, we turned to **H2L3** in an attempt to generate other porous frameworks with mononuclear nodes, through coordination of both carboxylate and imidazole groups. After screening a variety of synthesis conditions and metal ions, we found that reacting **H2L3** with cadmium nitrate tetrahydrate in N,N-dimethylacetamide at 100 °C gave orange rod crystals of complex **3** within 6 hours. Analysis by single crystal X-ray diffraction gave a structural model in the hexagonal space group *P*6522. As a consequence of the sixfold screw axis present, complex **3** exhibits an extremely long *c* unit cell edge of 100.2746(19) Å. While this caused practical difficulties in data collection, the data provide an unambiguous structural model. The asymmetric unit of **3** contains one doubly-deprotonated **L3** species coordinating to a single unique cadmium (II) ion. No additional solvent or guest molecules could be located from the Fourier residuals, and the data were treated with the SQUEEZE routine.15 The **L3** molecule exhibits minor crystallographic disorder on one carboxyphenyl ring, but is otherwise surprisingly well ordered, especially compared to **L2** in complex **2**. This observation is rationalised by considering the coordination mode of the ligand in complex **3**; all four donor groups are bound to crystallographically equivalent Cd sites, restricting the possible degrees of freedom of the ligand backbone. The ligand provides relatively symmetric bridging distances of 21.0882(3) and 21.8907(3) Å for carboxylate-carboxylate and imidazole-imidazole linkages, respectively. The structure of complex **3** is shown in Figure 5.



**Figure 5** (A) The ligand environment and coordination geometry in complex **3** with labelling scheme for unique heteroatoms; (B) Extended structure of complex **3** showing the connectivity of a single net viewed along *a*/*b*; (C) Topological representation of the two interpenetrated nets in the structure of **3**. All hydrogen atoms and ligand disorder are omitted for clarity.

Each cadmium ion links four equivalent molecules of **L3** and is coordinated in a distorted octahedral coordination geometry by the two partially chelating carboxylates and two monodentate imidazoles. This gives approximately tetrahedral character to the four-connected node defined by the metal site, while the four-connecting **L3** node is oriented in an approximately square planar fashion. Considering this, it is unsurprising that the overall network topology can be described by the **pts** net. However, unlike the highest symmetry (P42/mmc) form of **pts** in which the adjacent square planar nodes are oriented at 90° to one another *via* the tetrahedral nodes, in the hexagonal symmetry complex **3** each square planar (**L3**) node is twisted by 60° relative to its nearest neighbours along *c*, relating to the extremely large unit cell dimension along this axis. The very large windows present in an individual net of **3** lead to interpenetration; the complete structure of **3** is twofold interpenetrated, however as a non self-dual **pts** net, the interpenetrated nets are offset to one another and leave considerable solvent-accessible volume of 49%, in the form of intersecting three-dimensional channels permeating the entire structure. In keeping with the observations from complex **2** and the structures of the free ligands, the pyrrole core of **L3** within the structure does not undergo any substantial crystal packing interactions or significant close contacts with any other framework atoms. Only relatively minor offset face-to-face π-π contacts and C-H···O hydrogen bonding interactions are observed between adjacent imidazolyl and carboxylate groups from the interpenetrating nets.

Guest Exchange and Gas Adsorption Studies for Complexes 2 and 3

Given the readily accessible pore volumes in complexes **2** and **3**, and the tendency for TPP-derived molecules, including **L1**, to show solvatofluorochromic behaviour, we examined the guest exchange properties of these complexes, as well as probing the solid-state photoluminescence of **2** and **3** as a function of the exchanged guest. Solvent exchange and gas adsorption studies were undertaken on the two permanently porous materials to probe their utility as adsorbents. Firstly, the as-synthesised crystals of **2** were soaked in DMA for 12 hours to remove any residual reactants; digestion of the crystals with *d*1-TFA and NMR of the resulting solution in *d*6-DMSO showed only **H2L2** and DMA remained (Supporting Information, Figure S20). This digestion process also led to partial deuteration of the pyrrolic C-H group, as has also been observed for pyrazole derivatives.16

For complex **2**, the DMA-loaded crystals showed 45%mass loss below 250 °C by TGA; this was consistent with the findings from elemental analysis, and integration of the digested NMR sample (approximately 8 DMA molecules per **L2** group), all of which gave an approximate formula for the bulk solid of *poly*-[Zn4O(**L2**)3]·20DMA·10H20 (calculated volatile mass 47.8%). Transferring these crystals to MeCN and soaking for 24 hours, and refreshing the exchange solution after 12 hours, gave full exchange; TGA showed a complete loss of 37 wt% solvent by 50 °C. X-ray powder diffraction of the MeCN-exchanged material at 100 K revealed retention of crystallinity while the crystals remained solvated; however, drying in air for even a short period resulted in decomposition to a poorly crystalline phase.

