# Syntheses, Structures, and Photoluminescent Properties of a Series of Metal−Organic Frameworks Constructed by 5,5'-Bis(1*H*-imidazol-1-yl)-2,2'-Bithiophene and Various Carboxylate Ligands

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**Table S1.** Selected Bond Lengths (Å) and Angles (deg) for Compounds **1-7**.

| Compound **1** | | | |
|---|---|---|---|
| Co(1)-O(2) | 1.989(2) | Co(1)-N(1) | 2.049(3) |
| Co(1)-O(3)#1 | 1.908(7) | Co(1)-N(3) | 2.036(3) |
| O(2)-Co(1)-N(3) | 110.46(11) | O(2)-Co(1)-N(1) | 115.64(11) |
| N(1)-Co(1)-N(3) | 111.61(11) | O(2)-Co(1)-O(3)#1 | 107.6(2) |
| N(3)-Co(1)-O(3)#1 | 97.3(3) | N(1)-Co(1)-O(3)#1 | 112.7(3) |
| Symmetry codes: #1 = *x*, *y*, -1+*z*. | | | |
| Compound **2** | | | |
| Co(1)-O(1) | 2.1818(13) | Co(1)-O(2) | 2.2257(12) |
| Co(1)-N(1) | 2.1187(15) | Co(1)-O(5)#1 | 2.0642(13) |
| Co(1)-O(6)#2 | 2.0303(12) | Co(1)-N(4)#3 | 2.1423(15) |
| N(1)-Co(1)-O(2) | 87.84(5) | N(1)-Co(1)-O(1) | 93.82(5) |
| O(6)#2-Co(1)-O(5)#1 | 111.91(5) | O(6)#2-Co(1)-N(1) | 86.06(5) |

| | | | |
|---|---|---|---|
| O(5)#1-Co(1)-N(1) | 88.31(6) | O(6)#2-Co(1)-N(4)#3 | 90.53(5) |
| O(5)#1-Co(1)-N(4)#3 | 93.96(6) | N(1)-Co(1)-N(4)#3 | 176.43(5) |
| O(6)#2-Co(1)-O(1) | 99.40(5) | O(5)#1-Co(1)-O(1) | 148.68(5) |
| N(4)#3-Co(1)-O(2) | 94.96(5) | N(4)#3-Co(1)-O(1) | 85.69(5) |
| O(6)#2-Co(1)-O(2) | 157.92(5) | O(5)#1-Co(1)-O(2) | 89.07(5) |
| Symmetry codes: #1 = *x*, 1+*y*, *z*; #2 = 2-*x*, 1-*y*, -*z*; #3 = 1+*x*, -1+*y*, -1+*z*. | | | |
| Compound **3** | | | |
| Zn(1)-O(1) | 2.0475(12) | Zn(1)-N(1) | 2.1397(15) |
| Zn(1)-O(2)#1 | 2.0339(12) | Zn(1)-O(3)#2 | 2.0170(12) |
| Zn(1)-N(4)#3 | 2.1124(15) | | |
| O(1)-Zn(1)-N(1) | 89.91(6) | O(2)#1-Zn(1)-O(1) | 122.03(5) |
| O(2)#1-Zn(1)-N(1) | 92.77(6) | O(2)#1-Zn(1)-N(4)#3 | 88.72(6) |
| O(1)-Zn(1)-N(4)#3 | 84.70(5) | O(3)#2-Zn(1)-O(2)#1 | 128.75(5) |
| O(3)#2-Zn(1)-O(1) | 109.22(5) | O(3)#2-Zn(1)-N(1) | 87.28(6) |
| O(3)#2-Zn(1)-N(4)#3 | 96.02(6) | N(4)#3-Zn(1)-N(1) | 174.37(5) |
| Symmetry codes: #1 = 1-*x*, -*y*, 1-*z*; #2 = 1-*x*, 1-*y*, 1-*z*; #3 = 1+*x*, -1+*y*, -1+*z*. | | | |
| Compound **4** | | | |
| Cd(1)-O(1) | 2.2615(15) | Cd(1)-N(1) | 2.315(2) |
| Cd(1)-N(4)#1 | 2.300(2) | Cd(1)-O(2)#2 | 2.3062(17) |
| Cd(1)-O(3)#3 | 2.3641(15) | Cd(1)-O(4)#3 | 2.4291(17) |
| O(1)-Cd(1)-N(1) | 85.95(7) | O(1)-Cd(1)-N(4)#1 | 96.74(7) |
| O(1)-Cd(1)-O(2)#2 | 111.58(6) | N(4)#1-Cd(1)-O(2)#2 | 90.32(7) |
| N(4)#1-Cd(1)-N(1) | 169.71(7) | O(2)#2-Cd(1)-N(1) | 79.47(7) |
| O(1)-Cd(1)-O(3)#3 | 146.26(6) | N(4)#1-Cd(1)-O(3)#3 | 84.90(7) |
| O(2)#2-Cd(1)-O(3)#3 | 102.09(6) | N(1)-Cd(1)-O(3)#3 | 98.40(7) |
| O(1)-Cd(1)-O(4)#3 | 92.20(6) | N(4)#1-Cd(1)-O(4)#3 | 100.12(7) |

