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ARTICLE

Effect of π - π Stacking Interactions on the Emission Properties of Cadmium Metal-Organic Frameworks Based on 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene.

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Five multidimensional cadmium metal-organic frameworks based on the luminescent 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene linker and flexible dicarboxylate ligands have been synthesized by conventional routes. These MOFs show fascinating structures and display, in solid state and room temperature, intense and hypsochromic photoluminescence properties when packed as a 3D network, and bathochromic photoluminescence properties when arranged as 2D networks, as compared to the emission properties of the free luminescent 4-bpdb ligand. DFT calculations have revealed the establishment, on the 3D networks, of destabilizing p-p stacking interactions between pyridyl rings of neighbouring 4-bpdb aromatic linkers on the 3D networks synthesized, responsible for the unexpected hypsochromic emission. The absence of p-p stacking interactions in the 2D MOFs yields the expected bathochromic photoluminescence arising from metal coordination with the aromatic ligand.

1. Introduction.

In the last decade, design of coordination polymers has attracted great attention for their potential applications in the fields of luminescence, gas adsorption, catalysis, magnetism and electrical conductivity¹. An emerging class of crystalline multidimensional materials, Metal-organic frameworks (MOFs), are mostly constructed from clusters of transition-metal ions held in position in a lattice by ligation to organic molecules². Among the most sought ligands, multidentate N or O-donor building-blocks have drawn extensive attention in the construction of these new and unusual coordination polymers³ based on carboxylate and/or pyridine-based ligands⁴. Recently, we have designed and synthesized a new flexible MOF with Cu₂ paddle-wheels connected to glutarate and 1,3-bis(4-pyridyl)propane ligands leading to high adsorption capacity and outstanding CO₂ selectivity⁵. We believe that the conformational freedom of the glutarate ligand could promote the self-assembly of MOFs with alternative topologies and with properties pertaining to auxiliary ligands. In this context, and as a part of our continuing studies on nitrogen derivative ligands with different dicarboxylate flexible spacers, we have chosen the 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene linker (4-bpdb) to construct MOFs based on cadmium. Recent studies have demonstrated that the long conjugated 4-bpdb ligand is capable of coordinating transition metal centers with both terminal pyridyl nitrogen atoms forming new coordination polymers⁶. Further, complexes containing polynuclear d¹⁰ metals such as Cd²⁺, have attracted extensive interest in recent years due to

their abilities of exhibiting appealing structures⁷. The Cd²⁺ ion is particularly suited for the construction of coordination polymers since the absence of ligand field constrains associated with the d¹⁰ configuration provides a flexible coordination environment and, therefore, the variety of geometries achievable by these complexes can be finely tuned, easily generating multiple types of MOFs with various topologies. In this context, we present here the synthesis, structural characterization and analysis of the luminescence properties of three new cadmium based 3D MOFs (compounds **1-3**) and two new cadmium 2D MOFs (compounds **4-5**) with the 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene ligand (4-bpdb) and dicarboxylate flexible ligands. The former show unexpected hypsochromic emission bands as compared to the free 4-bpdb ligand, while the latter present bathochromic emission bands generated by coordination to metal ion. A deep analysis of the crystal structures of these five compounds revealed the existence of π - π stacking interactions between neighbouring 4-bpdb ligands in the former but not in the latter. Chromophore stacking guides to closely packed networks and generally leads to a significant quenching of the luminescent properties or generates bathochromic emissions⁸. The latter is due to a phenomenon commonly known as Aggregation Caused Quenching (ACQ) which provides non-radiative relaxation pathways to the system⁹ and diminish the intensity of the emission bands of the molecular complexes presenting it. Interestingly, Aggregation Induced Emission (AIE) has also been described¹⁰. With the aim to reveal the exact mechanism by which compounds 1-3 show an intense and blue shifted emission, a deep analysis of the π - π stacking interactions

occurring in our crystals was carried out. According to previous computational studies¹¹, π - π stacking interactions can be either highly, moderately or slightly stabilizing structures, but can also become destabilizing depending on the relative orientation and distance between the centroids of the involved aromatic rings. A theoretical DFT analysis on the interaction energy of π - π stacked pyridine dimers present on each of these mentioned 3D MOFs has proved to be useful to explain the origin of the mentioned unexpected hypsochromic light emission observed in the present study.

2. Experimental.

Reagents were purchased commercially and used without further purification.

