Supplementary Information

The Ubiquitous Paddle-Wheel Building Block in a Two-dimensional Coordination Polymer with Square Grid Structure

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Table S1. π - π Interaction in **1**, [Zn-BDC-Py].

π - π Interaction:				
Cg(I)...Cg(J)	d[Cg(I)...Cg(J)]Å	β -angle (°)	Symmetry code	Slippage
Cg(1)...Cg(1)	3.7476(3)	22.8	1-x,-y,-z	1.453
Cg(1)...Cg(2)	3.8951(4)	10.3	1-x,-1/2+y,1/2-z	
Cg(2)...Cg(1)	3.8951(2)	30.9	1-x,1/2+y,1/2-z	
β -angle = angle between Cg(I)-Cg(J) or Cg(I)->Me vector and normal to plane I. Centroid: Cg(1) = N(1)-C(9)-C(10)-C(11)-C(12)-C(13). Cg(2) = C(1)-C(2)-C(3)-C(4)-C(5)-C(6). Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Å).				

Table S2. Hydrogen bonds for **1**, [Zn-BDC-Py] [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle$ (DHA)
C(2)-H(2A)...O(4)#6	0.93	2.55	3.470(2)	171.8
C(5)-H(5A)...O(2)#7	0.93	2.59	3.5112(19)	172.2
C(9)-H(9A)...O(2)#8	0.93	2.54	3.405(2)	154.8

Symmetry transformations used to generate equivalent atoms:

#6 x,-y+3/2,z-1/2 ; #7 x,-y+3/2,z+1/2; #8 x-1,y,z

Table S3. π - π interaction in **2**, [Co-BDC-Py].

π - π Interaction:				
Cg(I)...Cg(J)	d[Cg(I)...Cg(J)]Å	β -angle (°)	Symmetry code	Slippage
Cg(1)...Cg(1)	3.7199(5)	21.5	1-x,-y,-z	1.499
Cg(1)...Cg(2)	3.9255(5)	10.7	1-x,-1/2+y,1/2-z	
Cg(2)...Cg(1)	3.9255(5)	32.3	1-x,1/2+y,1/2-z	
β -angle = angle between Cg(I)-Cg(J) vector and normal to plane I. Centroid: Cg(1) = N(1)-C(9)-C(10)-C(11)-C(12)-C(13). Cg(2) = C(1)-C(2)-C(3)-C(4)-C(5)-C(6). Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Å).				

Table S4. Hydrogen bonds for **2**, [Co-BDC-Py] [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle$ (DHA)
C(2)-H(2A)...O(4)#6	0.93	2.49	3.410(4)	173.5
C(5)-H(5A)...O(2)#7	0.93	2.51	3.433(4)	174.2
C(9)-H(9A)...O(2)#8	0.93	2.53	3.390(4)	154.9
C(13)-H(13A)...O(3)#3(Intra)	0.93	2.53	3.085(5)	117.7

Symmetry transformations used to generate equivalent atoms:

#3 -x+2,y-1/2,-z+1/2 ; #6 x,-y+3/2,z-1/2 ; #7 x,-y+3/2,z+1/2; #8 x-1,y,z

Table S5. π - π interaction in **3**, [Co-BDC-Mim]

π - π Interaction:				
Cg(I)...Cg(J)	d[Cg(I)...Cg(J)] Å	β -angle (°)	Symmetry code	Slippage
Cg(1)...Cg(1)	3.8747(10)	23.8	1-x,-y,-z	1.417
Cg(1)...Cg(2)	4.1219(11)	19.7	1-x,-1/2+y,1/2-z	
Cg(2)...Cg(1)	4.1219(11)	37.6	1-x,1/2+y,1/2-z	
β -angle = angle between Cg(I)-Cg(J) vector and normal to plane I. Centroid: Cg(1) = N(1)-C(9)-C(10)-C(11)-N(2)-C(11). Cg(2) = C(1)-C(2)-C(3)-C(4)-C(5)-C(6). Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Å).				