The MeCN-soaked crystals were evacuated at 75 °C under dynamic vacuum overnight (taking care to avoid contact of the dried crystals with air or moisture), and gas adsorption measurements were performed to probe the internal pore volume. Adsorption of N2 at 77 K provided a type-I isotherm typical for microporous materials of this type, although with slower equilibration on the adsorption branch possibly indicating some degree of pore constriction. The calculated BET surface area, taken from the smooth desorption branch is 717 m2/g. Similarly, adsorption of H2 at 77 K revealed smooth adsorption and desorption branches with a maximum uptake of 106 cc(STP)/g (*ca.* 1 wt%) at 1 atm, as shown in Figure 6. Adsorption of CO2 at 273K gave a maximum uptake of 42 cc(STP)/g at 1 atm (Figure 7), and using data from the 273 K, 283 K and 293 K isotherms (Supporting Information, Figure S16) the enthalpy of adsorption for CO2 at zero loading is estimated at approximately -24 kJ mol-1. These findings are consistent with a large open pore volume without strong adsorbent-adsorbate interactions (at least for these probe molecules), typical for “IRMOF”-type structures.17



**Figure 6** N2 (top) and H2 (bottom) adsorption isotherms for complexes **2** (green/yellow) and **3** (red/blue). All measurements were carried out at 77K.

For complex **3**, thermogravimetric analysis revealed a volatile mass of 28.5 wt%, lost in a gradual multi-step process plateauing above 200 °C. This offered excellent agreement with the calculated volatile mass from the molecular formula ascertained by elemental analysis of *poly*-[Cd**L3**]·2.5DMA·3.5H2O (calculated volatile mass 27.5 wt%). Soaking the material in acetonitrile overnight gave efficient guest exchange, with the acetonitrile-soaked material undergoing rapid loss of solvent initiating at room temperature and reaching a plateau by 100 °C. Both materials underwent gradual decomposition processes above 300 °C mostly centred on rapid mass losses initiating at *ca.* 420 °C.

The acetonitrile-exchanged material was evacuated under dynamic vacuum at 100 °C overnight, and the same gas uptake experiments as discussed above were performed. Complex **3** immediately revealed much improved gas uptake performance compared to **2** for all gasses and conditions studied. Adsorption of N2 at 77 K, shown in Figure 6, gave a maximum uptake of 387 cc(STP)/g at *P*/*P*0 = 0.99 and a calculated BET surface area of 1431 m2/g, approximately twice that observed for **2**. Similarly, the maximum H2 uptake of 264 cc(STP)/g at 77K and 1 atm (2.1 wt%, Figure 6) and CO2 uptake of 141 cc(STP)/g at 278K and 1 atm (22 wt%, Figure 7) are 2-3.5 times the corresponding values measured for complex **2**. The zero-loading enthalpy of adsorption for CO2 of approximately -25.5 kJ mol-1, estimated from adsorption isotherms at 278, 293 and 308 K, is similar to that of complex **2** and other non-functionalised MOF materials. X-ray powder diffraction revealed that the structures of the DMA and MeCN-loaded complex **3** were equivalent, and both proved relatively stable to air exposure, insofar as both measurements could be carried out in air without decomposition. In comparison, the relatively lower uptake capacity (despite a larger apparent pore volume), hysteretic adsorption of N2 and poor stability of complex **2** on drying in air may indicate this material exhibits relatively poorer stability following harsh evacuation conditions compared to complex **3**. In spite of this, complex **2** appears by X-ray powder diffraction to be indefinitely stable when immersed in aprotic solvents.



**Figure 7** CO2 adsorption isotherms for complexes **2** (top) and **3** (bottom), measured across three temperatures each as specified.

Photoluminescence of Complexes 2 and 3

The ability of compounds **2** and **3** to efficiently exchange guests, and the expectation that the adsorbed guests would come into close proximity of the fluorophore sites by the lack of strong packing interactions prompted an examination of the photoluminescence of the two MOFs as a function of the adsorbed guest. With the solid samples remaining immersed in the guest solvent at all times, emission spectra were recorded for complex **2** containing the original N,N-dimethylacetamide guest, as well as with acetonitrile and ethyl acetate guests. In the latter case, a stepwise exchange *via* acetonitrile was employed to ensure full exchange, confirmed by digestion and NMR of the solids (Supporting Information, Figures S21 and S22). As shown in Figure 8, with excitation at 380 nm, the original (DMA) material shows an emission maximum at 495 nm, while a slight red-shift is observed in acetonitrile to a maximum of 502 nm. Ethyl acetate effects a blue shift of the emission band, with a maximum of 482 nm. The direction of these deviations follows the expected variation in Stokes shift as a function of dielectric constant and refractive index of the guests.18 Although the magnitude of the shift in emission maxima between acetonitrile and ethyl acetate, approximately 820 cm-1, is less pronounced than those observed in solution for other fully organic TPP derivatives by Gryko *et al*.,7 the difference in emission colour between the two is clearly visible to the naked eye (Figure 8, inset).



**Figure 8** Emission spectra (λex = 380 nm) of complex **2** with N,N-dimethylacetamide (black, dashed), ethyl acetate (blue) and acetonitrile guests (green). Inset: Photographs of complex **2** under ethyl acetate or acetonitrile, respectively, under 366 nm irradiation.

The emission colour for each guest also proved fully reversible upon soaking the solid in fresh solvent, and no photoluminescence was detected from the supernatant, ruling out the possibility of fluorophore dissolution from the framework itself. In order to address the possibility of the variation in luminescence being coupled to a structural rearrangement, X-ray powder diffraction was carried out at 100 K on the solvated samples. The diffraction patterns for the MeCN and EtOAc soaked materials proved almost identical (Supporting Information, Figure S3), suggesting no significant structural rearrangement takes place to accompany the change in luminescence, and that the guest solvents are diffuse within the framework. This also implies that the photoluminescence behaviour arises from modulation of the bound fluorophore’s local electronic environment by the solvent, at least for the outer layers of the crystalline material.