2.1. Preparation of complexes.

[Cd₃(glu)₂(4-bpdb)₃(H₂O)₂](NO₃)₂·(4-bpdb)_{0.5}·(H₂O)₈ (1): an aqueous solution (5 ml) containing glutaric acid (**glu**) (13.2 mg 0.1 mmol) and cadmium nitrate tetrahydrate (0.1 mmol, 30.8 mg) was placed at the bottom of a test tube, and an interface of water/ethanol (50%, 3 ml) was added dropwise. Then an ethanolic solution (5 ml) of 4-bpdb (0.1 mmol, 21 mg) was dropped slowly on the interface. The tube was covered with parafilm and left at room temperature. X-ray quality crystals as yellow prisms were grown at the interface after a few days. Yield ca. 72%. Anal. Calcd for C₅₂H₆₇N₁₆O₂₄Cd₃: C, 38.14; H, 4.12; N, 13.68. Found: C, 38.27; H, 4.28; N, 13.51%.

[Cd(pim)(4-bpdb)] (2): compound **2** was prepared similar to that of compound **1**, but pimelic acid (**pim**) (16 mg, 0.1 mmol) was used instead of glutaric acid. Suitable crystals as yellow prisms were grown at the interface after a few days. Yield ca. 80%. Anal. Calcd for C₁₉H₂₀N₄O₄Cd: C, 47.46; H, 4.19; N, 11.65. Found: C, 47.58; H, 4.26; N, 11.92%.

[Cd(suc)(4-bpdb)] (3): compound **3** was prepared similar to that of compound **1**, but succinic acid (**suc**) (11.8 mg, 0.1 mmol) was used instead of glutaric acid. Suitable crystals as yellow prisms were grown at the interface after a few days. Yield ca. 81%. Anal. Calcd for C₁₆H₁₄N₄O₄Cd: C, 43.80; H, 3.22; N, 12.77. Found: C, 43.88; H, 3.28; N, 12.85%.

[Cd(glu)(4-bpdb)]·CH₃CH₂OH. (4): compound **4** was prepared similar to that of compound **1**, but 10.5 mg of 4-bpdb (0.05 mmol) was used. X-ray quality crystals as yellow prisms were grown at the interface after a few days. Yield ca. 76%. Anal. Calcd for C₁₉H₂₂N₄O₅Cd: C, 45.75; H, 4.45; N, 11.23. Found: C, 45.88; H, 4.48; N, 11.17%.

[Cd(3m-glu)(H₂O)(4-bpdb)]·H₂O (5): compound **5** was prepared similar to that of compound **4**, but 3-methylglutaric acid (**3m-glu**) (14.6 mg 0.1 mmol) was used instead of glutaric acid.

Yield ca. 68%. Anal. Calcd for C₁₈H₂₂N₄O₆Cd: C, 42.99; H, 4.41; N, 11.14. Found: C, 43.30; H, 4.13; N, 11.11%.

[Glu(4-bpdb)] (6): an aqueous solution (5 ml) containing glutaric acid (**glu**) (0.2 mmol, 26.2 mg) was placed at the bottom of a test tube, and an interface of water/ethanol (50%, 3 ml) was added dropwise. Then an ethanolic solution (5 ml) of 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (**4-bpdb**) (0.1 mmol, 21 mg) was dropped slowly on the interface. The tube was covered with parafilm and left at room temperature. X-ray quality crystals as yellow prisms were grown at the interface after a few days. Yield ca. 78%. Anal. Calcd. for C₁₇H₁₈N₄O₄: C, 59.64; H, 5.30; N, 16.37. Found: C, 59.78; H, 5.38; N, 16.27%.

Glu_{0.5}(4-bpdb)_{0.5} (7): compound **7** was prepared similar to that of compound **6**, but adipic acid (**adi**) (29.4 mg, 0.2 mmol) was used instead of glutaric acid. Suitable crystals as yellow prisms were grown at the interface after a few days. Yield ca. 72%. Anal. Calcd for C₁₈H₂₀N₄O₄: C, 60.67; H, 5.66; N, 15.72. Found: C, 60.82; H, 5.72; N, 15.61%.

2.2. Physical measurements.

Elemental analyses were carried out at the “Centro de Instrumentación Científica” (University of Granada) on a Fisons-Carlo Erba analyser model EA 1108.

2.3. Single-Crystal Structure Determination.

Suitable crystals of **1-7** were mounted on a glass fibre and used for data collection on a Bruker AXS APEX CCD area detector (compounds **1**, **2**, **5** and **7**) and on a Bruker Venture (compound **3**, **4** and **6**) equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Lorentz-polarization and empirical absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares calculations on F^2 using the program SHELXS97¹². Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. Attempts to identify the solvent molecules failed in compound **1**. Instead, a new set of F^2 (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON-94.¹³ Refinement reduced $R1$ to 0.089. Several crystals of **1** were measured and the structure was solved from the best data we were able to collect. Final $R(F)$, $wR(F2)$ and goodness of fit agreement factors, details on the data collection and analysis can be found in Table 1. Selected bond lengths and angles are given in Tables S1, S2, S3, S4 and S5 (ESI). CCDC reference numbers for the structures of **1-7** were 1032668-1032674. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336-033; e-mail, deposit@ccdc.cam.ac.uk). The crystal structure of 4-bpdb ligand was obtained from CCDC, reference number 146108.