| | | | |
|---|---|---|---|
| O(2)#2-Cd(1)-O(4)#3 | 152.80(6) | N(1)-Cd(1)-O(4)#3 | 89.68(7) |
| Symmetry codes: #1 = 1+*x*, -1+*y*, -1+*z*; #2 = 2-*x*, -*y*, -*z*; #3 = *x*, -1+*y*, *z*. | | | |
| Compound **5** | | | |
| Zn(1)-O(1) | 1.919(2) | Zn(1)-O(5) | 1.924(2) |
| Zn(1)-N(1) | 1.988(2) | Zn(2)-O(2) | 1.910(2) |
| Zn(2)-O(6) | 1.953(3) | Zn(2)-O(3)#1 | 1.902(2) |
| O(1)-Zn(1)-O(5) | 114.78(10) | O(1)-Zn(1)-N(1) | 104.16(10) |
| O(5)-Zn(1)-N(1) | 110.28(11) | O(2)-Zn(2)-O(6) | 110.26(12) |
| O(3)#1-Zn(2)-O(2) | 111.44(10) | O(3)#1-Zn(2)-O(6) | 104.53(11) |
| Symmetry codes: #1 = 1-*x*, 1+*y*, 1.5-*z*. | | | |
| Compound **6** | | | |
| Zn(1)-O(1) | 2.089(2) | Zn(1)-O(6) | 2.139(3) |
| Zn(2)- O(10) | 2.201(3) | Zn(2)-O(13) | 2.047(2) |
| Zn(3)- O(12) | 2.122(3) | Zn(3)-O(15)#5 | 2.324(3) |
| Zn(3)-O(16)#5 | 2.337(3) | Zn(4)-O(8) | 2.119(3) |
| Zn(4)-O(4)#5 | 1.964(3) | Zn(1)-N(1) | 2.033(3) |
| Zn(1)-N(11) | 2.032(3) | Zn(2)-N(4) | 2.002(3) |
| Zn(2)-N(9) | 2.037(3) | Zn(3)-N(5) | 2.023(3) |
| Zn(3)-N(13) | 2.013(3) | Zn(4)-N(7) | 2.038(3) |
| Zn(4)-N(15) | 2.033(3) | | |
| N(11)-Zn(1)-N(1) | 114.43(14) | N(11)-Zn(1)-O(1) | 98.01(11) |
| N(1)-Zn(1)-O(1) | 102.27(11) | N(11)-Zn(1)-O(6) | 90.65(12) |
| N(1)-Zn(1)-O(6) | 125.48(12) | O(1)-Zn(1)-O(6) | 122.11(11) |
| N(4)-Zn(2)-N(9) | 114.00(14) | N(4)-Zn(2)-O(13) | 97.76(12) |
| N(9)-Zn(2)-O(13) | 91.65(12) | N(4)-Zn(2)-O(10) | 96.36(12) |
| N(9)-Zn(2)-O(10) | 94.23(12) | O(13)-Zn(2)-O(10) | 160.95(11) |

| | | | |
|---|---|---|---|
| N(13)-Zn(3)-N(5) | 113.31(15) | N(13)-Zn(3)-O(12) | 90.54(12) |
| N(5)-Zn(3)-O(12) | 122.42(12) | N(15)-Zn(4)-N(7) | 113.05(14) |
| N(15)-Zn(4)-O(8) | 127.97(12) | N(7)-Zn(4)-O(8) | 91.62(12) |
| O(4)#5-Zn(4)-O(8) | 109.16(12) | O(12)-Zn(3)-O(16)#5 | 136.55(9) |
| O(12)-Zn(3)-O(15)#5 | 109.80(10) | O(15)#5-Zn(3)-O(16)#5 | 54.29(10) |
| O(4)#5-Zn(4)-N(7) | 109.80(10) | O(4)#5-Zn(4)-N(15) | 102.94(13) |
| N(5)-Zn(3)-O(15)#5 | 88.08(13) | N(5)-Zn(3)-O(16)#5 | 98.85(11) |
| N(13)-Zn(3)-O(15)#5 | 136.63(13) | N(13)-Zn(3)-O(16)#5 | 84.36(11) |
| Symmetry codes: #5 = -1+*x*, *y*, *z*. | | | |
| Compound 7 | | | |
| Zn(1)-O(1) | 1.966(3) | Zn(1)-N(1) | 2.041(3) |
| Zn(1)-N(3) | 2.032(4) | Zn(1)-O(4)#1 | 1.980(3) |
| O(1)-Zn(1)-N(3) | 121.33(14) | O(1)-Zn(1)-N(1) | 95.18(13) |
| N(3)-Zn(1)-N(1) | 101.71(14) | O(1)-Zn(1)-O(4)#1 | 108.90(12) |
| O(4)#1-Zn(1)-N(1) | 127.40(12) | O(4)#1-Zn(1)-N(3) | 103.92(12) |
| Symmetry codes: #1 = -1+*x*, 1.5-*y*, -0.5+*z*. | | | |

