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**Structural trends in coordination polymers containing
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3 Structural trends in coordination polymers containing perfluorinated dicarboxylates and
4 4,4'-bipyridine
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Abstract

A new family of coordination polymers has been synthesized using cobalt or zinc, 4,4'-bipyridine (4,4'-bpy), and the perfluorinated dicarboxylates tetrafluoroterephthalate (tftpa), tetrafluorophthalate (tfpha), tetrafluoroisophthalate (tfipa), and tetrafluorosuccinate (tfsuc). These materials form under similar conditions and all display similar octahedral metal coordination environments despite significant differences in their structures. Compounds **1**, $M(4,4'\text{-bpy})(\text{tftpa})(\text{H}_2\text{O})_2$ ($M = \text{Co}, \text{Zn}$), and **2**, $M(4,4'\text{-bpy})(\text{tfpha})(\text{H}_2\text{O})_2$ ($M = \text{Co}, \text{Zn}$) are two-dimensional layered structures. Compounds **3**, $\text{Co}(4,4'\text{-bpy})(\text{tfsuc})(\text{H}_2\text{O})_2$ and **4**, $M(4,4'\text{-bpy})(\text{tfipa})(\text{H}_2\text{O})_2$ ($M = \text{Co}, \text{Zn}$) display three-dimensional connectivity built up from two types of interconnected chains.

Keywords: Coordination polymers, perfluorinated ligands, structure trends, 4,4'-bipyridine

Introduction

The field of inorganic-organic framework materials has seen rapid growth over the past two decades in response to their interesting catalytic [1], gas storage [2-4], and optical properties [5]. Structures containing many types of coordinating organic molecules have been synthesized [6], but the use of perfluorinated molecules or even partially-fluorinated molecules as ligands has been largely ignored to date. Recently, reports by ourselves and Omary have indicated that porous materials containing exposed fluorine atoms display interesting hydrogen storage properties [7-9]. There have also been examples of interesting luminescence and catalytic properties in lanthanide materials containing large trifluoromethyl-substituted ligands [10-13]. In light of these promising results, we are continuing to investigate materials incorporating perfluorinated dicarboxylates.

As with most other classes of ligands used in the synthesis of hybrid framework materials, perfluorinated ligands can be used to make a diverse and interesting range of structures [7-9, 14-20]. We have found that a second, non-fluorinated ligand is usually necessary to facilitate the incorporation of perfluorinated dicarboxylates into hybrid structures. We have previously reported structures containing triazole [9], imidazole [19],

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3 and 2,2'-bipyridine [20] as second ligands, and herein extend this work to include
4 materials using 4,4'-bipyridine (4,4'-bpy). The 4,4'-bpy molecule has been extensively
5 utilized in hybrid synthesis for its ability to increase dimensionality as a bridging ligand
6 [21-23]. We report seven new materials using Co^{2+} and Zn^{2+} in conjunction with 4,4'-bpy
7 and the perfluorinated dicarboxylates tetrafluoroterephthalate (tftpa), tetrafluorophthalate
8 (tfpha), tetrafluorosuccinate (tfsuc), and tetrafluoroisophthalate (tfipa). All of these
9 materials contain similar octahedral metal coordination environments and yet display
10 significantly different structures due to the differences in bridging angles in the
11 dicarboxylates.
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20 21 Results and Discussion