2.4. Luminescence measurement.

A Varian Cary-Eclipse Fluorescence Spectrofluorimeter was used to obtain the fluorescence spectra. The spectrofluorimeter was equipped with a xenon discharge lamp (peak power equivalent to 75 kW), Czerny-Turner monochromators, R-928 photomultiplier tube which is red sensitive (even 900 nm) with manual or automatic voltage controlled using the Cary Eclipse software for Windows 95/98/NT system. The photomultiplier detector voltage was 700 V and the instrument excitation and emission slits were set at 5 and 5 nm, respectively.

2.5. Computational calculations.

All calculations were carried out using the Gaussian 09 software package¹⁴. Single-point energy calculations were performed by using second-order perturbation theory (MP2) and Dunning's aug-cc-pVTZ, basis sets¹⁵. The coordinates of each type of π - π stacked pyridine dimer, trimer or tetramer present in compounds **1-3** were isolated from the cif files of the corresponding crystal structures. The (de)stabilization energy associated to the formation of each pyridine dimer, trimer or tetramer was computed as the energy difference between the corresponding oligomer and two, three or four pyridine monomers, respectively

3. Results and Discussion.

Crystallographic structures

Three different 3D-MOFs and two two-dimensional coordination polymers have been obtained with cadmium(II) as the metallic center, the 4-bpdb spacer and different dicarboxylate anions as ligands; in all cases the bond distances and angles in the coordination sphere are the expected ones for these types of compounds¹⁶.

Metal-bound three dimensional MOFs:

The structure of **1** consists of a cationic three-dimensional MOF formed by metal bound glutarate and 4-bpdb spacers. Two different big channels are observed along the *b* axis ($5.139 \times 14.308 \text{ \AA}^2$ and $4.989 \times 13.423 \text{ \AA}^2$ approx), which are occupied by nitrate anions and non-coordinated 4-bpdb ligands, and nitrate anions and solvent water molecules, respectively (Figure 1). The asymmetric unit shows three crystallographically independent Cd^{2+} centers, two glutarate ligands, two coordination water molecules and three 4-bpdb spacers together with half molecule of the non-coordinated 4-bpdb, two nitrate anions and 8 crystallization water molecules. Two of the three different cadmium atoms (Cd1 and Cd3 in Figure S1) display a distorted octahedral geometry, CdN_2O_4 , however for Cd3 all the oxygen-donor ligands are glutarate anions and for Cd1 one of the ligands is a coordinated molecule of water. The remaining cadmium atom, Cd2, shows a distorted pentagonal bipyramidal environment, CdN_2O_5 , formed by 4-bpdb, glutarate and one molecule of coordinated water (Figure S1A and Table S1). The crystalline structure can be described as sheets of cadmium-glutarate interconnected by 4-bpdb ligands in the *c* axis and this network consists in **6,8-c** topology net with a point symbol $\{3^2.4^{11}.5.6\}\{3^4.4^{13}.5^8.6^3\}$ (Figure S1). In these sheets formed by glutarate and cadmium ions, half of the glutarates