**Table S2.** Hydrogen bond lengths (Å) and angles(°) for the Compounds **2**, **3**, **and 6**

| D–H···A | d(D–H) | d(H···A) | d(D···A) | ∠DHA | Symmetry code |
|---|---|---|---|---|---|
| Compound **2** | | | | | |
| O(3)–H(3A)···O(2) | 0.82 | 1.85 | 2.6451(17) | 162.4 | 2-*x*, 1-*y*, 1-*z* |
| Compound **3** | | | | | |
| O(5)–H(5)···O(4) | 0.82 | 1.84 | 2.6568(18) | 173.6 | 1-*x*, 1-*y*, 2-*z* |
| Compound **6** | | | | | |
| C(12)–H(12)···O(5) | 0.93 | 2.08 | 2.918(5) | 149.8 | 1-*x*, 1-*y*, -*z* |
| C(17)–H(17)···O(3) | 0.93 | 2.29 | 3.216(5) | 173.9 | 1-*x*, 1/2+*y*, 1/2-*z* |

**Table S3.** Luminescence data for organic ligands and coordination polymers in the solid state.

| Compound | λex[nm] | λem[nm] | Ligand | λex[nm] | λem[nm] |
|---|---|---|---|---|---|
| 3 | 394 | 508 | BIBP | 354 | 496 |
| 4 | 397 | 513 | $H_2$hfipbb | 290 | 325 |
| 5 | 392 | 526 | $H_2$bdc | 276 | 380 |
| 6 | 393 | 520 | 5-OH-$H_2$bdc | 289 | 368 |
| 7 | 390 | 485 | | | |