22 **Structure of $M(4,4'\text{-bpy})(\text{tftpa})(\text{H}_2\text{O})$, ($M = \text{Co}, \text{Zn}$), **1**.** The structure of **1** contains a
23 single unique cobalt atom octahedrally coordinated to two water molecules (Co-O
24 distance 2.120(5) Å), two 4,4'-bpy ligands (Co-N distances 2.148(8) Å and 2.157(8) Å),
25 and two tftpa ligands (Co-O distance 2.094(5) Å). The pairs of ligands are all *trans* to
26 each other across the metal center, forming the overall two-dimensional coordination
27 polymer with the 4,4'-bpy and tftpa ligands serving as linear linkers between cobalt
28 atoms (Figure 1). The two water molecules prevent connectivity between the layers
29 (Figure 2). The layers are oriented perpendicular to the *b*-axis and exhibit ABAB
30 stacking. Because of the large open window in each layer, the closest layer-layer
31 interactions are actually from one layer to the second layer above it, as the coordinated
32 water molecule and unbound carboxylate oxygen atom point directly into this window
33 towards that of the next "A" layer. This allows for a hydrogen bonding interaction
34 between the water molecule and the unbound carboxylate oxygen atom from two layers
35 above (O-H...O distance 2.876(10) Å). Reactions were attempted at higher temperatures
36 (up to 150 °C) with the aim of reducing the water content and potentially increasing the
37 dimensionality of **1**, but these reactions were unsuccessful due to decomposition of the
38 fluorinated ligand.
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3 **Structure of $M(4,4'$ -bpy)(tfpha)(H_2O)₂ ($M = Co, Zn$), **2**.** The structure of **2** also contains
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5 octahedrally coordinated metal centers with *trans* pairs of water molecules, 4,4'-bpy
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7 ligands, and singly coordinated carboxylate groups from tfpha ligands (Zn-O_{water} distance
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9 2.099(3) Å, Zn-O_{tfpha} distance 2.122(3) Å, Zn-N distances 2.190(4) Å and 2.213(4) Å).
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11 The 4,4'-bpy ligands act as linear linkers between metal atoms, as seen in **1**. The tfpha
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13 ligands also serve as linear linkers between metal atoms, but the two carboxylate groups
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15 on the ligand only extend coordination along the *a*-axis. This results in another two-
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17 dimensional coordination polymer, as the water molecules prevent connectivity between
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19 the layers (Figure 3). The layers are held together by a hydrogen bonding interaction
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21 between the unbound carboxylates oxygen atom on the tfpha ligand and the coordinated
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23 water molecule on the next layer (O-H ··· O distance 2.745(4) Å). The layers stack in an
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25 ABAB manner much like in **1**. As seen with **1**, efforts to increase the dimensionality of **2**
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27 by performing reactions at higher temperatures led to decomposition of the fluorinated
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29 ligand.
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41 **Structure of $Co(4,4'$ -bpy)(tfsuc)(H_2O)₂, **3**.** Like the previous materials, the structure of **3**
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43 is built up from octahedral cobalt centers with *trans* pairs of water molecules, 4,4'-bpy
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45 ligands, and the fluorinated ligand, in this case tfsuc (Co-O_{water} distance 2.104(3) Å; Co-
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47 O_{tfsuc} distance 2.122(3) Å; Co-N distance 2.129(3) Å). There are two types of one-
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49 dimensional chains in **3**; one involving the Co-4,4'-bpy connectivity, and the other
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51 involving the Co-tfsuc connectivity (Figure 4). There are two sets of 4,4'-bpy-containing
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53 chains, both existing perpendicular to the *c*-axis. One chain lies at approximately $c = \frac{1}{2}$
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55 (horizontal chains in left of Figure 4) and the other at $c = 0$, such that they are canted at
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57 an angle of approximately 62° to each other (angled chains in left of Figure 4). The Co-
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59 tfsuc chains (Middle, Figure 4) follow a zig-zag path perpendicular to the *b*-axis and
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3 between the *a* and *c* axes. All the Co-tfsuc chains run parallel to each other. These chains
4 link the two types of 4,4'-bpy chains together and complete the three-dimensional
5 connectivity of **3** (Right, Figure 4).
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12 **Structure of $M(4,4'\text{-bpy})(\text{tfipa})(\text{H}_2\text{O})_2$ ($M = \text{Co}, \text{Zn}$), **4**.** Compound **4** contains a similar
13 structure to that of **3**. The zinc atom is also octahedrally coordinated to *trans* pairs of
14 water molecules, 4,4'-bpy ligands, and tfipa ligands (Zn-O_{water} distance 2.150(4) Å; Zn-
15 O_{tfipa} distance 2.124(3) Å; Zn-N distance 2.126(4) Å). There are again two different one
16 dimensional chains; one linear M-4,4'-bpy chain and one zig-zag M-tfipa chain. As with
17 **3**, there are two orientations of the M-4,4'-bpy chains; however, in **4** the angle between
18 the chain at $c = 0$ and $c = \frac{1}{2}$ is approximately 90° (Left, Figure 5). Also as in **4**, the M-
19 tfipa chains run perpendicular to the *b*-axis (Middle, Figure 5), and link together the two
20 orientations of M-4,4'-bpy chains to form the overall 3-D structure (Right, Figure 5).
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30 31 32 **Comparison of structures**