Table 1. Crystallographic Data and Structural Refinement Details for **1-7**

compound	1	2	3	4	5	6	7
chemical formula	$\text{C}_{52}\text{H}_{67}\text{N}_{16}\text{O}_{24}\text{Cd}_3$	$\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_4\text{Cd}$	$\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_4\text{Cd}$	$\text{C}_{19}\text{H}_{22}\text{N}_4\text{O}_5\text{Cd}$	$\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_6\text{Cd}$	$\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_4$	$\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_4$
M/gmol ⁻¹	1637.42	480.79	438.71	498.81	502.80	342.35	356.38
T(K)	100	100(2)	100(2)	100	100	100(2)	100(2)
$\lambda/\text{\AA}$	0.71073	0.71069	0.71069	0.71073	0.71073	0.71069	0.71069
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>P21/c</i>	<i>P21/c</i>	<i>P-1</i>	<i>Cc</i>	<i>C2/c</i>	<i>P21/c</i>
<i>a</i> /\AA	46.216(4)	10.8281(3)	10.667(6)	8.6168(5)	16.9914(7)	40.33(9)	4.8452(4)
<i>b</i> /\AA	12.3840(11)	11.4808(4)	11.908(6)	10.0838(6)	15.7268(8)	4.629(13)	10.3656(10)
<i>c</i> /\AA	31.040(3)	15.8705(4)	13.161(7)	12.9388(8)	9.2125(9)	20.38(5)	17.3307(17)
α/deg	90	90	90	93.318(2)	90	90	90
β/deg	131.459(2)	109.3510(10)	109.602(6)	108.249(2)	120.503(3)	117.50(3)	97.778(4)
γ/deg	90	90	90	110.455(2)	90	90	90
<i>V</i> /\AA ³	13314(2)	1861.49(10)	1574.8(15)	982.54(10)	2121.1(2)	3375(15)	862.40(14)
<i>Z</i>	8	4	4	2	4	8	2
ρ (g cm ⁻³)	1.634	1.716	1.850	1.686	1.575	1.347	1.372
μ (mm ⁻¹)	1.038	1.208	1.418	1.151	1.070	0.098	0.099
Unique reflections	147539	25826	8157	20293	12633	2480	8178
R(<i>int</i>)	0.157	0.0471	0.0453	0.091	0.046	0.0765	0.0819
GOF on F ²	1.177	1.042	1.062	1.025	1.083	0.991	1.005
R1 [<i>I</i> > 2 σ (<i>I</i>)]	0.109	0.0263	0.0373	0.048	0.043	0.0772	0.0546
wR2 [<i>I</i> > 2 σ (<i>I</i>)]	0.254	0.0566	0.0849	0.091	0.109	0.1756	0.1075

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR(F^2) = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum wF^4]^{1/2}}$$

are in an anti-gauche conformation (torsion angles $-175(2)^\circ$ and $61(2)^\circ$), while the other half display a more stable anti-anti conformation (torsion angles $-173(2)^\circ$ and $-179(2)^\circ$). The glutarate displaying the anti-anti conformation binds four metals with both carboxylates binding in a syn-syn-anti fashion. Meanwhile, in the other type of glutarates, one of the carboxylates binds only two metal ions in a syn-syn mode, while the other one binds three metal ions in a syn-syn-anti mode (Figure S1). These sheets formed by cadmium and glutarate are linked by the 4-bpdb ligand, which in all cases shows the more favorable *trans* conformation.

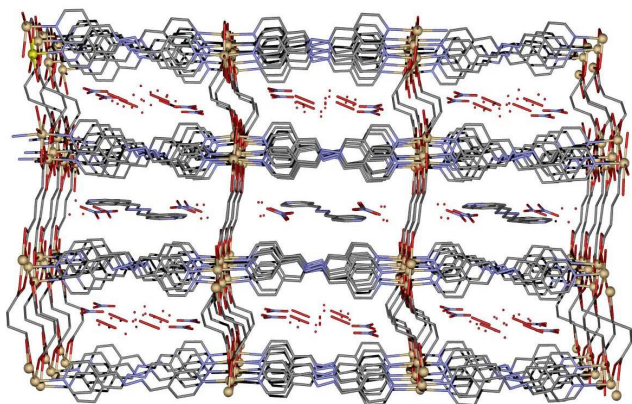


Figure 1. View down to the *b* axis of the three-dimensional network in compound **1**. Hydrogen atoms have been omitted for clarity.

Compound **2** is a 3D structure that can be described as sheets of pimelate ligands interconnected by 4-bpdb ligands in the *a* axis, generating small rectangular channels in the *b* direction (Figure 2), forming a *pcu* type net with point symbol $(4^{12}, 6^3)$. The asymmetric unit consists of one Cd^{2+} cation, and single pimelate and 4-bpdb ligands. In the extended structure, Cd^{2+} atoms form dimers where each metal center shows a CdN_2O_5 coordination mode generating an environment of distorted pentagonal bipyramid (Figure S2), arising from the coordination of five oxygen atoms belonging to three pimelate dianions and two nitrogen atoms in *trans* position belonging to two 4-bpdb ligands (Figure S2 and Table S2). The pimelate ligand adopts an *gauche-anti-anti-gauche* conformation (torsion angles $-65.0(2)^\circ$, $-168.0(2)^\circ$, $178.0(2)^\circ$ and $-61.4(2)^\circ$), and each pimelate binds three metals, one end binds a metal in a chelate mode, while the other carboxylate binds two metals in a *syn-syn-anti* fashion (Figure S2). Meanwhile the 4-bpdb ligand adopts the most stable *trans* conformation.