Having observed this guest-dependent emission behaviour in complex **2**, we turned our attention to complex **3** to test for similar behaviour. However, to our surprise, complex **3** as prepared exhibits no detectable photoluminescence. Following our methodology described above, we sequentially exchanged the internal guest molecules for MeCN, followed by EtOAc. Nonetheless, all three materials failed to exhibit any significant fluorescence, either at room temperature or on cooling to 77K, implying complex **3** is intrinsically non-emissive.

Discussion

The structural chemistry of the TPP derivatives described above is an encouraging prospect for future developments in this area. It is already relatively well understood that rigid linear and square-planar ligand molecules are good candidates for forming robust and highly porous framework materials.19 However, incorporating intense photoluminescence functionality within the relatively compact ligand core without the need for any additional pendant functionality is a useful aspect of this versatile ligand system. The tendency of the TPP derivatives above to avoid strong π-π interactions in the solid state is a key consideration for designing fluorescent porous materials, particularly for chemical sensing applications requiring direct contact between analyte and fluorophore.

Several explanations can be put forward to explain the discrepancy between the highly fluorescent free ligand **H2L3** and the non-emissive complex **3**. In contrast to complexes **1** and **2**, the coordination through the pyrrolic N-substituent is the distinctive feature of complex **3**. Coordination of a metal cation at this position will most likely reduce the electron donor capacity of the central electron-rich core and reduce the electron donor capacity of the imidazolylphenyl substituent, which is known to be a key element in the fluorescence of these compounds.7 Additionally, conjugation of the heavy Cd(II) ion in this way may influence the excited-state lifetime of the fluorophore,18 which would be expected to make efficient quenching through non-radiative decay pathways (for example, aromatic ring rotations20 allowed by the loose packing mode in the porous framework) more influential.

Conclusions

The capability for TPP fluorophores to form 3-dimensional coordination polymers with prominent luminescence and permanent porosity is an extremely encouraging result in the search for MOF-based fluorescent sensor devices. Here, we have shown that metal-coordinating functionality can be readily appended to the TPP fluorophore core, and used to transfer responsive photoluminescence properties into a porous framework. As the basis of MOF linker molecules, the TPP moiety provides several useful features; as well as structural rigidity, the relatively small and electron-rich central π-surface flanked by twisted phenyl groups may serve to dissuade aggregation through face-to-face π-π interactions which can often lead to dense packing modes in other fluorophore species. Indeed, fully exposing the fluorophore core to the internal pore volume in microporous materials is a key consideration in extracting the maximum performance of heterogeneous chemical sensors of this type. By combining the structural and photophysical properties of the TPP core with the selective adsorption and concentration effects at play in microporous hosts, a new generation of sensitive and versatile sensor platforms may become a reality, with numerous potential applications.

Experimental

Materials and Methods

All starting materials, reagents and solvents were purchased from Sigma/Merck, Fluorochem or Alfa Aesar, and were used as received without further purification. Synthesis of the ligands was adapted from the general synthesis reported by Gryko *et al.*7 NMR spectra were recorded using a Bruker AVANCE III instrument operating at 400 MHz for 1H and 100 MHz for 13C, using *d*6-DMSO as the solvent. Chemical shifts are reported in ppm with the residual solvent as the internal reference. For the digestion experiments, solid samples of each complex (*ca*. 5 mg) were decomposed with 1-2 drops of *d*1-TFA and the resulting mixture was diluted using *d*6-DMSO to obtain spectra. Mass spectra were acquired using a Micromass time of flight mass spectrometer (tof), interfaced to a Waters 2690 HPLC, with samples dissolved in HPLC-grade MeOH or MeCN, with trace methanolic NaOH added to **2** and **3** to aid solubility. The instrument was operated in positive or negative mode as required. Leucine Enkephalin was used as an internal lock mass. Masses were recorded over the range 100-1000 m/z. Melting points were determined using an Electrothermal IA9000 digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a PerkinElmer Spectrum One FTIR spectrometer in the range 4000 - 550 cm-1. Thermogravimetric analysis was performed on a PerkinElmer Pyris 1 TGA in the temperature ranges specified, with a scan rate 5 °C min-1 under a nitrogen atmosphere with N2 flow rate 20 mL/min. All photophysical measurements were performed at 298 K in spectrophotometric grade solvents. UV-Vis absorption spectra were measured in 1 cm quartz cuvettes on a Varian Cary 50 spectrophotometer or a Thermo Scientific Evolution 220 spectrophotometer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorimeter. All solution-phase emission spectra were recorded with excitation wavelength 366 nm (in order to match excitation intensity with the Quinine Sulfate standard), and comparison with the emission spectra recorded with λex = λmax(abs) showed no change in emission band position or shape. Quantum yields were calculated by comparison with quinine sulfate in 2M H2SO4 with excitation at 366 nm using an excitation slit width of 2.5 nm for all samples, and emission integrated across the range 380 – 600 nm. Solid-state emission spectra were measured at room temperature with solid samples (*ca.* 20 mg) covered by a layer of clean solvent in a sample holder mounted within a fluorescence cuvette; in all cases, no measurable photoluminescence was observed from the solvent layer above the samples. Gas adsorption isotherms were measured using a Quantachrome Autosorb IQ gas sorption analyser. Chemically pure (CP, N4.5) grade He, N2, H2 and CO2 gases from BOC gases were used for the measurements. The samples of acetonitrile-exchanged complexes **2** and **3** were de-gassed under dynamic vacuum at 75 °C and 100 °C, respectively, for 24 hours prior to the measurements. Datapoints for BET analysis were selected based on established criteria.21