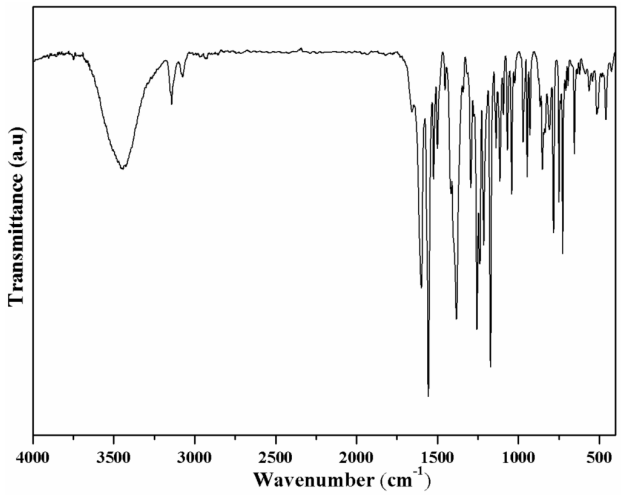



**Figure S1**. IR spectra of compound **1**

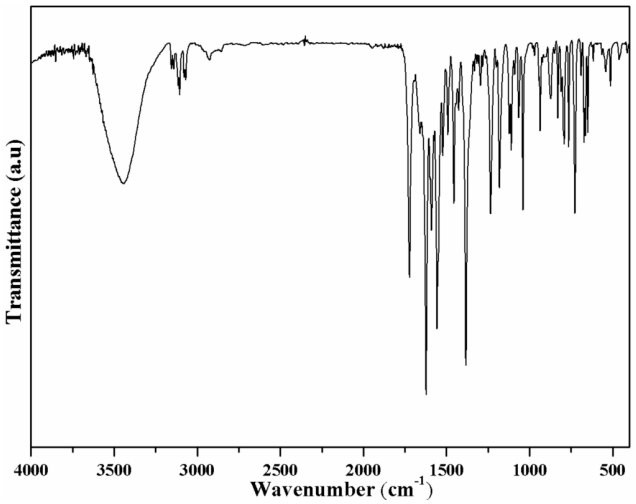



**Figure S2**. IR spectra of compound **2**

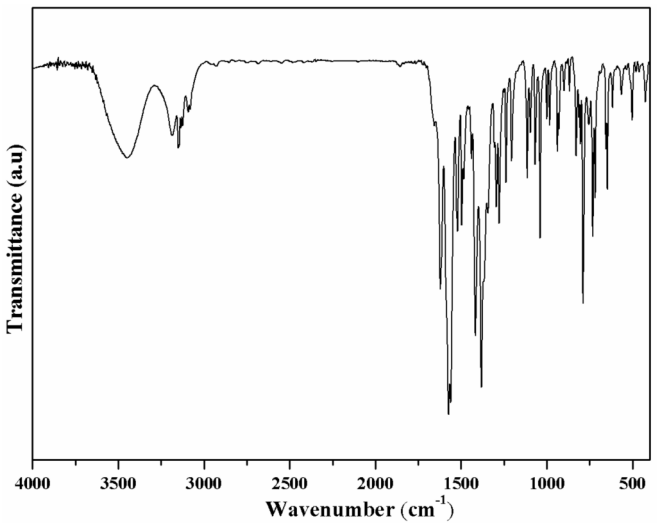



**Figure S3**. IR spectra of compound **3**

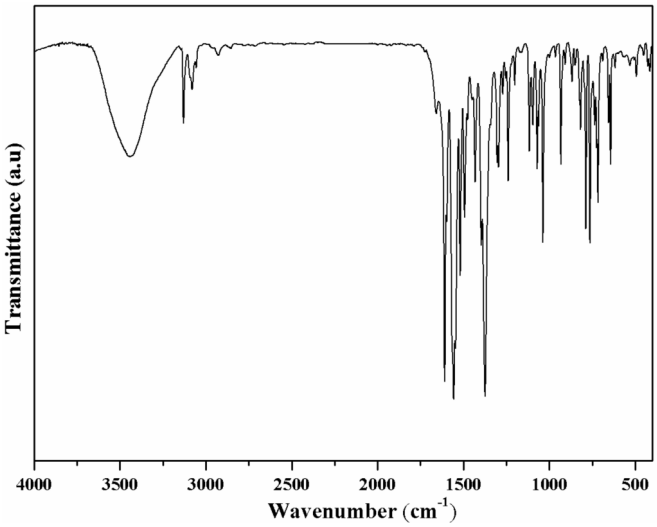