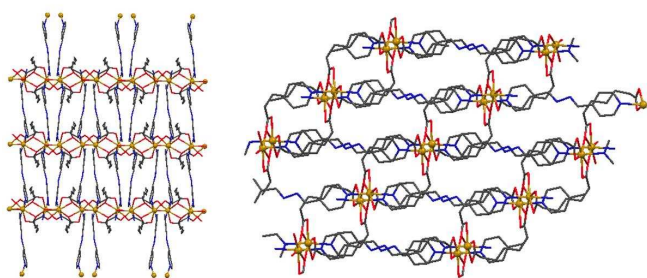


Figure 2. View down to the *c* axis (left) and the *b* axis (right) of the three-dimensional network in compound **2**.

Compound **3** is a 3D MOF that can be described as cadmium-succinate zig-zag sheets along *c* axis linked by 4-bpdb ligands, respectively (Figure 3), which has a *mab* topology with point symbol $(4^4.6^{10}.8)$ (Figure S3). The asymmetric unit is very similar to that of **2**. It consists of one Cd^{2+} cation, and a single succinate and 4-bpdb ligands. In the extended structure, the Cd^{2+} atom shows a CdN_2O_5 coordination mode and a distorted pentagonal bipyramidal geometry, arising from the coordination of five oxygen atoms belonging to three succinate dianions and two nitrogen atoms in *trans* position belonging to two 4-bpdb ligands. Analogously to **2**, one carboxylate of the succinate chelates one metal, while the other carboxylate binds two metals in a *syn-syn-anti* fashion (Figure S3 and Table S3). To achieve this, the chain of the succinate ligand adopts a *gauche* conformation ($-63.9(5)^\circ$). As in **2** the 4-bpdb ligand also adopts the more favourable *trans* configuration.

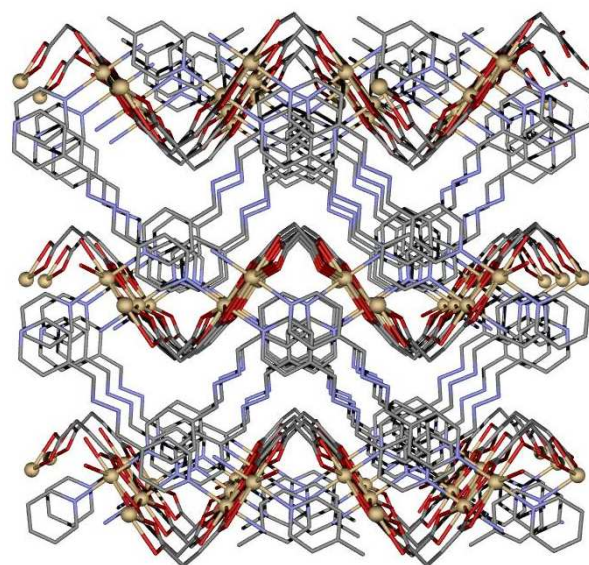


Figure 3. View down the *c* axis of the three-dimensional network present in compound **3**.

Metal-bound two-dimensional MOFs:

Compound **4** is a 2D structure that can be described as double chains along *a* axis formed by cadmium dimers and glutarate anions that are linked by 4-bpdb ligands (Figure 4). The environment around the Cd^{2+} is very similar to that displayed by **2** and **3**, it shows a CdN_2O_5 coordination mode in a distorted pentagonal bipyramidal geometry (Figure S4 and Table S4). This arises from the coordination of five oxygen atoms belonging to three glutaric dianions and two nitrogen atoms in *trans* position belonging to two 4-bpdb ligands (Figure S4). The glutarate anion binds three different metals, it binds one in a chelate mode through one of the carboxylates and binds two through the other carboxylate in a *syn-syn-anti* fashion. However, unlike in **1**, where despite having the same components a 3D net appears, the glutarate anion adopts a *gauche-gauche* conformation (torsion angles $-71(3)^\circ$ for both cases).

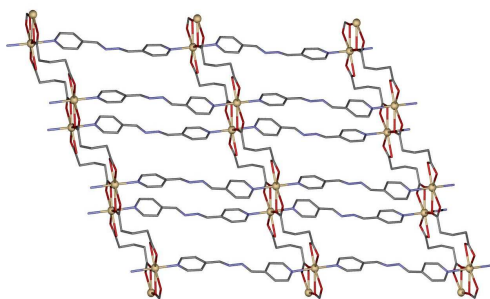


Figure 4. Perspective view of the double sheets present in **4**.