33 All the structures presented above contain the same octahedral metal coordination
34 environment with *trans* pairs of 4,4'-bpy, dicarboxylate, and water ligands. They can all
35 be described as having two types of chains connected through the metal atom. One chain
36 involves the 4,4'-bpy ligands and is linear in all the structures. In **1** and **2**, there is only
37 one orientation of these chains, whereas in **3** and **4** there are two different orientations of
38 the same unique chain. The second chain involves the dicarboxylates and is also linear in
39 all the structures, but those in **3** and **4** follow a zig-zag pattern down the chain axis. The
40 dimensionality of these structures can be directly related to the metal-dicarboxylate-metal
41 bridging angles seen in these chains. These angles have been calculated using the
42 midpoint of the two carboxylate carbon atoms. In **1** and **2**, this angle is approximately
43 linear (180° and 175° respectively), and these chains run perpendicular to the M-4,4'-bpy
44 chains, resulting in two-dimensional coordination polymers. In **3** and **4**, these angles are
45 124° and 137°, respectively, which allows these chains to intersect the two different
46 orientations of M-4,4'-bpy chains and achieve three-dimensional connectivity.
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5 There have been a number of studies reporting differences in families of materials based
6 on phthalate, isophthalate, and terephthalate with second ligands [24-29], but none of
7 these families display identical metal coordination environments regardless of the
8 dicarboxylate isomer, as seen in **1-4**. In most of these reports, dimensionality tends to
9 increase from phthalate to isophthalate to terephthalate. These materials also tend to
10 involve multi-dentate coordination through the carboxylate groups to form double chains
11 or dimeric units, which is not seen in **1-4**. When comparing the specific structures to
12 previous reports with their non-fluorinated analogs and 4,4'-bpy, we find that compound **2**
13 is analogous to a previously reported phase [26]. To our knowledge this is the first hybrid
14 framework material where the perfluorinated carboxylate forms a similar structure to that
15 of its non-fluorinated analog. There are two isomorphous structures containing succinate
16 and 4,4'-bpy that are similar to **3**; however, these structures have three orientations of M-
17 4,4'-bpy chains and helical M-succinate-M chains connecting them [30-31].
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30 **Conclusion**

31 We have extended our family of coordination polymers containing perfluorinated
32 dicarboxylates to include the seven new materials presented here with 4,4'-bipyridine as
33 a co-ligand. All these materials contain similar octahedral metal coordination
34 environments, yet display vastly different structure types. For the first time, we have
35 synthesized a material analogous to a structure containing the non-fluorinated analog of
36 one of these dicarboxylates. It is also clear that the diversity of phases obtained using
37 perfluorinated ligands demands that these ligands continue to be investigated in hybrid
38 synthesis.
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48 **Experimental Section**

