Supporting Information

Exploration of Cd(II)/pseudohalide/di-2-pyridyl ketone chemistry – Rational synthesis, structural analysis and photoluminescence

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Figure S9. IR spectrum of 1.
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Figure S27. Perspective views of the asymmetric unit of 8 (a), 9a (b) and 9b (c) showing the atom numbering. Displacement ellipsoids are drawn at 50% probability.

Figure S28. The solid state absorption electronic spectra of (py)2CO and the Cd(II) coordination compounds.

Figure S29. The UV-Vis spectra of the free ligand and Cd(II) compounds in acetonitrile solution (10⁻⁴ M).
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<td>2861 (Rint=0.0363)</td>
<td>2862 (Rint=0.0366)</td>
<td>2968 (Rint=0.0335)</td>
<td>2977 (Rint=0.0325)</td>
<td>2986 (Rint=0.0360)</td>
<td>2986 (Rint=0.0405)</td>
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<td><strong>Completeness to 2θ=50° [%]</strong></td>
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<td>99.7</td>
<td>99.7</td>
<td>99.7</td>
<td>99.5</td>
<td>99.7</td>
<td>99.6</td>
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</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>1.000 and 0.798</td>
<td>1.000 and 0.783</td>
<td>1.000 and 0.733</td>
<td>1.000 and 0.638</td>
<td>1.000 and 0.478</td>
<td>1.000 and 0.644</td>
<td>1.000 and 0.583</td>
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<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>2971 / 0 / 210</td>
<td>2861 / 0 / 210</td>
<td>2862 / 0 / 210</td>
<td>2968 / 0 / 210</td>
<td>2977 / 0 / 210</td>
<td>2986 / 0 / 210</td>
<td>2921 / 0 / 210</td>
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<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
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<td>1.092</td>
<td>1.166</td>
<td>1.064</td>
<td>1.059</td>
<td>1.159</td>
<td>1.100</td>
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<tr>
<td><strong>Final R indices [1=2σ(I)]</strong></td>
<td>R1 = 0.0341</td>
<td>R1 = 0.0368</td>
<td>R1 = 0.0391</td>
<td>R1 = 0.0305</td>
<td>R1 = 0.0268</td>
<td>R1 = 0.0312</td>
<td>R1 = 0.0418</td>
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<tr>
<td></td>
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<td>wR2 = 0.0797</td>
<td>wR2 = 0.0711</td>
<td>wR2 = 0.0613</td>
<td>wR2 = 0.0486</td>
<td>wR2 = 0.0729</td>
<td>wR2 = 0.1011</td>
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<tr>
<td><strong>R indices (all data)</strong></td>
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<td>R1 = 0.0465</td>
<td>R1 = 0.0495</td>
<td>R1 = 0.0387</td>
<td>R1 = 0.0312</td>
<td>R1 = 0.0359</td>
<td>R1 = 0.0503</td>
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<td></td>
<td>wR2 = 0.1224</td>
<td>wR2 = 0.0833</td>
<td>wR2 = 0.0944</td>
<td>wR2 = 0.0647</td>
<td>wR2 = 0.0501</td>
<td>wR2 = 0.0747</td>
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<td><strong>Absolute structure parameter</strong></td>
<td>-0.01(5)</td>
<td>-0.03(4)</td>
<td>0.06(6)</td>
<td>-0.06(3)</td>
<td>-0.02(2)</td>
<td>0.04(4)</td>
<td>0.00(5)</td>
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<tr>
<td><strong>Largest diff. peak and hole [e Å⁻³]</strong></td>
<td>0.593 and -0.370</td>
<td>0.686 and -0.400</td>
<td>0.445 and -0.594</td>
<td>0.536 and -0.321</td>
<td>0.239 and -0.249</td>
<td>0.464 and -0.311</td>
<td>0.821 and -0.577</td>
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Table S3. Short intra- and intermolecular contacts detected in the structures 2-9.