Compound **5** is a 2D MOF constituted by anti-parallel interpenetrated sheets formed by 3Methyl-glutarate, 4-bpdb ligands and Cd^{2+} atoms, that can be described as 1D cadmium-glutarate polymers along *c* axis linked by 4-bpdb ligands (Figure 5). The environment around the cadmium atoms is CdN_2O_5 with a distorted pentagonal bipyramidal geometry, however unlike other structures in this article with the same geometry both ends of the glutarate dianion bind the metal in a chelate fashion and the fifth equatorial coordination position is filled with a molecule of water and no dimers are formed (Figure S5 and Table S5). Also, unlike the glutarate dianion in **4**, which is also a 2D polymer, 3Methyl-glutarate adopts a similar conformation to the glutarate dianion in **1**, a *gauche-anti* conformation (torsion angles $71.8(3)^\circ$ and $176(2)^\circ$).

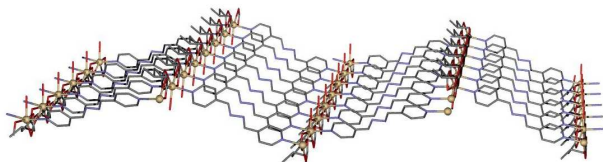


Figure 5. Perspective view of two-dimensional coordination polymer found on the extended structure of compound **5**.

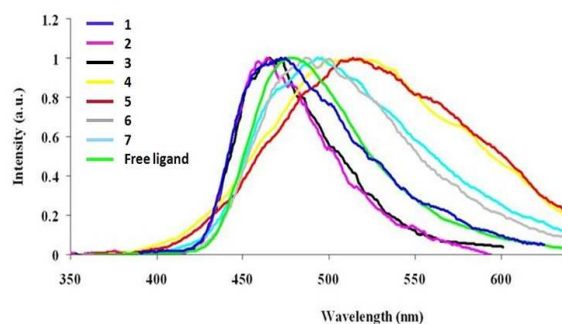
Metal-free networks:

Compound **6** consists of a zig-zag H-bond network of 4-bpdb and glutaric acid ligands (Figure S6), for this the glutaric acid does not adopt the most favorable *anti-anti* conformation but a *gauche-anti* conformation (torsion angles $-76(1)^\circ$ and $175.2(8)^\circ$). However when the diacid of choice is adipic acid (compound **7**) the H-bond network formed consists on parallel sheets of coplanar 4-bpdb and glutaric acid ligands (Figure S7), where the adipic acid adopts the most stable *anti-anti-anti* conformation (torsion angles $-175.0(1)^\circ$, $-180.0(2)^\circ$ and $175.0(1)^\circ$).

3.2. Luminescence Studies.

Due to its extended aromaticity, 4-bpdb ligand is a good candidate for enhanced emissive properties; for this reason we decided to carry out an experimental-theoretical study of luminescent properties of compounds **1-5** in solid state at room temperature (Figure 6). Using a 330 nm incident radiation, compound **1** showed an intense emission at 468 nm, as did compounds **2** and **3**, with intense emission at 463 and 464 nm, respectively. These emission bands are significantly blue-shifted with respect to the free ligand (480 nm). Emission bands for these

type of aromatic ligands generally originate from $p^* \rightarrow s$ and/or $p^* \rightarrow p$ photon relaxation; this energy gap generally decreases (red-shifted emission or bathochromic emission) upon ligand coordination to metals due to the increased rigidity provided to the system¹⁷. The mentioned hypsochromic emission of MOFs **1-3** must therefore arise from either structural and/or electronic features resulting from events other than metal coordination; such an event must provoke an increase on the $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ energy gap of the light emitting ligand. A deeper analysis of the crystal structure of compounds **1-3** revealed the existence of an interesting π - π stacking interaction pattern between pyridyl rings of neighboring 4-bpdb ligands, which is not observed in the crystal structure of the free 4-bpdb ligand¹⁸. In this line, compound **1** contains nearly-parallel pyridine dimmers where the measured distances and angles for the stacked pyridyl groups are slightly different parameters at both ends of the 4-bpdb dimmers (scheme 1a). On the other hand, the relative position of the non-stacked (embedded) and the mentioned stacked 4-bpdb ligands reveals a lack of interaction of the former with the stacking geometry of the latter (see Figure S8). The same is true for the embedded water molecules and nitrate ions. Therefore, guest molecules were not included in the theoretical calculations that were aimed at identifying any possible effect of ligand stacking on peak position. According to our DFT calculations, these distorted parallel sandwich pyridine dimers with large vertical displacements (4.2 Å in one end of the 4-bpdb ligand and 4.0 Å in the other end), account for an unfavourable interaction energy of 0.78 kcal/mol each. This moderate destabilizing packing effect on compound **1** would in part account for its blue-shifted emission as compared to the luminescent properties of the free ligand, whose X-ray structure shows a complete lack of π - π stacking interactions. Nevertheless, the non-coordinated 4-bpdb ligands present in the big channels observed in **1**, would shift the emission of **1** to higher wavelengths and, therefore, would oppose the blue-shifting effect of the destabilizing π - π stacking interactions.