49 The chemicals used in the synthesis of all compounds ($\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$,
50 $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, tetrafluoroterephthalic acid, tetrafluorophthalic acid,
51 tetrafluorosuccinic acid, tetrafluoroisophthalic acid, and 4,4'-bipyridine) were all used as
52 received from Aldrich.
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4 **Synthesis of $M(4,4'$ -bpy)(tftpa)(H₂O)₂ ($M = Co, Zn$), 1.** A mixture of 0.1 mmol
5 Co(CH₃CO₂)₂ • 4H₂O or Zn(CH₃CO₂)₂, 0.1 mmol tetrafluoroterephthalic acid, 0.1 mmol
6 4,4'-bipyridine, and 3 mL H₂O was heated in a 23 mL Teflon-lined Parr autoclave at 100
7 °C for 24 h. The resulting solids were isolated by filtration, washed with water and
8 acetone, and dried in air. Elemental analysis was carried out by the Marine Sciences
9 Institute Analytical Laboratory at UCSB. Anal. found for Co analog (wt %): C, 44.2; H,
10 2.53; N, 5.75. Calculated (wt %): C, 44.4; H, 2.48; N, 5.75. Anal. found for Zn analog
11 (wt %): C, 43.8; H, 2.50; N, 5.71. Calculated (wt %): C, 43.8; H, 2.45; N, 5.67.
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19 **Synthesis of $M(4,4'$ -bpy)(tfpha)(H₂O)₂ ($M = Co, Zn$), 2.** A mixture of 0.1 mmol
20 Co(CH₃CO₂)₂ • 4H₂O or Zn(CH₃CO₂)₂, 0.1 mmol tetrafluorophthalic acid, 0.1 mmol
21 4,4'-bipyridine, and 3 mL H₂O was heated in a 23 mL Teflon-lined Parr autoclave at 100
22 °C for 24 h. The resulting solids were isolated by filtration, washed with water and
23 acetone, and dried in air. Anal. found for Co analog (wt %): C, 44.3; H, 2.29; N, 5.86.
24 Calculated (wt %): C, 44.4; H, 2.48; N, 5.75. Anal. found for Zn analog (wt %): C, 44.0;
25 H, 2.54; N, 5.64. Calculated (wt %): C, 43.8; H, 2.45; N, 5.67.
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33 **Synthesis of $Co(4,4'$ -bpy)(tfsuc)(H₂O)₂, 3.** A mixture of 0.1 mmol Co(CH₃CO₂)₂ • 4H₂O,
34 0.1 mmol tetrafluorosuccinic acid, 0.1 mmol 4,4'-bipyridine, and 3 mL H₂O was heated
35 in a 23 mL Teflon-lined Parr autoclave at 100 °C for 24 h. The resulting solids were
36 isolated by filtration, washed with water and acetone, and dried in air. Anal. found (wt
37 %): C, 38.3; H, 2.82; N, 6.29. Calculated (wt %): C, 38.3; H, 2.75; N, 6.38.
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44 **Synthesis of $M(4,4'$ -bpy)(tfipa)(H₂O)₂ ($M = Co, Zn$), 4.** A mixture of 0.1 mmol
45 Co(CH₃CO₂)₂ • 4H₂O or Zn(CH₃CO₂)₂, 0.1 mmol tetrafluoroisophthalic acid, 0.1 mmol
46 4,4'-bipyridine, and 3 mL H₂O was heated in a 23 mL Teflon-lined Parr autoclave at 100
47 °C for 24 h. The resulting solids were isolated by filtration, washed with water and
48 acetone, and dried in air. Anal. found for Co analog (wt %): C, 44.4; H, 2.56; N, 5.86.
49 Calculated (wt %): C, 44.4; H, 2.48; N, 5.75. Anal. found for Zn analog (wt %): C, 43.8;
50 H, 2.37; N, 5.73. Calculated (wt %): C, 43.8; H, 2.45; N, 5.67.
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Structure determination

Structures **1-4** were determined using single crystal X-ray diffraction. Data were collected on a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$) operating at 45 kV and 35 mA. Suitable single crystals were selected under a polarizing microscope and glued to a glass fiber. A hemisphere of intensity data was collected at room temperature.

Absorption corrections were made using SADABS [32]. All structures were then solved by direct methods and difference Fourier synthesis and were refined against $|F|^2$ using the SHELXTL software package [33]. The relevant details of structure determination are shown in Table 1. All extinction coefficients refined to within three esd's of zero and were therefore removed from the refinement. Non-hydrogen atoms were refined anisotropically. Riding hydrogens were assigned to the carbon atoms on the 4,4'-bpy ligands. Hydrogen atoms on the water molecules in were found in the Fourier difference map and were refined isotropically. CCDC 737133-737139 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 1. Crystal data and refinement parameters for **1-4**.

