From 1D to 2D Cd(II) and Zn(II) Coordination Networks by Replacing Monocarboxylate with Dicarboxylates in Partnership with Azine Ligands: Synthesis, Crystal Structures, Inclusion, and Emission Properties

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Table S1. Bond lengths [Å] and angles [°] for 1-8

|   |  |   |
|---|---|---|
| Cd(1)-N(5)#1 | Cd(1)-O(2) | Cd(1)-N(6) |
| Cd(1)-N(2) | 2.340(3) | 2.391(3) |
| Cd(1)-O(1) | 2.348(3) | 2.398(3) |
| Cd(1)-N(6)#1 | 2.316(6) | 2.332(6) |
| Cd(1)-O(1) | 2.316(5) | 2.332(6) |
| Cd(1)-N(3) | 2.303(6) | 2.322(5) |
| Cd(1)-N(6)#1 | 2.316(6) | 2.332(6) |
| Cd(1)-O(1) | 2.316(5) | 2.336(5) |

Symmetry transformations used to generate equivalent atoms: #1 x, y, z-1
| Bond                  | Length  | Bond                  | Length  |
|----------------------|---------|----------------------|---------|
| Cd(1)-O(3)           | 2.323(5)| Cd(2)-N(10)          | 2.354(6) |
| Cd(1)-O(4)#2         | 2.378(5)| Cd(2)-O(6)#3         | 2.416(6) |
| Cd(1)-O(2)           | 2.465(6)| Cd(2)-O(7)           | 2.448(7) |
| Cd(1)-O(4)           | 2.580(5)| Cd(2)-O(6)           | 2.542(6) |
| N(3)-Cd(1)-N(6)#1    | 174.4(2)| N(9)-Cd(2)-O(8)      | 97.3(2)  |
| N(3)-Cd(1)-O(1)      | 93.5(2) | N(9)-Cd(2)-O(5)      | 92.8(2)  |
| N(6)#1-Cd(1)-O(1)    | 89.9(2) | O(8)-Cd(2)-O(5)      | 140.3(2) |
| N(3)-Cd(1)-O(3)      | 90.2(2) | N(9)-Cd(2)-N(10)     | 173.5(2) |
| N(6)#1-Cd(1)-O(3)    | 90.1(2) | O(8)-Cd(2)-N(10)     | 83.6(2)  |
| O(1)-Cd(1)-O(3)      | 139.5(2)| O(5)-Cd(2)-N(10)     | 90.5(2)  |
| N(3)-Cd(1)-O(4)#2    | 85.4(2) | N(9)-Cd(2)-O(6)#3    | 84.9(2)  |
| N(6)#1-Cd(1)-O(4)#2  | 90.1(2) | O(8)-Cd(2)-O(6)#3    | 89.4(2)  |
| O(1)-Cd(1)-O(4)#2    | 91.62(19)| O(5)-Cd(2)-O(6)#3    | 129.8(2) |
| O(3)-Cd(1)-O(4)#2    | 128.88(19)| N(10)-Cd(2)-O(6)#3   | 88.7(2)  |
| O(2)-Cd(1)-O(4)      | 137.41(18)| N(9)-Cd(2)-O(7)      | 94.0(2)  |
| N(3)-Cd(1)-O(2)      | 91.7(2) | O(8)-Cd(2)-O(7)      | 54.0(2)  |
| N(6)#1-Cd(1)-O(2)    | 93.9(2) | O(5)-Cd(2)-O(7)      | 87.2(2)  |
| O(1)-Cd(1)-O(2)      | 53.86(19)| N(10)-Cd(2)-O(7)     | 91.7(2)  |
| O(3)-Cd(1)-O(2)      | 85.75(19)| O(6)#3-Cd(2)-O(7)    | 143.0(2) |
| O(4)#2-Cd(1)-O(2)    | 145.17(19)| N(9)-Cd(2)-O(6)      | 86.58(19) |
| N(3)-Cd(1)-O(4)      | 81.45(19)| O(8)-Cd(2)-O(6)      | 165.2(2) |
| N(6)#1-Cd(1)-O(4)    | 94.33(19)| O(5)-Cd(2)-O(6)      | 53.12(19) |
| O(1)-Cd(1)-O(4)      | 167.37(19)| N(10)-Cd(2)-O(6)    | 91.0(2)  |
| O(3)-Cd(1)-O(4)      | 52.54(18)| O(6)#3-Cd(2)-O(6)    | 76.70(19) |
| O(4)#2-Cd(1)-O(4)    | 76.49(18)| O(7)-Cd(2)-O(6)      | 140.3(2) |