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<tbody>
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<td>O(2)—H(1A)•••N(98) _#1</td>
<td>0.82</td>
<td>1.96</td>
<td>2.769(7)</td>
<td>167.0</td>
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<tr>
<td>C(12)—H(12C)•••O(2)</td>
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<td>2.45</td>
<td>2.791(7)</td>
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<td>C(8)—H(8)•••N(97) _#2</td>
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<td>172.0</td>
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<tr>
<td>C(8)—H(8)•••O(2) _#3</td>
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<tr>
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<td>3.413(9)</td>
<td>145.0</td>
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<td>2.44</td>
<td>2.767(6)</td>
<td>100.0</td>
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<td>2.667(8)</td>
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<td>2.58</td>
<td>2.916(10)</td>
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<tr>
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<td>2.738(7)</td>
<td>171.0</td>
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<tr>
<td>C(2)—H(2)•••O(7) _#9</td>
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<td>2.31</td>
<td>3.080(10)</td>
<td>140.0</td>
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<tr>
<td>C(4)—H(4)•••O(2)</td>
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<td>2.47</td>
<td>2.788(10)</td>
<td>100.0</td>
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<td>C(20)—H(20)•••O(4)</td>
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<td>2.761(9)</td>
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<td>2.712(4)</td>
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<td>2.31</td>
<td>3.080(10)</td>
<td>140.0</td>
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<td>C(4)—H(4)•••O(2)</td>
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<td>2.47</td>
<td>2.788(7)</td>
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<td>C(20)—H(20)•••O(4)</td>
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<td>2.761(9)</td>
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<td>3.114(11)</td>
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<td>1.90</td>
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<td>2.788(7)</td>
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<td>2.45</td>
<td>2.772(6)</td>
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<td>C(23)—H(23)•••O(5)</td>
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<td>2.49</td>
<td>3.114(11)</td>
<td>125.0</td>
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<tr>
<td>O(4)—H(4A)•••O(1) _#1</td>
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<td>1.90</td>
<td>2.705(6)</td>
<td>177.0</td>
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<td>3.250(12)</td>
<td>129.0</td>
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<td>C(14)—H(14)•••O(2)</td>
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<td>2.45</td>
<td>2.773(10)</td>
<td>101.0</td>
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Symmetry transformations used to generate equivalent atoms: #1: -x,2-y,1-z; #2: 5/4-y,3/4-x,-1/4+z; #3: 1-x,1/2-y,z; #4: -x,1-y,1-z; #5: x,1+y,z; #6: ½-x,1/2+y,1/2-z; #7: 1-x,1-y,-z; #8: 1-x,-y,1-z; #9: x,-1+y,z; #10: 1/2-x,-1/2+y,3/2-z; #11: 2-x,1-y,1-z; #12: -1/2+x,y,3/2-z; #13: -1/2+x,1/2-y,1-z; #14:1-x,1-y,1-z
Table S4. The selected bond lengths [Å] and angles [°] for 1.

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<th>Bond lengths</th>
<th>Bond angles</th>
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<td>Cd(1)--N(2)</td>
<td>2.322(3)</td>
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<td>Cd(1)--O(1)</td>
<td>2.603(3)</td>
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<td>Cd(1)--N(98)</td>
<td>2.273(4)</td>
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<td>Cd(1)--N(99)</td>
<td>2.287(4)</td>
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<td>Cd(1)--S(99)</td>
<td>2.5756(12)</td>
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<td>N(98)--C(98)</td>
<td>1.129(6)</td>
</tr>
<tr>
<td>C(98)--S(98)</td>
<td>1.639(5)</td>
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<td>C(99)--N(99)</td>
<td>1.138(6)</td>
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<tr>
<td>C(99)--S(99)</td>
<td>1.642(5)</td>
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<td>S(99)--C(99)</td>
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<th>Bond angles</th>
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<td>N(1)--Cd(1)--O(1)</td>
<td>65.67(10)</td>
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<td>64.62(10)</td>
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<td>169.88(14)</td>
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<td>O(1)--Cd(1)--N(99)</td>
<td>148.02(12)</td>
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<td>O(1)--Cd(1)--S(99)</td>
<td>94.64(7)</td>
</tr>
<tr>
<td>N(98)--Cd(1)--N(99)</td>
<td>92.64(16)</td>
</tr>
<tr>
<td>N(98)--Cd(1)--S(99)</td>
<td>88.44(12)</td>
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<td>N(99)--Cd(1)--S(99)</td>
<td>104.39(11)</td>
</tr>
<tr>
<td>C(99)--N(99)--Cd(1)</td>
<td>164.7(4)</td>
</tr>
<tr>
<td>C(99)--S(99)--Cd(1)</td>
<td>101.84(16)</td>
</tr>
<tr>
<td>N(99)--C(99)--S(99)</td>
<td>179.0(5)</td>
</tr>
<tr>
<td>N(99)--C(99)--S(99')</td>
<td>177.3(4)</td>
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Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+1/2,-z+1  #2 x-1/2,-y+1/2,-z+1

Table S5. The selected bond lengths [Å] and angles [°] for 2.

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<td>Cd(1)--O(1)</td>
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<td>Cd(1)--N(99)#1</td>
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<td>Cd(1)--S(98)</td>
<td>2.5953(15)</td>
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<td>C(98)--N(98)</td>
<td>1.142(7)</td>
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<td>C(98)--S(98)</td>
<td>1.663(6)</td>
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<td>C(99)--N(99)</td>
<td>1.148(6)</td>
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<td>C(99)--S(99)</td>
<td>1.641(5)</td>
</tr>
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<td>N(99)#1--Cd(1)--N(2)</td>
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<td>66.67(12)</td>
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<td>N(2)--Cd(1)--O(1)</td>
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<td>N(99)#1--Cd(1)--N(1)</td>
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<tr>
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<td>N(1)--Cd(1)--S(99)</td>
<td>92.45(11)</td>
</tr>
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<td>N(99)--Cd(1)--S(99)</td>
<td>94.64(7)</td>
</tr>
<tr>
<td>O(1)--Cd(1)--N(99)</td>
<td>148.02(12)</td>
</tr>
<tr>
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</tr>
<tr>
<td>N(98)--Cd(1)--N(99)</td>
<td>92.64(16)</td>
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<td>C(99)--N(99)--Cd(1)</td>
<td>164.7(4)</td>
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<td>C(99)--S(99)--Cd(1)</td>
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<td>N(99)--C(99)--S(99)</td>
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<td>N(99)--C(99)--S(99')</td>
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Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

#1 x+1/2,-y+1/2,-z+1  #2 x-1/2,-y+1/2,-z+1
Table S6. The experimental and calculated bond lengths [Å] and angles [°] for 4.