	1-Co	1-Zn	2-Co
Formula	CoC ₁₈ H ₁₂ F ₄ N ₂ O ₆	ZnC ₁₈ H ₁₂ F ₄ N ₂ O ₆	CoC ₁₈ H ₁₂ F ₄ N ₂ O ₆
Molecular Weight	487.23	493.69	487.23
Crystal System	Monoclinic	Monoclinic	Orthorhombic
Space Group	<i>C2/c</i>	<i>C2/c</i>	<i>Pccn</i>
<i>a</i> / \AA	11.632(3)	11.632(5)	7.4994(6)
<i>b</i> / \AA	11.421(3)	11.374(5)	10.6535(9)
<i>c</i> / \AA	14.269(4)	14.303(7)	22.9116(19)
β	109.656(6) $^\circ$	109.979(7) $^\circ$	90
<i>V</i> / \AA^3	1785.3(8)	1778.6(14)	1830.5(3)
<i>Z</i>	4	4	4

$\rho/\text{g cm}^{-3}$	1.813	1.844	1.768
μ/mm^{-1}	1.045	1.465	1.019
2θ range collected	5.16-49.42°	5.16-51.36°	3.56-51.34°
Data/restraints/parameters	1539 / 4 / 151	1681 / 4 / 151	1738 / 2 / 155
R_{int}	0.1092	0.1262	0.0629
$R_1, wR_2 (I > 2\sigma(I))$	0.0678, 0.1613	0.0780, 0.1548	0.0588, 0.1268
R (all data)	0.1194, 0.1908	0.1345, 0.1826	0.0822, 0.1382

	2-Zn	3	4-Co
Formula	ZnC ₁₈ H ₁₂ F ₄ N ₂ O ₆	CoC ₁₄ H ₁₂ F ₄ N ₂ O ₆	CoC ₁₈ H ₁₂ F ₄ N ₂ O ₆
Molecular Weight	493.69	439.19	487.23
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group	<i>Pccn</i>	<i>C2/c</i>	<i>C2/c</i>
$a/\text{Å}$	7.575(7)	11.6719(15)	15.871(5)
$b/\text{Å}$	10.760(11)	19.364(2)	16.217(5)
$c/\text{Å}$	23.042(17)	6.9849(10)	7.168(2)
β	90	90.326(3)°	100.910(5)°
$V/\text{Å}^3$	1878(3)	1578.7(3)	1811.4(10)
Z	4	4	4
$\rho/\text{g cm}^{-3}$	1.746	1.848	1.787
μ/mm^{-1}	1.388	1.170	1.030
2θ range collected	3.54-52.72°	4.08-52.74°	3.62-52.70°
Data/restraints/parameters	1928 / 4 / 155	1600 / 10 / 148	1829 / 3 / 156
R_{int}	0.0882	0.0612	0.0553
$R_1, wR_2 (I > 2\sigma(I))$	0.0472, 0.0942	0.0513, 0.1238	0.0771, 0.1579
R (all data)	0.0859, 0.1052	0.0843, 0.1424	0.1136, 0.1754

	4-Zn
Formula	ZnC ₁₈ H ₁₂ F ₄ N ₂ O ₆
Molecular Weight	493.69
Crystal System	Monoclinic
Space Group	<i>C2/c</i>
<i>a</i> /Å	15.941(2)
<i>b</i> /Å	16.076(2)
<i>c</i> /Å	7.2110(10)
β	101.171(4) [°]
<i>V</i> /Å ³	1812.9(4)
<i>Z</i>	4
ρ /g cm ⁻³	1.809
μ /mm ⁻¹	1.437
2 θ range collected	3.64-52.74 [°]
Data/restraints/parameters	1816 / 4 / 152
<i>R</i> _{int}	0.0648
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0641, 0.1441
<i>R</i> (all data)	0.1104, 0.1648