Symmetry transformations used to generate equivalent atoms: #1 x, y-1, z; #2 2-x, -y, 1-z; #3 1-x, 1-y, 2-z

| Bond                  | Length  | Bond                  | Length  |
|----------------------|---------|----------------------|---------|
| Cd(1)-O(3)#1         | 2.331(4)| Cd(1)-O(1)           | 2.384(4) |
| Cd(1)-N(4)#2         | 2.336(4)| Cd(1)-O(4)#3         | 2.416(3) |
| Cd(1)-N(1)           | 2.348(4)| Cd(1)-O(3)#3         | 2.466(4) |
| Cd(1)-O(2)           | 2.361(4)|                     |         |
| O(3)#1-Cd(1)-N(4)#2  | 89.57(13)| O(2)-Cd(1)-O(1)     | 54.84(13) |
| O(3)#1-Cd(1)-N(1)    | 89.92(13)| O(3)#1-Cd(1)-O(4)#3  | 126.27(14) |
| N(4)#2-Cd(1)-N(1)    | 178.45(14)| N(4)#2-Cd(1)-O(4)#3  | 90.22(12) |
| O(3)#1-Cd(1)-O(2)    | 144.94(13)| N(1)-Cd(1)-O(4)#3   | 88.89(12) |
| N(4)#2-Cd(1)-O(2)    | 96.75(14)| O(2)-Cd(1)-O(4)#3    | 88.29(14) |
| N(1)-Cd(1)-O(2)      | 84.50(14)| O(1)-Cd(1)-O(4)#3    | 142.98(15) |
| O(3)#1-Cd(1)-O(1)    | 90.74(14)| O(3)#1-Cd(1)-O(3)#3  | 73.76(13) |
| N(4)#2-Cd(1)-O(1)    | 90.98(13)| N(4)#2-Cd(1)-O(3)#3  | 89.40(13) |
| N(1)-Cd(1)-O(1)      | 90.49(13)| N(1)-Cd(1)-O(3)#3    | 89.05(13) |
| O(2)-Cd(1)-O(3)#3    | 140.42(12)| O(1)-Cd(1)-O(3)#3   | 164.50(13) |
| Bond | Distance (Å) |
|------|-------------|
| O(4)#3-Cd(1)-O(3)#3 | 2.344(2) |

Symmetry transformations used to generate equivalent atoms: #1 2-x, 1-y, 1-z; #2 x+1, y, z+1; #3 x, y, z+1

| Bond | Distance (Å) |
|------|-------------|
| Cd(1)-O(3)#3 | 2.310(2) |
| Cd(1)-N(4)#2 | 2.390(19) |
| Cd(1)-N(1) | 2.456(2) |

Symmetry transformations used to generate equivalent atoms: #1 x, y, z+1; #2 x+1, y, z+1; #3 x, y, 2-z

| Bond | Distance (Å) |
|------|-------------|
| Cd(1)-O(3)#1 | 2.232(2) |
| Cd(1)-N(4)#3 | 2.322(3) |

Symmetry transformations used to generate equivalent atoms: #1 x, y, z+1; #2 x+1, y, z+1; #3 1-x, 1-y, 2-z

| Bond | Distance (Å) |
|------|-------------|
| Zn(1)-O(3)#1 | 2.0246(16) |
| Zn(1)-N(1) | 2.163(2) |

Symmetry transformations used to generate equivalent atoms: #1 1-x, -y, 2-z; #2 x+1, y, z; #3 x+1, y, z+1

| Bond | Distance (Å) |
|------|-------------|
| Zn(1)-N(4)#2 | 2.0538(16) |
| Zn(1)-O(2) | 2.1446(17) |

Symmetry transformations used to generate equivalent atoms: #1 1-x, -y, 2-z; #2 x+1, y, z; #3 x+1, y, z+1

| Bond | Distance (Å) |
|------|-------------|
| O(3)#1-Zn(1)-O(4)#2 | 117.42(7) |
| O(3)#1-Zn(1)-O(2) | 152.02(7) |