**Figure S4**. IR spectra of compound **4**

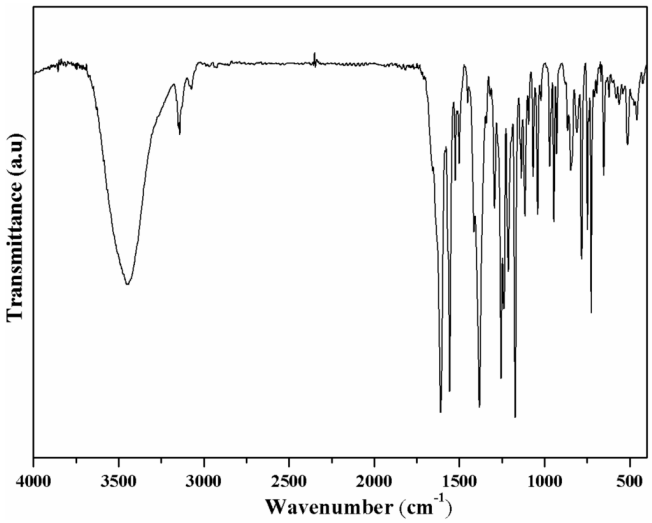



**Figure S5**. IR spectra of compound **5**

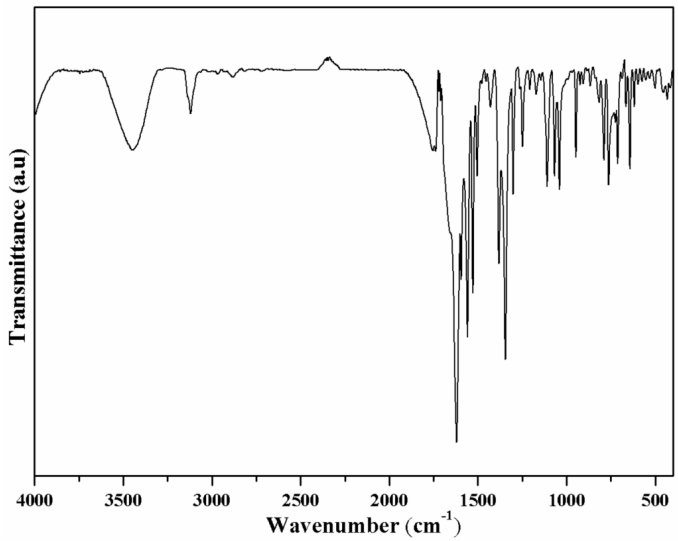



**Figure S6**. IR spectra of compound **6**

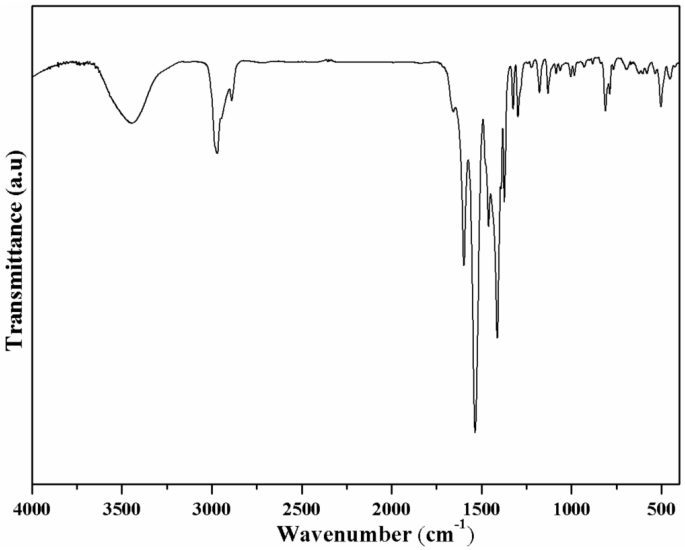
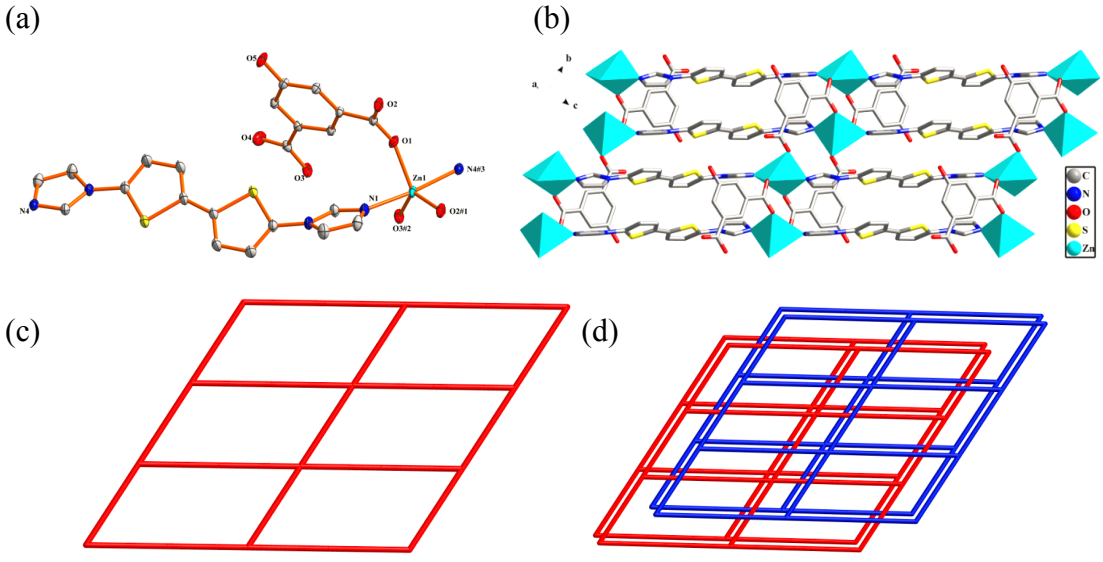