X-ray powder diffraction patterns for complex **1** and the air-decomposed complex **2** were recorded with a Bruker D2 Phaser instrument using Cu-Kα (λ = 1.5405 Å) radiation at room temperature. Raw data were compared with the simulated patterns from the single crystal data collections carried out at 100 K. For the fresh and solvent-exchanged complex **2**, X-ray powder diffraction patterns were measured using a Bruker APEX-II Duo operating at Cu-Kα wavelength (λ = 1.5405 Å). Samples, slurried in their exchange solvent, were ground together with a small quantity of NVH immersion oil and the resulting mass was immediately transferred to the cryostream of the instrument (T = 100 K). Data were collected using three 360 ° scans in φ covering the 2θ range 3 – 55 °, which were subsequently merged and the Debye rings integrated in Bruker APEX-3, with baseline corrections then applied in DIFFRAC.EVA.22, 23

X-ray Crystallography

Crystal and refinement data are presented in Table 2. CCDC 1818940-1818943 and 1840308-1840309. All datasets were collected on a Bruker APEX-II Duo dual-source instrument using microfocus Cu-Kα radiation (λ = 1.5405 Å). The four datasets were each collected using ω and φ scans. Single crystals were mounted on Mitegen micromounts in NVH immersion oil, and maintained at a temperature of 100 K using a Cobra cryostream. The diffraction data were reduced and processed using the Bruker APEX suite of programs.22 Multi-scan absorption corrections were applied using SADABS.24 The data were solved using the Intrinsic Phasing routine in SHELXT and refined with full-matrix least squares procedures using SHELXL-2015 within the OLEX-2 GUI.25-27. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined with a riding model, with isotropic displacement parameters equal to either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. Specific collection and refinement strategies are further outlined in the combined crystallographic information file (cif) under the \_refine\_special\_details heading. The solvate structures of **L1**, **H2L2, H2L3** and the structure of complex **1** could be fully refined to convergence with only minimal restraints, mostly to maintain chemical geometry for the partial-occupancy or disordered solvent molecules in the two ligand structures. Complex **3** was refined to convergence with only minor functional group disorder. The SQUEEZE routine was employed for complexes **2** and **3**;15 in both cases, solvation was better determined by supporting methods, a combination of elemental analysis, thermogravimetric analysis and, in the case of complex **2**, digestion of the crystals and guest quantification with NMR. The extremely long *c* unit cell edge in complex **3** necessitated a 90 mm crystal-to-detector distance; under these conditions it was not feasible to collect data beyond a resolution of *ca.* 0.9 Å.

In the case of complex **2**, while the metal sites and two of the three ligand molecules (C1-C40 and C41-C80) were well ordered, and could be modelled with only minor restraints on the Uij parameters of the *tert*-butyl groups, the remaining residue (C81-C120) exhibited significant disorder. This was manifest as one major geometric contributor overlapped by several others at low occupancy, indicative of both a bowing of the central pyrrolopyrrole unit and a rotation of this group about the fixed carboxyphenyl groups. This issue was also exacerbated by relatively poor diffraction characteristics, commonly observed in open framework materials of this type. The other contributors could not be reasonably modelled without over-refinement, and the geometry of the main contributor was fixed using rigid group AFIX cards for the two outer phenyl rings and one of the two pyrrole units. The remaining distances and angles were restrained with DFIX commands, and ISOR and RIGU restraints and EADP constraints were used to maintain these groups as a chemically sound model. As such, bond length and angle calculations from the fragment C81-C120 are considerably less meaningful than those derived from the remainder of the structure.

Synthesis

Synthesis of L1

4-Formylbenzonitrile (500 mg; 3.8 mmol), 4-tert-butyl aniline (610 μL; 3.8 mmol) and para-toluenesulfonic acid (70 mg; 0.4 mmol) were combined in glacial acetic acid (3 mL) and heated at 90 °C for 30 minutes in air. Following this period, 2,3-butanedione (170 μL; 1.9 mmol) was added dropwise, and the mixture was stirred at 90 °C for a further 3 hours. After this period, the mixture was cooled to room temperature, filtered, and the yellow solids were washed with methanol. The solids were slurried in 50 mL of hot ethyl acetate and filtered, and the solids washed with 2×50 mL of ethyl acetate, giving the product as a bright yellow solid. Yield 135 mg (12%); m.p. >300 °C; Found C, 83.42; H, 6.34; N, 9.71; Calculated for C40H36N4 C, 83.88; H, 6.34; N, 9.78%; δH (CDCl3, 400 MHz) 1.37 (s, 18H, H6), 6.49 (s, 2H, H3), 7.18 (d, 4H, 3*J* = 8.5 Hz, H4), 7.29 (d, 4H, 3*J* = 8.4 Hz, H2), 7.43 (d, 4H, 3*J* = 8.4 Hz, H5), 7.48 (d, 4H, 3*J* = 8.3 Hz, H1); δC (CDCl3, 100 MHz) 31.37, 34.64, 96.08, 109.01, 119.16, 124.79, 126.40, 127.84, 131.94, 133.42, 135.02, 136.63, 137.75, 149.70; *m/z* (HR-ESMS) 573.3006 ([M+H]+, calculated for C40H37N4 573.3013); νmax (ATR, cm-1) 2960m, 2904m, 2866m, 2224s, 1600s, 1515s, 1463m, 1413m, 1379m, 1270m, 1170m, 1143w, 1108w, 1018w sh, 833s sh, 773s, 749m, 721w, 679m, 634w. A single crystal of the title compound as a toluene solvate for X-ray diffraction was grown by slow evaporation from toluene.