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Figure Captions

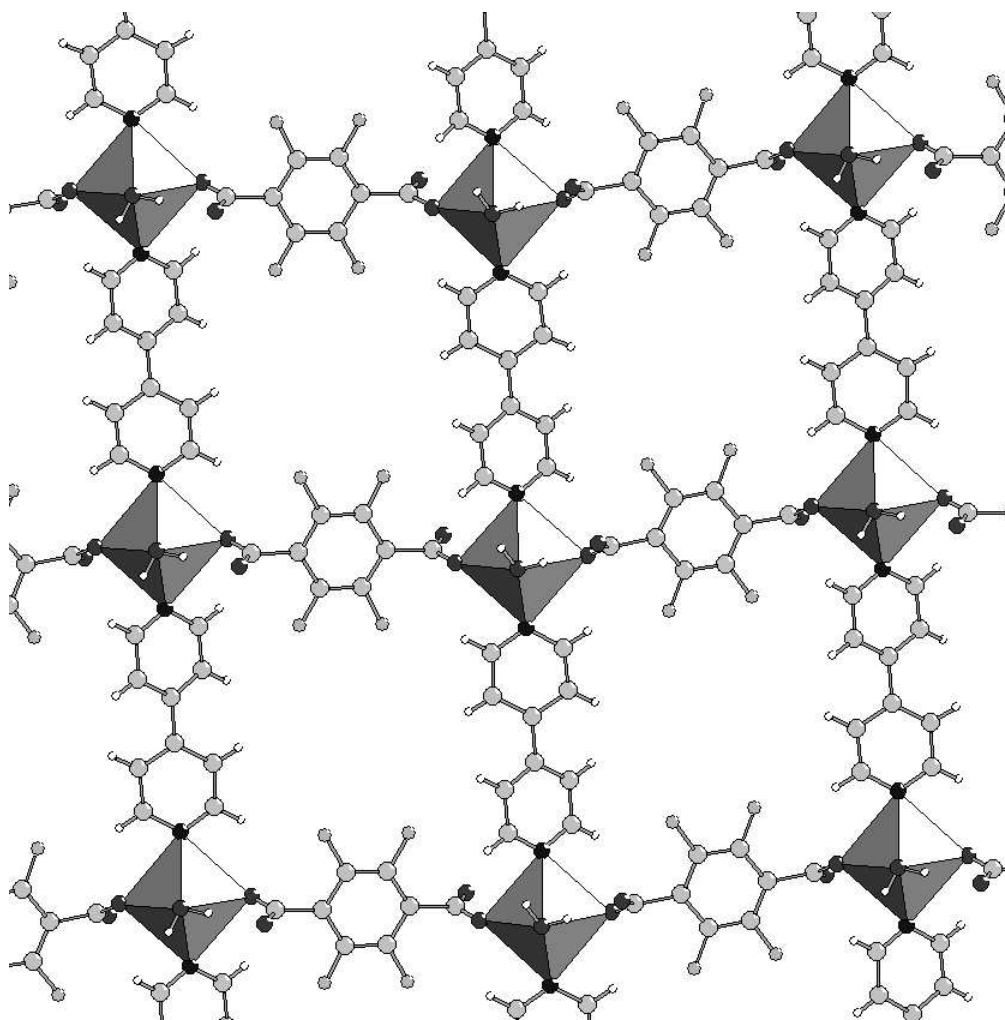
Figure 1. View of single layer of **1** from above, towards *b*-axis.

Figure 2. Layer packing in **1**, viewed down the *b*-axis.

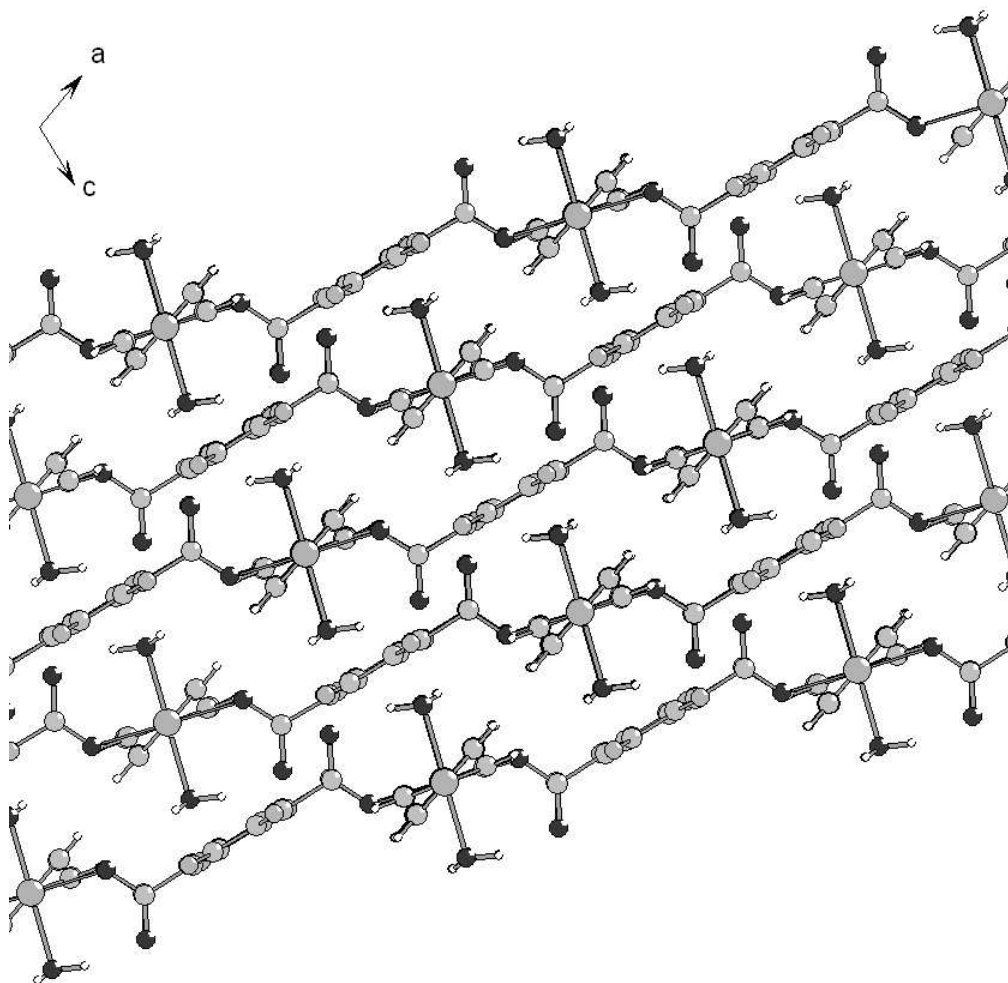
Figure 3. Single layer view of **2** down *b*-axis.

