Supplementary Information

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

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Table of Contents:

| Sl. No | Contents                                                                 | Page No. |
|-------|--------------------------------------------------------------------------|----------|
| 1     | Table S1. π-π Interaction in 1                                             | S2       |
| 2     | Table S2. Hydrogen bonds for 1                                             | S2       |
| 3     | Table S3. π-π Interaction in 2                                             | S2       |
| 4     | Table S4. Hydrogen bonds for 2                                             | S2       |
| 5     | Table S5. π-π Interaction in 3                                             | S3       |
| 6     | Table S6. Hydrogen bonds for 4                                             | S3       |
| 7     | Table S7. Hydrogen bonds for 5                                             | S3       |
| 8     | Table S8. CH…π Interaction in 6                                            | S3       |
| 9     | Table S9. Hydrogen bonds for 6                                             | S4       |
| 10    | Table S10. Dihedral angle θ between the benzene ring and carboxylate group of BDC moiety in the paddle wheel structure of 1 – 6. | S4       |
| 10    | Figure S1. Structure of [Co(BDC)(Py)](2).                                 | S5       |
| 11    | Figure S2. Space filled model for 1 showing 1-D channels                  | S6       |
| 12    | Figure S3. Structure of [Zn(BDC)(DMF)] (5).                               | S6       |
Table S1. π-π Interaction in 1, [Zn-BDC-Py].

| 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) | <(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].

| 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) | <(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]

| 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) | <(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) | <(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].

| X-H…Cg(J)       | d(H…Cg) \(\text{Å}\) | γ-angle \(^{\circ}\) | X-H…Cg \(^{\circ}\) | X…Cg \(\text{Å}\) | 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).

53
Table S9. Hydrogen bonds for 6, [Zn-AmBDC-DMF] [Å and °].

| D-H...A       | d(D-H) | d(H...A) | d(D...A) | <(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 (°) | Reference                  |
|----------|--------------------|----------------------------|
|          | θ₁                | θ₂                        |
| 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 et. al. Chem Commun 2001, 2532 |
| MOF-46   | 25                 | 25                        | Yaghi et. al. Chem Commun 2001, 2532 |
Structure of 2:

Figure S1. Structure of [Co(BDC)(Py)](2). (a) Asymmetric unit of 2 at 50% probability level. (b) Paddle-wheeled coordination unit of 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 (6 1 10) plane.

Structure of 5:

Figure S3: Structure of [Zn(BDC)(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.