Synthesis of H2L2

A mixture of 4-formylbenzoic acid (900 mg, 6.0 mmol), 4-tert-butyl aniline (950 μL, 5.9 mmol) and para-toluenesulfonic acid (110 mg, 0.6 mmol) in glacial acetic acid (5 mL) was heated at 90 °C for 30 minutes. To the thick yellow mixture was added 2,3-butanedione (260 μL, 2.9 mmol) and the mixture was heated at 90 °C, during which time the original thick paste dispersed into a freely stirring suspension. On completion, the reaction mixture was cooled to room temperature, filtered, washed with 5 mL of glacial acetic acid and 2×10 mL of methanol, and the solids air dried. The solids were then dispersed in 100 mL of boiling ethyl acetate, and filtered, washed with 2×50 mL of ethyl acetate and 2×50 mL of methanol, and driedin air. Yield 669 mg (1.1 mmol, 37%); m.p. > 300 °C; Found C, 77.48; H, 6.16; N, 4.48; Calculated for C40H38N2O4·0.5H2O C, 77.52; H, 6.34; N, 4.52; δH (*d*6-DMSO, 400 MHz) 1.31 (s, 18H, H6), 6.60 (S, 2H, H3), 7.21 (d, 4H, 3*J* = 8.6 Hz, H4), 7.30 (d, 4H, 3*J* = 8.3 Hz, H2), 7.47 (d, 4H, 3*J* = 8.6 Hz, H5), 7.78 (d, 4H, 3*J* = 8.3 Hz, H1), 12.84 (br s, H7); Due to the very poor solubility of the title compound we were unable to obtain a satisfactory 13C NMR spectrum; *m/z* (APCI) 609.2734 ([M-H]-, calculated for C40H37N2O4 609.2759); νmax (ATR, cm-1) 2960m, 2868w, 2817 m br, 1674s, 1599s, 1563w, 1518m, 1462m, 1418m br, 1375m, 1318m, 1290s sh, 1186s, 1146w, 1107w, 1055w, 1015w, 942m br, 844s, 751s, 704m, 671w. A single crystal of the title compound as a dimethylacetamide solvate for X-ray diffraction was obtained from a mixture of **H2L1** (20 mg) in N,N-dimethylacetamide (1 mL) heated at 100 °C and cooled to room temperature.

Synthesis of H2L3

A mixture of 4-formylbenzoic acid (900 mg, 6.0 mmol), 4-(*1H*-imidazol-1-yl)-aniline (950 mg; 6.0 mmol) and para-toluenesulfonic acid (110 mg, 0.6 mmol) in 5 mL of glacial acetic acid was heated to 90 °C and held at this temperature with stirring for 30 minutes. Following this period, 2,3-butanedione (260 μL, 2.9 mmol) was added dropwise. The mixture was stirred at 90 °C for a further 3 hours, before being cooled to room temperature and filtered. The solids were washed with a further 5 mL of acetic acid and two 5 mL portions of methanol, and the crude solids were dried in air. The solids were then dispersed in 50 mL of boiling ethyl acetate, filtered, and washed with ethyl acetate (50 mL), methanol (50 mL) and diethyl ether (50 mL), leaving a bright yellow solid. Yield 225 mg (12%); m.p. >300 °C; Found C, 69.05; H, 3.90; N, 12.46; Calculated for C38H26N6O4·1.5H2O C, 69.40; H, 4.45; N, 12.78%; δH (d6-DMSO, 400 MHz) 6.71 (s, 2H, H3), 7.13 (s, 2H, H6), 7.37 (d, 4H, *J* = 8.3 Hz, H4), 7.44 (2, 4H, *J* = 8.7 Hz, H2), 7.76 – 7.85 (m, 10H, H1 + H5 + H7), 8.32 (s, 2H, H8), 12.8 (br s, 2H, H9); we were unable to obtain a satisfactory 13C NMR due to the extremely poor solubility of the compound, which tended to precipitate from d6-DMSO during the experiment; *m/z* (APCI) 629.1928 ([M-H]-, calculated for C38H25N6O4 629.1943; νmax (ATR, cm-1) 3407w br, 3116w, 3079w, 1690s sh, 1601s, 1564w, 1514s, 1468m sh, 1408m sh, 1377w, 1363w, 1273m sh, 1233m, 1175s, 1139w, 1102m sh, 1054s, 1013w, 964w, 829s sh, 786w, 746m, 727s, 702m, 671w, 649m. Single crystals of the tetrakis-DMSO solvate were prepared in small quantities by recrystallization from hot DMSO.