Table S6. Hydrogen bonds for **4**, [Cu-BDC-DMF] [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle$ (DHA)
C(5)-H(5A)...O(2)#6	0.93	2.53	3.355(4)	148.6
C(9)-H(9A)...O(1)	0.93	2.38	3.016(4)	125.2
C(11)-H(11A)...O(5)	0.96	2.38	2.791(6)	105.1

Symmetry transformations used to generate equivalent atoms:

#6 x,-y+1/2,z-1/2

Table S7. Hydrogen bonds for **5**, [Zn-BDC-DMF] [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle$ (DHA)
C(5)-H(5A)...O(2)#6	0.93	2.53	3.327(3)	143.3
C(9)-H(9A)...O(1)	0.93	2.38	3.007(3)	124.7
C(11)-H(11A)...O(5)	0.96	2.35	2.767(4)	105.3

Symmetry transformations used to generate equivalent atoms:

#6 x,-y+1/2,z-1/2

Table S8. CH... π interaction in **6**, [Zn-AmBDC-DMF].

CH... π Interaction:					
X-H...Cg(J)	d(H...Cg) Å	γ -angle (°)	X-H...Cg (°)	X...Cg Å	Symmetry code
C(6)-H(6C)...Cg(1)	2.86	23.27	142	3.6646(6)	x,y,-1+z
C(6)-H(6C)...Cg(1)	2.86	23.27	142	3.6646(6)	1/2-x,1/2-y,-z
Cg(J) = center of gravity of ring J; γ -angle = angle between Cg-H vector and ring J normal. Centroid: Cg(1) = C(2)-C(3)-C(4)'-C(2)'-C(3)'-C(4).					

Table S9. Hydrogen bonds for **6**, [Zn-AmBDC-DMF] [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1A)...O(2)#1	0.86	2.45	3.32937(5)	165
N(1)-H(1B)...O(1) (intra)	0.86	2.09	2.7109(4)	128
C(5)-H(5)...O(1) (intra)	0.96	2.60	3.3430(5)	135
C(6)-H(6A)...N(1)#2	0.96	2.60	3.0011(5)	105
C(6)-H(6B)...N(2)#2	0.96	2.33	3.1456(5)	143

Symmetry transformations used to generate equivalent atoms:

#2= 1-x, y, -z; #1= 1/2+x, -1/2-y, -z

Table S10. Dihedral angle θ between the benzene ring and carboxylate group of BDC moiety in the paddle wheel structure.

MOFs	Dihedral angle ($^\circ$)		Reference
	θ_1	θ_2	
1	19.7	22.9	This work
2	19.9	23.8	This work
3	19.1	22.9	This work
4	23.5	26.3	This work
5	23.1	25.6	This work
6	25.6	25.6	This work
MOF-2	5.5	5.5	Yaghi <i>et. al.</i> Chem Commun 2001, 2532
MOF- 46	25	25	Yaghi <i>et. al.</i> Chem Commun 2001, 2532

Structure of **2**:

Figure S1. Structure of $[\text{Co}(\text{BDC})(\text{Py})](\mathbf{2})$. (a) Asymmetric unit of $\mathbf{2}$ at 50% probability level. (b) Paddle-wheel coordination unit of $\mathbf{2}$ and (c) 2-D polymeric arrangement viewed along the c -direction. Color codes - cobalt: green; nitrogen: blue; oxygen: red and carbon: dark grey. Hydrogens are omitted from (b) and (c) for clarity.

Fig S2. Space-filled model showing 3D supramolecular array in isostructural **1** or **2** showing 1-D channel viewed towards $(\bar{6} \ 1 \ 10)$ plane.

Structure of **5**:

Figure S3: Structure of $[\text{Zn}(\text{BDC})(\text{DMF})]$ (**5**). (a) Asymmetric unit of **5** shown at 50% probability level. (b) Paddle-wheeled coordination unit of **5** and (c) 2D polymeric arrangement viewed along c -directions. Color code; zinc: turquoise; nitrogen: blue; oxygen: red and carbon; dark grey. Hydrogen atoms are omitted from (b) and (c) for clarity.