**Figure S7**. IR spectra of compound **7**



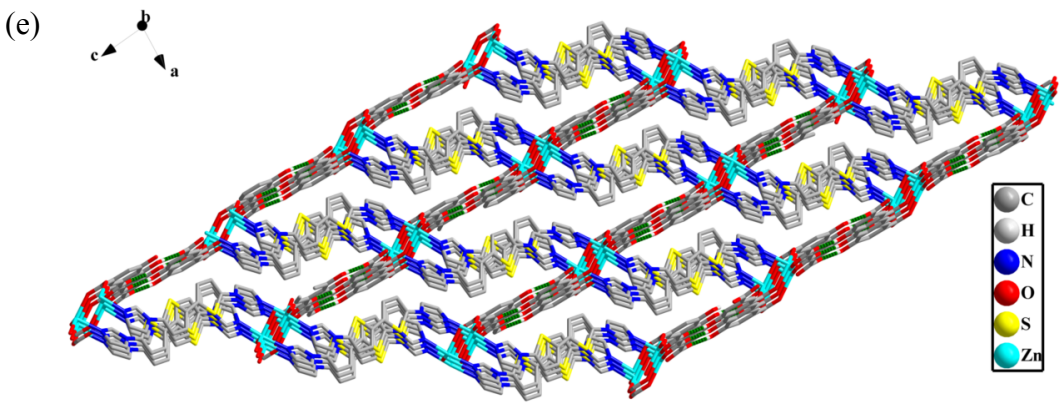



**Figure S8**. (a) Coordination environment of the Zn(II) cation in **3** (30% probability displacement ellipsoids). The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = 1-*x*, -*y*, 1-*z*; #2 = 1-*x*, 1-*y*, 1-*z*; #3 = 1+*x*, -1+*y*, -1+*z*. (b) Polyhedral view of the 2D coordination network of **3**. (c) View of an **sql** type net of **3**. (d) Packing diagram showing the ABAB type offset stacks of 2D sheets in **3**. (e) Schematic representation the 3D supramolecular framework of **3** via the hydrogen bonds (green dashed line).