Synthesis of *poly*-[AgL12]SbF6·3THF·2H2O 1

Ligand **L1** (10 mg, 17 μmol) was slurried in 5 mL of THF, and combined with a solution of silver hexafluoroantimonate (6 mg, 17 μmol) in 5 mL of THF, with exclusion of ambient light. The mixture was sealed and left to stand for 48 hours, yielding orange crystals of the title compound. Yield 6.9 mg (46 %); m.p >300 °C (decomp.); Found C, 63.35; H, 5.62; N, 6.29; Calculated for [Ag**L1**2]SbF6·3THF·2H2O (C92H100AgF6N8O5Sb] C, 63.45; H, 5.79; N, 6.43%; νmax (ATR, cm-1) 3341 w br, 2953m, 2901w, 2864w, 2236s, 1592s, 1553w, 1515s, 1458m, 1412m, 1376m sh, 1269w, 1238w, 1175s, 1144w, 1114w, 1060m, 1020w, 901w, 841s, 797w, 766w, 721w, 684w, 653s. Phase purity was confirmed by X-ray powder diffraction.

Synthesis of *poly*-[Zn4O(L2)3]·20DMA·10H2O 2

A mixture of **H2L2** (10 mg, 16 μmol), zinc nitrate hexahydrate (10 mg; 34 μmol) and DABCO (5 mg, 45 μmol) was combined in 2 mL of a 2:1 mixture of N,N-dimethylacetamide and ethanol. The resulting suspension was homogenised with brief sonication, sealed, and heated at 100 °C for 6 hours, agitating the sample after 1 hour. The resulting yellow crystals were filtered hot, washed with 2×5 mL of N,N-dimethylacetamide, and air dried. Samples for gas adsorption or solvent exchange studies were immediately transferred into their respective exchange solvents without allowing the solids to dry. Yield 7 mg (32%); m.p. >300 °C; Found C, 59.18; H, 7.05; N, 8.61; calculated for [Zn4O(**L2**)3]·20DMA·10H2O C, 59.66; H, 7.71; N, 9.04%; νmax (ATR, cm-1) 3424w br, 2955m, 2868m, 1601s sh, 1549w, 1513m, 1462w, 1391s sh, 1265m, 1182m, 1140w, 1104w, 1058w, 1014m, 842m, 788m, 757m, 707w, 674w. Phase purity was confirmed by X-ray powder diffraction.

Synthesis of *poly*-[CdL3]·2.5DMA·3.5H2O 3

Ligand H2L3 (10 mg, 16 µmol) and cadmium nitrate tetrahydrate (10 mg, 32 µmol) were combined in 2 mL of N,N-dimethylacetamide, and the turbid yellow mixture was homogenised by sonication. The mixture was sealed and heated at 100 °C for 6 hours, at which point the orange crystals of the product were isolated by filtration and washed with N,N-dimethylacetamide. Yield 5.0 mg (31%); m.p. > 300 °C; Found C, 56.10; H, 4.75; N, 11.94; Calculated for C38H24N6O4Cd·2.5DMA·2.5H2O C, 56.42; H, 5.28; N, 11.65%; νmax (ATR, cm-1) 3415w, 3116w, 2932w, 1627s, sh, 1606s, 1588s, 1522s, 1382s, 1366m, 1263m, 1172w sh, 1134w, 1060m, 1013m, 962m, 933w, 852s, 754s, 716w, 651m. Phase purity was confirmed by X-ray powder diffraction.