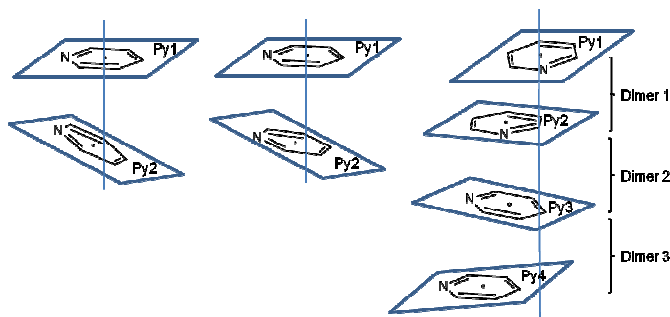


	Emission maxima (nm)
1	468
2	463
3	464
4	518
5	518
6	489
7	495
4-bpdb	480

Figure 6. The emission maxima values (left) and experimental emission spectra (right) of compounds **1-7** and free 4-bpdb ligand after excitation at 330 nm in solid state at room temperature.

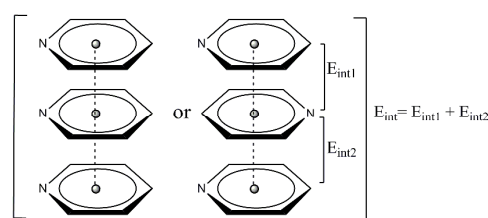
In compounds **2** and **3** the nature of the π - π stacking interactions established between neighboring pyridyl rings is modulated by the substitution of the glutarate ligand present in compound **1** by the equally flexible pimelate and succinate ligands present in MOFs **2** and **3**, respectively. A deep structural analysis of compound **2** revealed the existence of stacked pyridyl groups, arranged as parallel displaced sandwich structures (scheme 1); the measured distances and angles for the stacked pyridyl groups are identical at both ends of the 4-bpdb dimmers and are shown in scheme 1 (vertical and horizontal displacements, 3.7 Å and 1.4 Å, respectively). The latter, differ from those supposed to be maximally stabilizing (3.5 and 1.6 Å, respectively) according to the potential energy surfaces reported for displaced parallel pyridine sandwiches by Sathyamurthy et al.^{11b} and Sherryl et al.^{11c}. Our DFT calculations revealed that the pyridine dimers present in compound **2** are highly destabilizing and account for a desfavoured interaction energy of 5 kcal/mol approximately.

Compound **3** contains tetramers of interacting 4-bpdb ligands forming distorted column-like structures where three different types of p-p stacked pyridine dimers are observed (Scheme 1): dimer 1 (pyridines 1 and 2) and dimer 3 (pyridines 3 and 4), both with a parallel displaced sandwich configuration and dimer 2 (pyridines 2 and 3) with a non-parallel sandwich configuration. The measured distances and angles for the stacked pyridyl groups are identical at both ends of the 4-bpdb tetramers. As previously reported^{11b}, the interaction energy computed for p-p stacked pyridine oligomers is the sum of the interaction energy of each constitutive pyridine dimer (scheme 2). The same additive property was described for the π - π stacking interaction established among DNA base pair tetramers¹⁹.



Scheme 1. Top: Schematic representation of the π - π stacking configurations adopted by the pyridyl groups of neighbouring 4-bpdb ligands in compounds **1** (left), **2** (middle) and **3** (right). Bottom: Tabulated crystallographic parameters; c-c (intercentroid distances, in Å), p-p (interplanar angles, in degrees); hd (horizontal displacement: the distance between the centroids of a pyridyl group and the axis horizontal to the plane containing Py1 and centered on its centroid, in Å); vd (vertical displacement: distance between the centroid of a pyridyl group and the plane containing the neighbouring pyridyl group, in Å).

According to our DFT calculations, dimers 1 and 3, with vertical displacement distances of 3.3 each (Scheme 1), would each account for an interaction energy close to 5.2 kcal/mol. In the same line, dimer 2, a non-parallel pyridine sandwich with a vertical displacement of 3.3 Å (scheme 1), accounts for a destabilization energy of 6.66 kcal/mol. To evaluate the accuracy of our calculations, the additive property of the interaction energy on oligomers of stacked aromatic rings was checked in our system; with that goal in mind the energy of the trimer (dimer 1 + dimer 2) and the tetramer (dimer 1 + dimer 2 + dimer 3) was also calculated at the MP2 level of theory, which revealed a destabilization energy of 11.86 kcal/mol for the former and a destabilization energy of 16.47 kcal/mol for the latter; these values equal the sum of the interaction energies computed for the corresponding constitutive dimers. A mathematical calculation of the average contribution of each dimer on the tetramer in compound **3** would yield a destabilization energy of c.a. 5.5 kcal/mol.