Symmetry transformations used to generate equivalent atoms: #1 1-x, -y, 2-z; #2 x+1, y, z; #3 x+1, y, z+1

| Bond | Distance (Å) |
|------|-------------|
| O(4)#2-Zn(1)-O(2) | 90.32(7) |

Symmetry transformations used to generate equivalent atoms: #1 1-x, -y, 2-z; #2 x+1, y, z; #3 x+1, y, z+1
| Bond                      | Distance (Å) | Bond                      | Distance (Å) |
|---------------------------|--------------|---------------------------|--------------|
| O(3)#1-Zn(1)-N(1)         | 89.79(8)     | O(4)#2-Zn(1)-O(1)         | 148.43(7)    |
| O(4)#2-Zn(1)-N(1)         | 86.59(8)     | O(2)-Zn(1)-O(1)           | 58.11(6)     |
| O(2)-Zn(1)-N(1)           | 88.26(8)     | N(1)-Zn(1)-O(1)           | 91.49(8)     |
| O(3)#1-Zn(1)-N(4)#3       | 91.75(8)     | N(4)#3-Zn(1)-O(1)         | 91.24(8)     |
| O(4)#2-Zn(1)-N(4)#3       | 90.17(8)     |                           |              |
| Symmetry transformations used to generate equivalent atoms: #1 x, y+1, z; #2 -x, 2-y, 2-z; #3 x, y+1, z+1 |

| Bond                      | Distance (Å) | Bond                      | Distance (Å) |
|---------------------------|--------------|---------------------------|--------------|
| Cd(1)-O(2)#1              | 2.225(3)     | Cd(1)-N(4)#3              | 2.33(3)      |
| Cd(1)-O(1)#2              | 2.278(4)     | Cd(1)-O(4)                | 2.380(4)     |
| Cd(1)-N(1)                | 2.307(5)     | Cd(1)-O(3)                | 2.390(13)    |
| O(2)#1-Cd(1)-O(1)#2       | 122.27(14)   | O(2)#1-Cd(1)-O(4)         | 91.86(13)    |
| O(2)#1-Cd(1)-N(1)         | 89.7(2)      | O(1)#2-Cd(1)-O(4)         | 144.95(13)   |
| O(1)#2-Cd(1)-N(1)         | 86.5(2)      | N(1)-Cd(1)-O(4)           | 102.7(2)     |
| O(2)#1-Cd(1)-N(4)#3       | 84(2)        | N(4)#3-Cd(1)-O(4)         | 87(2)        |
| O(1)#2-Cd(1)-N(4)#3       | 88(2)        | O(2)#1-Cd(1)-O(3)         | 141.7(3)     |
| N(1)-Cd(1)-N(4)#3         | 168(2)       | O(1)#2-Cd(1)-O(3)         | 93.5(3)      |
| N(1)-Cd(1)-O(3)           | 107.2(3)     | N(4)#3-Cd(1)-O(3)         | 84(2)        |
| O(4)-Cd(1)-O(3)           | 51.4(3)      |                           |              |
| Symmetry transformations used to generate equivalent atoms: #1 x, y-1, z; #2 1-x, 1-y, 1-z; #3 x-1, y, z+1 |

| Bond                      | Distance (Å) | Bond                      | Distance (Å) |
|---------------------------|--------------|---------------------------|--------------|
| Cd(1)-N(1)                | 2.337(2)     | Cd(1)-O(1)                | 2.326(4)     |
| Cd(1)-N(3)                | 2.363(2)     |                           |              |
| N(1)-Cd(1)-N(3)           | 93.94(8)     | N(1)#1-Cd(1)-O(1)         | 90.36(13)    |
| N(1)#1-Cd(1)-N(3)         | 86.06(8)     | N(3)#1-Cd(1)-O(1)         | 100.58(15)   |
| N(1)-Cd(1)-O(1)           | 89.64(13)    | N(3)-Cd(1)-O(1)           | 79.42(15)    |
| Symmetry transformations used to generate equivalent atoms: #1 2-x, 2-y, 1-z |
Figure S1. Infrared spectra of compounds 1-8
Figure S2. XRPD patterns for compound 2: (a) simulated; (b) as-synthesized; (c) desolvated product; (d) product after keeping the crystals in MeOH solvent; (e) product after keeping the crystals in EtOH solvent; (f) product after keeping the crystals in H$_2$O solvent.