Figure 4. Left: View of **3** down *c*-axis showing only Co-4,4'-bpy connectivity. Middle: Same view of **3** showing only Co-tfsuc connectivity. Right: Simplified picture of **3**; pink and blue lines represent Co-4,4'-bpy chains; green lines represent Co-tfsuc chains; black line is one Co-tfsuc chain showing extension of the chain down the *c*-axis to complete three-dimensional connectivity.

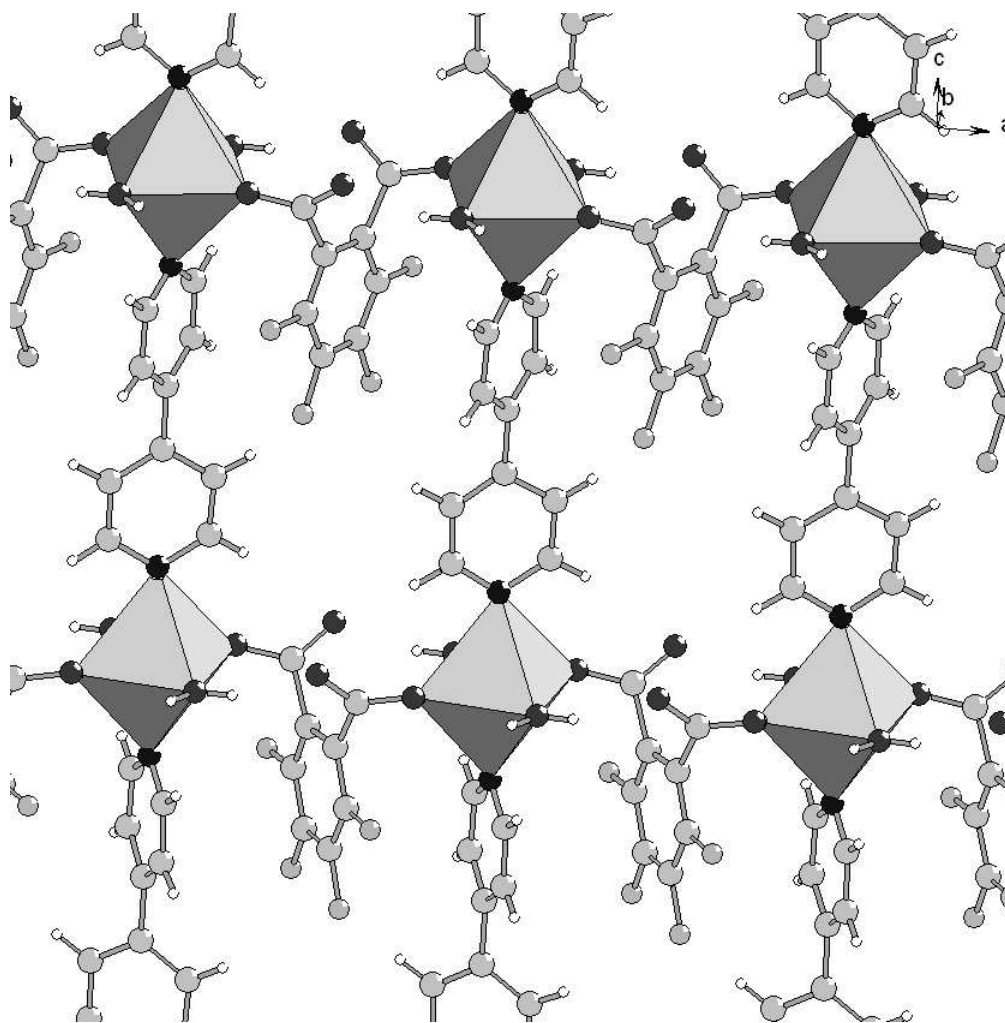
Figure 5. Left: View of **4** down *c*-axis showing only M-4,4'-bpy connectivity. Middle: View of **4** showing only M-tfipa connectivity, with independent chains in different shades of green. Right: Simplified picture of **4**; pink and blue lines represent M-4,4'-bpy chains; green lines represent M-tfipa chains; black line is one M-tfipa chain showing extension of the chain down the *c*-axis to complete three-dimensional connectivity.