Scheme 2. The total interaction energy in a pyridine oligomer can be approximated as the sum of the interaction energy of each dimer.

In summary, a quantitative analysis of the interaction energy of the differently stacked 4-bpdb dimers in MOFs **1-3** revealed that the mentioned packing forces are in fact destabilizing and, therefore, an aggregation derived signal quenching and/or bathochromic shift should not be expected. In this line, to the best of our knowledge, previously reported signal quenches derived from molecular aggregation provoked by aromatic ring stacking, were all related to packing of single molecules or two-dimensional polymers⁸⁻⁹, which were therefore able to adopt the maximally stabilizing π stacking geometries. Being our systems 3D networks, they lack such a flexibility and are therefore forced to “aggregate” in a manner that is not necessarily linked to favourable π - π stacking interactions.

This apparent key role of the destabilizing π - π stacking interactions on the hypsochromic emission of compounds **1-3** was further confirmed by the analysis of the emissive properties of compounds **4** and **5**, which, in the absence of any stabilizing or destabilizing π - π stacking interaction, showed a traditional bathochromic or red-shifted behaviour. In this sense, the analysis of the crystallographic structure of compound **4**, a cadmium based 2D network of glutarate and 4-bpdb ligands, revealed the absence of any significantly stacked pyridyl dimers. In addition, the bathochromic emission observed for this particular molecular network (518 nm, Figure 6), was shown to be independent from the nature of the dicarboxylic ligand used, as concluded from the analysis of the emission properties of compound **5**, a 2D MOF formed by metal-coordinated 3-methy-glutarate and 4-bpdb ligands. Again, this polymer lacks any p-p stacking interaction between neighbouring

pyridyl rings and, as observed for compound **4**, its emission is also red-shifted (518 nm) with respect to the free 4-bpdb ligand. The absence of destabilizing p-p stacking interactions seems therefore to prevent the hypsochromic effect from happening, while the observed bathochromic luminescence is generally derived from ligand coordination to metals. Metal coordination generally causes a loss of energy through non-radiative pathways, caused by the enhanced “rigidity” of the ligand²⁰. The latter was confirmed by the analysis of the emissive properties of compound **6** (489nm), a metal free 2D H-network of glutaric acid and 4-bpdb ligand. As observed in Figure 6, in the absence of any metal coordination or p-stacking interactions, the maximum emission wavelength stays mainly undisturbed with respect to the free ligand. In addition, it was observed that the latter was not influenced by the electronic and/or geometric properties of the dicarboxylic ligand present, as concluded by the analysis of the emission properties of compound **7** (495 nm), a metal free 2D H-network of adipic acid and 4-bpdb ligand, that, similar to compound **6**, lacks both 4-bpdb ligand coordination to metal and any significant p-stacking interactions between pyridyl rings of neighbouring 4-bpdb ligands.

Conclusions

In summary, we have synthesized and characterized the structural and luminescent properties of five new multidimensional cadmium metal-organic frameworks based on the luminescent 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene linker and flexible dicarboxylate ligands. These MOFs display, in solid state at room temperature, intense and hypsochromic photoluminescence properties when packed as 3D networks, and intense and bathochromic photoluminescence properties when arranged as 2D structures, as compared to the emission properties of the free 4-bpdb ligand. DFT calculations at MP2 level aided in the design of a rational explanation of the interesting luminescent properties encountered. In this line, the establishment of destabilizing π - π stacking interactions between pyridyl groups of neighbouring 4-bpdb ligands (compounds 1-3) was shown to be able to provoke and finely tune the mentioned hypsochromic emission, while metal coordination only, provokes the expected bathochromic behaviours (compounds 4 and 5). Work along this line using other metals and XR measures with pressure are in progress in our lab. We are also working in the use of supercritical activation process to allow the removal of solvent molecules from the compound 1 and evaluate for their ability to selectively retain different organic molecules and, therefore, be potentially developed as advanced materials for the purification of gas mixtures.

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† CCDC 1032668-1032674 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Effect of π - π Stacking Interactions on the Emission Properties of Novel Cadmium Metal-Organic Frameworks Based on 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene.

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Five novel multidimensional cadmium metal-organic frameworks based on the luminescent 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene linker and flexible dicarboxylate ligands have been synthesized by conventional routes. These MOFs show fascinating structures and display, in solid state and room temperature, intense and hypsochromic photoluminescence properties when packed as a 3D network, and bathochromic photoluminescence properties when arranged as 2D networks, as compared to the emission properties of the free luminescent 4-bpdb ligand.