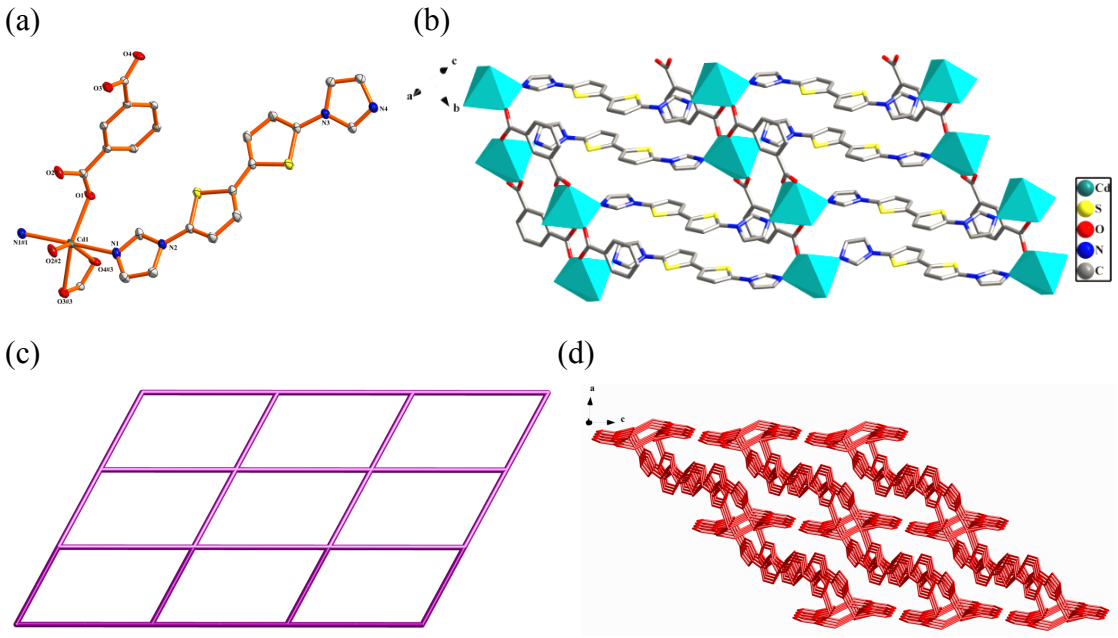
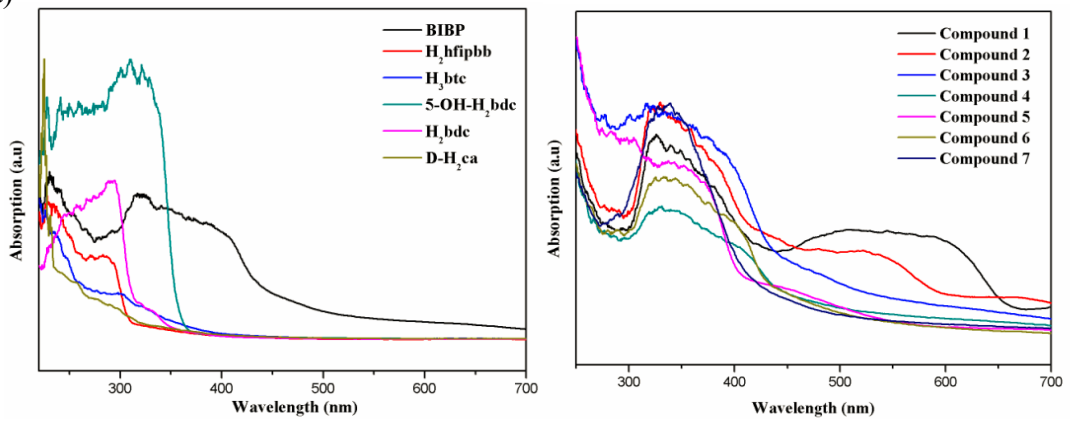
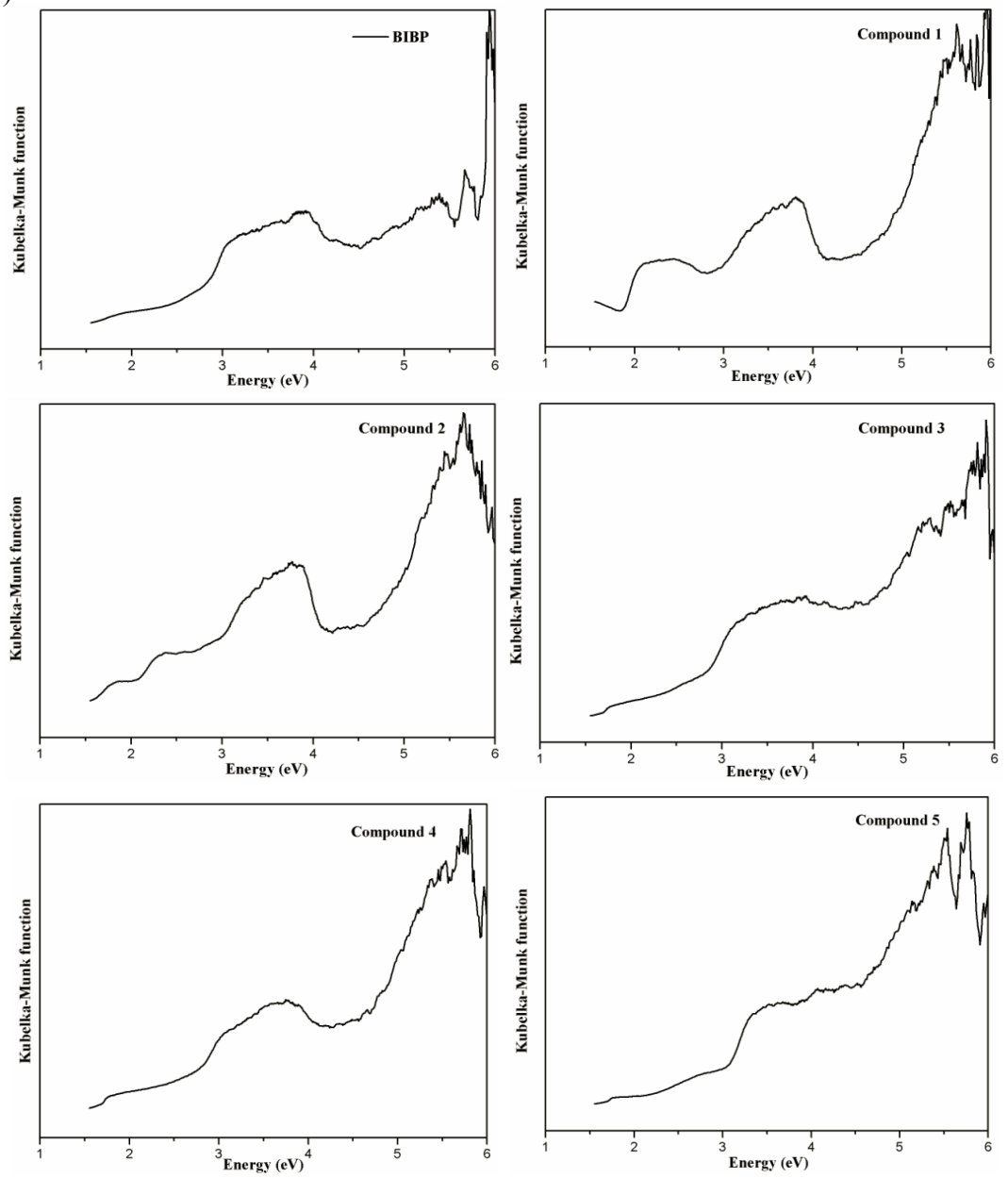



**Figure S9**. (a) Coordination environment of the Cd(II) cation in **4** (30% probability displacement ellipsoids). The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = 1+*x*, -1+*y*, -1+*z*; #2 = 2-*x*, -*y*, -*z*; #3 = *x*, -1+*y*, *z*. (b) Polyhedral view of the 2D coordination network of **4**. (c) View of an **sql** type net of **4**. (d) Packing diagram showing the AAAA type offset stacks of 2D sheets in **4**.