Figure S3. XRPD patterns of compound 7: (a) simulated; (b) as-synthesized; (c) desolvated product.
Figure S4. N\textsubscript{2} adsorption-desorption isotherms for desolvated compounds 2d and 7d at 77K.
| Compound | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|
| CCDC number | 2022947 | 2022948 | 2022949 | 2022950 | 2022951 | 2022952 | 2022953 | 2022954 |
| Empirical formula | CsH8CaN6O6 | CsH8CaN6O6 | CsH8CaN6O6 | CsH8CaN6O6 | CsH8CaN6O6 | CsH8CaN6O6 | CsH8CaN6O6 | CsH8CaN6O6 |
| Formula weight | 697.98 | 649.72 | 540.88 | 568.93 | 500.78 | 499.81 | 546.84 | 841.13 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | P-1 | P-1 | P-1 | P-1 | P-1 | P-1 | P-1 | P-1 |
| a, Å | 10.200(7) | 15.089(8) | 10.076(8) | 10.012(6) | 7.9286(5) | 9.1741(5) | 9.8636(6) | 9.5960(7) |
| b, Å | 10.538(4) | 15.885(7) | 10.1625(7) | 11.3491(7) | 10.2530(7) | 10.0959(6) | 10.3856(5) | 10.0623(8) |
| c, Å | 15.937(10) | 15.8843(7) | 12.7653(7) | 12.8116(8) | 13.8228(7) | 12.7739(6) | 11.9413(8) | 10.2938(8) |
| α, ° | 77.209(5) | 60.650(5) | 106.911(5) | 97.992(5) | 94.035(5) | 103.514(5) | 101.408(5) | 66.957(8) |
| β, ° | 88.096(5) | 65.928(5) | 91.992(5) | 97.620(5) | 100.886(5) | 95.606(4) | 92.074(5) | 88.604(7) |
| γ, ° | 84.390(5) | 65.649(5) | 109.708(7) | 114.365(6) | 111.823(6) | 104.631(5) | 104.721(5) | 87.270(7) |
| Volume, Å³ | 1631.03(17) | 2915.2(3) | 1164.57(15) | 1283.84(15) | 1012.12(12) | 1097.52(11) | 1154.90(13) | 913.58(14) |
| Z | 4 | 4 | 2 | 2 | 2 | 2 | 2 | 1 |
| D(calcd) Mg/m³ | 1.421 | 1.479 | 1.542 | 1.472 | 1.643 | 1.512 | 1.573 | 1.529 |
| μ, mm⁻¹ | 0.717 | 0.797 | 0.977 | 0.891 | 1.114 | 1.162 | 0.987 | 0.662 |
| F(000) | 708 | 1318 | 552 | 584 | 500 | 516 | 552 | 428 |
| Reflections collected | 10,619 | 18,829 | 6319 | 8185 | 5443 | 7355 | 7156 | 4900 |
| Independent reflections | 5723 | 10,524 | 4061 | 4767 | 3563 | 4062 | 4281 | 3196 |
| | R(int) = 0.0378 | R(int) = 0.0354 | R(int) = 0.0326 | R(int) = 0.0296 | R(int) = 0.0230 | R(int) = 0.0263 | R(int) = 0.0319 | R(int) = 0.0215 |
| Reflections with | 4776 | 7264 | 3182 | 4057 | 3126 | 3428 | 3619 | 2927 |
| | I > 2σ(I) | | | | | | | |
| Data/restraints/parameters | 5723/72/431 | 10,521/320/833 | 4061/3/322 | 4767/30/310 | 3563/0/271 | 4062/38/323 | 4281/97/436 | 3196/24/287 |
| Goodness-of-fit on F² | 0.991 | 1.002 | 1.009 | 1.039 | 1.008 | 1.077 | 1.000 | 1.030 |
| Final R indices | 0.0404, 0.0852 | 0.0612, 0.1640 | 0.0646, 0.0813 | 0.0340, 0.0669 | 0.0322, 0.0575 | 0.0370, 0.0839 | 0.0446, 0.0161 | 0.0338, 0.0721 |
| | R(int) = 0.0378 | R(int) = 0.0354 | R(int) = 0.0326 | R(int) = 0.0296 | R(int) = 0.0230 | R(int) = 0.0263 | R(int) = 0.0319 | R(int) = 0.0215 |
| R indices (all data) | 0.0506, 0.0915 | 0.0958, 0.1857 | 0.0649, 0.0907 | 0.0438, 0.0708 | 0.0397, 0.0615 | 0.0480, 0.0898 | 0.0562, 0.1141 | 0.0395, 0.0756 |
| Largest diff. peak and hole e. Å⁻³ | 0.735 and −0.476 | 0.843 and −0.670 | 0.789 and −0.496 | 0.489 and −0.460 | 0.441 and −0.483 | 0.330 and −0.255 | 0.710 and −0.501 | 0.396 and −0.431 |