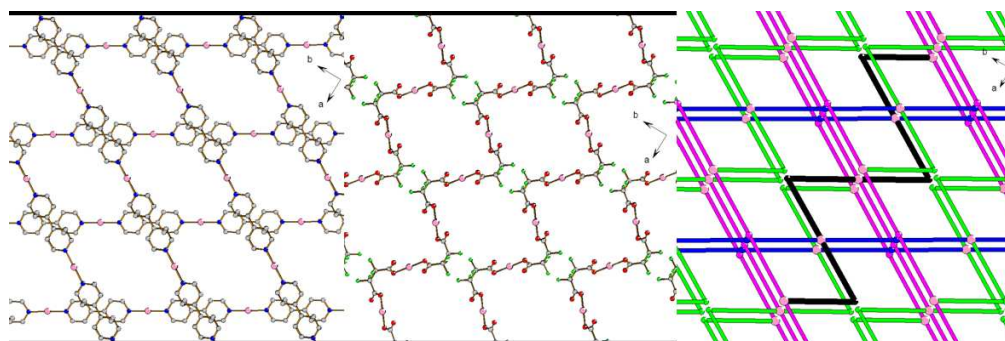
220x222mm (96 x 96 DPI)



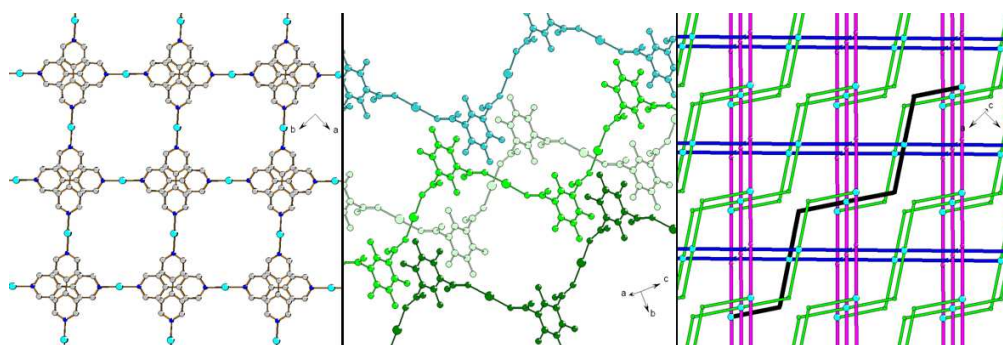
220x222mm (96 x 96 DPI)



220x222mm (96 x 96 DPI)



198x66mm (150 x 150 DPI)



199x66mm (150 x 150 DPI)