Conflicts of interest

There are no conflicts to declare

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Notes and references

1. I. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorf and R. Ameloot, *Chem. Soc. Rev.* 2017, **46**, 3185-3241; N. S. Bobbitt, M. L. Mendonca, A. J. Howarth, T. Islamoglu, J. T. Hupp, O. K. Farha and R. Q. Snurr, *Chem. Soc. Rev.* 2017, **46**, 3357-3385; D. O’Nolan, A. Kumar and M. J. Zaworotko, *J. Am. Chem. Soc.* 2017, **139**, 8508-8513.
2. X. Zhao, X. Bu, T. Wu, S.-T. Zheng, L. Wang and P. Feng, *Nature Commun.* 2013, **4**, 2344; B. Van de Voorde, B. Bueken, J. Denayer and D. De Vos, *Chem. Soc. Rev.* 2014, **43**, 5766-5778; K. A. Cychosz, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.* 2008, **130**, 6938-6939.
3. M. Hoshino, A. Khutia, H. Xing, Y. Inokuma and M. Fujita, *IUCrJ*, 2016, **3**, 139-151.
4. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.* 2012, **112**, 1105-1125; S. G. Dunning, A. J. Nuñez, M. D. Moore, A. Steiner, V. M. Lynch, J. L. Sessler, B. J. Holliday and S. M. Humphrey, *Chem* 2017, **2**, 579-589; G. Tobin, S. Comby, N. Zhu, R. Clérac, T. Gunnlaugsson and W. Schmitt, *Chem. Commun.* 2015, **51**, 13313-13316; D. Wu, A. C. Sedgwick, T. Gunnlaugsson, E. U. Akkaya, J. Yoon and T. D. James, *Chem. Soc. Rev.* 2017, **46**, 7105-7123.
5. S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem. Int. Ed.* 2013, **52**, 2881-2885.
6. Y. Takashima, V. M. Martínez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto and S. Kitagawa, *Nature Commun.* 2010, **2**, 168; J. Cui, Y. Li, Z. Guo and H. Zheng, *Chem. Commun.* 2013, **49**, 555-557.
7. D. H. Friese, A. Mikhaylov, M. Krzeszewski, Y. M. Poronik, A. Rebane, K. Ruud and D. T. Gryko, *Chem. Eur. J.* 2015, **21**, 18364–18374.
8. M. Kaur and D. H. Choi, *Chem. Soc. Rev.* 2014, **44**, 58-77.
9. M. Krzeszewski, D. Gryko and D. T. Gryko, *Acc. Chem. Res.* **2017**, *50*, 2334-2345; B. Dereka, A. Rosspeintner, M. Krzeszewski, D. T. Gryko and E. Vauthey, *Angew. Chem. Int. Ed.* 2016, **55**,15624-15628.
10. K. Li, Y. Liu, Y. Li, Q. Feng, H. Hou and B. Z. Tang, *Chem. Sci.* 2017, **8**, 7258-7267.
11. M. Du, C.-P. Li, C.-S. Liu and S.-M. Fang, *Coord. Chem. Rev.* 2013, **257**, 1282-1305; Z. Yin, Y.-L. Zhou, M.-H. Zeng and M. Kurmoo, *Dalton Trans.* 2015, **44**, 5258-5275; C. S. Hawes, R. Babarao, M. R. Hill, K. F. White, B. F. Abrahams and P. E. Kruger, *Chem. Commun.* 2012, **48**, 11558-11560
12. U. Rösch, S. Yao, R. Worthmann and F. Würthner, *Angew. Chem. Int. Ed.* 2006, **118**, 7184-7188; S. Kim, M. Fujitsuka, N. Tohnai, T. Tachikawa, I. Hisaki, M. Miyata and T. Majima, *Chem. Commun.* 2015, **51**, 11580-11583; Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.* 2011, **40**, 5361-5388.
13. L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.* 2007, 955-964.
14. C. S. Hawes, K. Byrne, W. Schmitt and T. Gunnlaugsson, *Inorg. Chem.* 2016, **55**, 11570-11582; J. A. Kitchen, P. N. Martinho, G. G. Morgan and T. Gunnlaugsson, *Dalton Trans.* 2014, **43**, 6468-6479; D. L. Reger, A. Debreczeni, J. J. Horger and M. D. Smith, *Cryst. Growth Des.* 2011, **11**, 4068-4079; A. B. Carter, R. J. Laverick, D. J. Wales, S. O. Akponasa, A. J. Scott, T. D. Keene and J. A. Kitchen, *Cryst. Growth Des.* 2017, **17**, 5129-5144
15. A. L. Spek, *Acta Crystallogr. Sect. C.* 2015, **71**, 9-18
16. B. M. Ahmed and G. Mezei, *J. Org. Chem.* 2018, **83**, 1649-1653
17. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe and O. M. Yaghi, *Science* 2002, **295**, 469-472
18. J. R. Lacowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, U.S.A., 2006.
19. D. Zhao, D. J. Timmons, D. Yuan and H.-C. Zhou, *Acc. Chem. Res.* 2011, **44**, 123-133; P. Deria, J. E. Mondloch, E. Tylianakis, P. Ghosh, W. Bury, R. Q. Snurr, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.* 2013, **135**, 16801-16804; B. F. Abrahams, R. W. Elliott, T. A. Hudson, R. Robson and A. L. Sutton, *CrystEngComm* 2018, *In Press*, DOI: 10.1039/C8CE00413G

20 M. K. Kurimova, G. Yahioglu, J. A. Levitt and K. Suhling, *J. Am. Chem. Soc.* 2008, **130**, 6672-6673; A. F. Henwood, S. Evariste, A. M. Z. Slawin and E. Zysman-Colman, *Faraday Discuss.* 2014, **174**, 165-182; M. A. Haidekker, T. P. Brady, D. Lichlyter and E. A. Theodorakis, *J. Am. Chem. Soc.* 2006, **128**, 398-399

21 D. A. Gómez-Gualdrón, P. Z. Moghadam, J. T. Hupp, O. K. Farha and R. Q. Snurr, *J. Am. Chem. Soc.* 2016, **138**, 215-224; Y. Zhu, H. Long and W. Zhang, *Chem. Mater.* 2013, **25**, 1630-1635