(a)




(b)



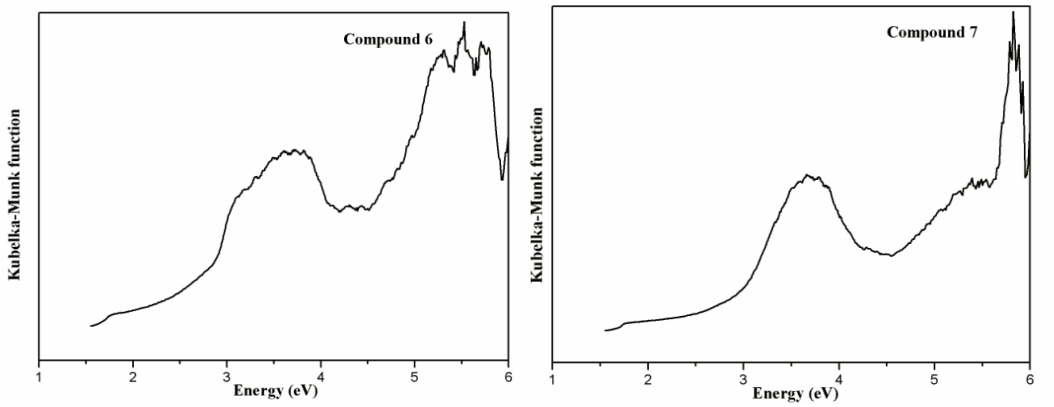



**Figure S10.** (a) UV-vis absorbance spectra and (b) Plot of Kubelka-Munk as a function of energy of the compounds and the free ligands at room temperature.

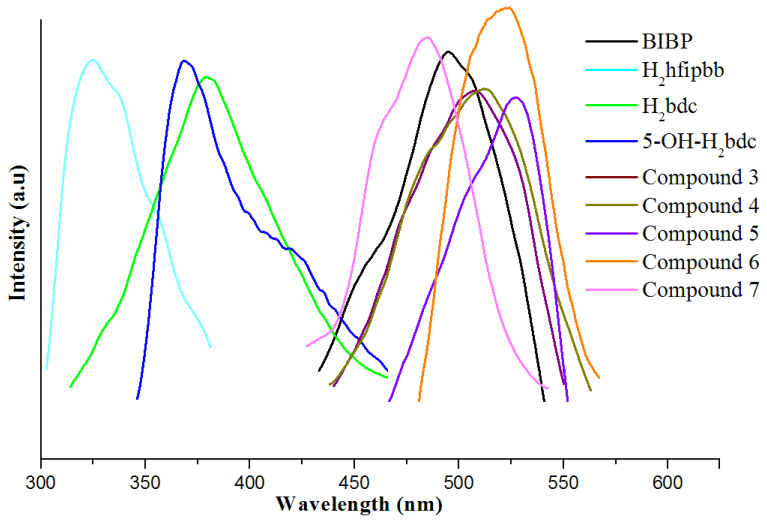



**Figure S11**. Solid-state photoluminescent spectra of **3**, **4**, **5**, **6**, **7** and corresponding ligands at room temperature.

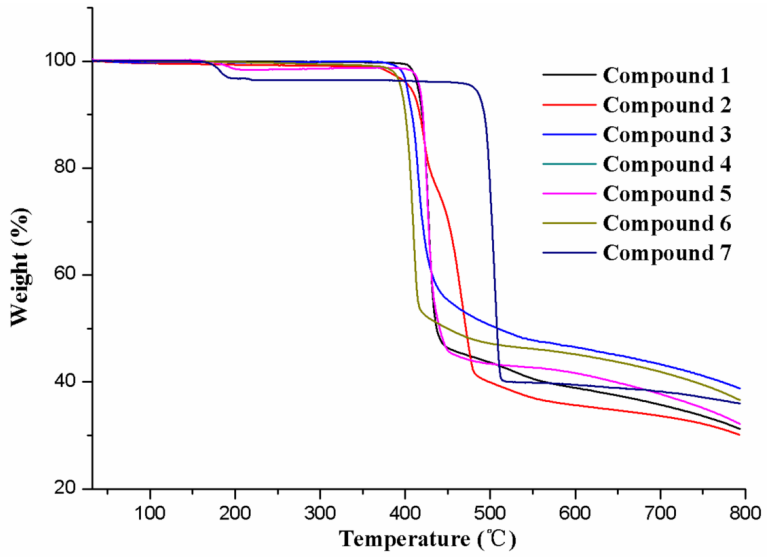



**Figure S12.** TGA curves of compounds **1**-**7**.