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<td>99.51(18)</td>
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<td>N(99)–Cd(1)–N(1)</td>
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<td>2.373(5)</td>
<td>87.87(19)</td>
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<td>Cd(1)–N(99)</td>
<td>N(99)–Cd(1)–N(2)</td>
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<td>2.247(5)</td>
<td>92.64(19)</td>
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<td>Cd(1)–O(1)</td>
<td>N(1)–Cd(1)–O(1)</td>
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<td>68.98(14)</td>
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<td>N(1)–Cd(1)–O(1)</td>
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<td>145.16(14)</td>
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<td>N(99)–Cd(1)–O(1)</td>
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<td>118.63(17)</td>
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<td>101.74(14)</td>
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<td>70.78(14)</td>
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<td>79.37(13)</td>
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Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1/2,z;  #2 y+1/4,-x+3/4,-z+1/4;  #3 -y+3/4,x-1/4,-z+1/4
Table S7. The selected bond lengths [Å] and angles [°] for 5.

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Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1
Table S8. The experimental and calculated bond lengths [Å] and angles [°] for 6.

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Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1/2,z  #2 y+1/4,-x+3/4,-z+5/4  #3 -y+3/4,x-1/4,-z+5/4
Table S9. The selected bond lengths [Å] and angles [°] for 7.

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Symmetry transformations used to generate equivalent atoms:
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Table S10. The selected bond lengths [Å] and angles [°] for 8.

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<td>Symmetry transformations used to generate equivalent atoms:</td>
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#1 -x+1,-y,-z+1
Table S11. The selected bond lengths [Å] and angles [°] for 9a.

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Bond lengths: 2.291(5) – 2.435(6) Å  
Bond angles: 106.86(18) – 147.66(17)°

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1
Table S12. The selected bond lengths [Å] and angles [°] for 9b.

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Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1
**Figure S1.** The XRPD spectrum (Cu–Kα radiation) of 1 (black), together with the calculated pattern from the single crystal data (red).

**Figure S2.** The XRPD spectrum (Cu–Kα radiation) of 2 (black), together with the calculated pattern from the single crystal data (red).
Figure S3. The XRPD spectrum (Co–Kα radiation) of 4 (black), together with the calculated pattern from the single crystal data (red).

Figure S4. The XRPD spectrum (Cu–Kα radiation) of 5 (black), together with the calculated pattern from the single crystal data (red).
**Figure S5.** The XRPD spectrum (Co–Kα radiation) of 6 (black), together with the calculated pattern from the single crystal data (red).

**Figure S6.** The XRPD spectrum (Cu–Kα radiation) of 7 (black), together with the calculated pattern from the single crystal data (red).
Figure S7. The XRPD spectrum (Co–Kα radiation) of 8 (black), together with the calculated pattern from the single crystal data (red).
Figure S8. a) The XRPD spectra (Cu–Kα radiation) of 9 (a+b) (black), together with the calculated pattern from the single crystal data (red for 9a and blue for 9b). b) The powder XRD pattern of compound 9(a+b) (black), together with the calculated pattern from the single crystal data of 9a (red); c) The powder XRD pattern of compound 9(a+b) (black), together with the calculated pattern from the single crystal data of 9b (red).
Figure S9. IR spectrum of 1.

Figure S10. IR spectrum of 2.
Figure S11. IR spectrum of 4.

Figure S12. IR spectrum of 5.
Figure S13. IR spectrum of 6.

Figure S14. IR spectrum of 7.
Figure S15. IR spectrum of 8.

Figure S16. IR spectrum of 9(a+b).
Figure S17. DSC curve of 1.

Figure S18. DSC curve of 2.
Figure S19. DSC curve of 4.

Figure S20. DSC curve of 5.
Figure S21. DSC curve of 6.

Figure S22. DSC curve of 7.
Figure S23. DSC curve of 8.

Figure S24. DSC curve of 9(a+b).
Figure S25. Perspective views of the asymmetric unit of 4 (a) and 6 (b) showing the atom numbering. Displacement ellipsoids are drawn at 50% probability.

Figure S26. Perspective views of the asymmetric unit of 5 (a) and 7 (b) showing the atom numbering. Displacement ellipsoids are drawn at 50% probability.
Figure S27. Perspective views of the asymmetric unit of 8 (a), 9a (b) and 9b (c) showing the atom numbering. Displacement ellipsoids are drawn at 50% probability.
Figure S28. The solid state absorption electronic spectra of (py)$_2$CO and the Cd(II) coordination compounds.

Figure S29. The UV-Vis spectra of the free ligand and Cd(II) compounds in acetonitrile solution ($10^{-4}$ M).