22 *Bruker APEX-3*, Bruker-AXS Inc., Madison, WI, 2016

23 *Bruker DIFFRAC.EVA*, Bruker-AXS Inc., Madison, WI, 2016

24 *SADABS*. Bruker-AXS Inc., Madison, WI, 2016

25 G. M. Sheldrick, *Acta Crystallogr. Sect. A.* 2015, **71**, 3-8

26 G. M. Sheldrick, *Acta Crystallogr. Sect. C.* 2015, **71**, 3-8

27 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339-341

**Table 2** Crystal and refinement data for all structures

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Identification code | **L1·PhMe** | **H2L2·2DMA** | **H2L3·4DMSO** | **1** | **2** | **3** |
| Empirical formula | C47H44N4 | C48H56N4O6 | C46H50N6O8S4 | C80H72AgF6N8Sb | C120H108N6O13Zn4 | C38H24CdN6O4 |
| Formula weight | 664.86 | 784.96 | 943.16 | 1489.07 | 2103.6 | 741.03 |
| Temperature/K | 100 | 100 | 120 | 100 | 100 | 100 |
| Crystal system | triclinic | monoclinic | triclinic | orthorhombic | triclinic | hexagonal |
| Space group | *P*-1 | *P*21/*c* | *P*-1 | C*cca* | *P*-1 | *P*6522 |
| a/Å | 6.259(3) | 6.1199(2) | 5.5946(3) | 10.7985(3) | 22.5696(8) | 13.4720(3) |
| b/Å | 10.267(5) | 11.6124(4) | 11.5848(6) | 29.4144(9) | 22.7345(8) | 13.4720(3) |
| c/Å | 14.832(8) | 28.9629(9) | 18.1469(9) | 25.9424(8) | 22.7582(8) | 100.2746(19) |
| α/° | 94.749(17) | 90 | 84.9420(10) | 90 | 89.484(2) | 90 |
| β/° | 94.10(2) | 92.694(2) | 81.7040(10) | 90 | 75.944(2) | 90 |
| γ/° | 102.130(17) | 90 | 88.700(2) | 90 | 87.829(2) | 120 |
| Volume/Å3 | 924.7(8) | 2056.02(12) | 1159.24(10) | 8240.1(4) | 11319.7(7) | 15761.1(8) |
| Z | 1 | 2 | 1 | 4 | 2 | 12 |
| ρcalcg/cm3 | 1.194 | 1.268 | 1.351 | 1.200 | 0.617 | 0.937 |
| μ/mm‑1 | 0.535 | 0.668 | 0.264 | 4.966 | 0.725 | 3.593 |
| F(000) | 354 | 840 | 496 | 3040 | 2188 | 4488 |
| Crystal size/mm3 | 0.18 × 0.05 × 0.04 | 0.2 × 0.06 × 0.03 | 0.25 × 0.12 × 0.04 | 0.11 × 0.04 × 0.04 | 0.16 × 0.16 × 0.11 | 0.26 × 0.08 × 0.06 |
| Radiation | Cu Kα (λ = 1.54178) | Cu Kα (λ = 1.54178) | Mo Kα (λ = 0.71073) | Cu Kα (λ = 1.54178) | Cu Kα (λ = 1.54178) | Cu Kα (λ = 1.54178) |
| 2Θ range for data collection/° | 8.854 to 136.086 | 6.11 to 136.662 | 3.53 to 56.732 | 6.01 to 136.87 | 3.89 to 108.672 | 5.288 to 117.904 |
| Index ranges | -7 ≤ h ≤ 7, -12 ≤ k ≤ 11, -17 ≤ l ≤ 17 | -7 ≤ h ≤ 7, -13 ≤ k ≤ 13, -21 ≤ l ≤ 34 | -7 ≤ h ≤ 7, -15 ≤ k ≤ 11, -24 ≤ l ≤ 23 | -11 ≤ h ≤ 12, -34 ≤ k ≤ 35, -25 ≤ l ≤ 31 | -23 ≤ h ≤ 23, -23 ≤ k ≤ 21, -23 ≤ l ≤ 23 | -14 ≤ h ≤ 12, -14 ≤ k ≤ 14, -111 ≤ l ≤ 111 |
| Reflections collected | 10234 | 14305 | 11850 | 31802 | 63193 | 71590 |
| Independent reflections | 3350 [Rint = 0.0323, Rsigma = 0.0348] | 3755 [Rint = 0.0430, Rsigma = 0.0408] | 5789 [Rint = 0.0255, Rsigma = 0.0454] | 3737 [Rint = 0.0703, Rsigma = 0.0437] | 27389 [Rint = 0.0369, Rsigma = 0.0575] | 7532 [Rint = 0.0983, Rsigma = 0.0543] |
| Data/restraints/parameters | 3350/0/266 | 3755/6/286 | 5789/0/296 | 3737/105/271 | 27389/388/1225 | 7532/138/515 |
| Reflns Obs. [I>=2σ (I)] | 2786 | 3112 | 4162 | 3051 | 18928 | 6647 |
| Goodness-of-fit on F2 | 1.029 | 1.034 | 1.036 | 1.043 | 0.988 | 1.037 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0464, wR2 = 0.1265 | R1 = 0.0489, wR2 = 0.1325 | R1 = 0.0444, wR2 = 0.1011 | R1 = 0.0795, wR2 = 0.2415 | R1 = 0.0700, wR2 = 0.2148 | R1 = 0.0550, wR2 = 0.1415 |
| Final R indexes [all data] | R1 = 0.0545, wR2 = 0.1342 | R1 = 0.0581, wR2 = 0.1404 | R1 = 0.0708, wR2 = 0.1114 | R1 = 0.0915, wR2 = 0.2591 | R1 = 0.0886, wR2 = 0.2307 | R1 = 0.0614, wR2 = 0.1458 |
| Largest diff. peak/hole / e Å-3 | 0.22/-0.25 | 0.28/-0.22 | 0.36/-0.50 | 1.63/-1.31 | 0.79/-0.57 | 0.58/-0.73 |
| CCDC No. | 1818940 | 1818941 | 1840309 | 1818942 | 1818943 | 1840308 |