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**Supporting Information**

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

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**Table S1**. Crystal data and structure refinement for **1**, **2** and **4-9** complexes.

| | **1** | **2** | **4** | **5** | **6** | **7** | **8** | **9a** | **9b** |
|---|---|---|---|---|---|---|---|---|---|
| Empirical formula | $C_{14}H_{12}CdN_4O_2S_2$ | $C_{28}H_{24}Cd_2N_8O_4S_4$ | $C_{48}H_{44}Cd_4N_{20}O_8$ | $C_{46}H_{40}Cd_4N_{20}O_8$ | $C_{52}H_{44}Cd_4N_{12}O_{12}$ | $C_{50}H_{40}Cd_4N_{12}O_{12}$ | $C_{46}H_{40}Cd_4N_{16}O_{14}$ | $C_{48}H_{40}Cd_4N_{12}O_{16}$ | $C_{48}H_{40}Cd_4N_{12}O_{16}$ |
| Formula weight | 444.80 | 889.59 | 1478.63 | 1450.58 | 1478.59 | 1450.54 | 1490.54 | 1490.52 | 1490.52 |
| Temperature [K] | 293.0(2) | 293.0(2) | 293.0(2) | 293.0(2) | 293.0(2) | 293.0(2) | 293.0(2) | 293.0(2) | 293.0(2) |
| Wavelength [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | orthorhombic | triclinic | tetragonal | monoclinic | tetragonal | monoclinic | monoclinic | monoclinic | orthorhombic |
| Space group | $P2_12_12_1$ | P-1 | $I4_1/acd$ | $P2_1/n$ | $I4_1/acd$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | Pbca |
| Unit cell dimensions [Å, °] | a = 8.5167(4)<br>b = 8.9163(4)<br>c = 22.2579(10) | a = 8.5984(6)<br>b = 9.9463(7)<br>c = 10.6576(6)<br>α = 100.460(5)<br>β = 108.911(5)<br>γ= 92.653(5) | a = 18.4180(5)<br>b = 18.4180(5)<br>c = 30.698(2) | a = 13.4980(5)<br>b = 12.6484(6)<br>c = 15.9441(6)<br>β = 107.628(4) | a = 18.4690(7)<br>b = 18.4690(7)<br>c = 30.558(2) | a = 13.4790(9)<br>b = 12.6998(6)<br>c = 15.9841(13)<br>β = 106.524(8) | a = 13.4664(6)<br>b = 12.4449(5)<br>c = 16.1614(7)<br>β = 100.398(5) | a = 13.3914(6)<br>b = 12.5725(5)<br>c = 16.1350(9)<br>β = 101.274(4) | a = 12.5084(5)<br>b = 19.1468(9)<br>c = 22.4328(9) |
| Volume [$Å^3$] | 1690.22(13) | 842.50(9) | 10413.6(8) | 2594.29(19) | 10423.4(9) | 2623.2(3) | 2664.00(19) | 2664.1(2) | 5372.6(4) |
| Z | 4 | 1 | 8 | 2 | 8 | 2 | 2 | 2 | 4 |
| Density (calculated) [$Mg/m^3$] | 1.748 | 1.753 | 1.886 | 1.857 | 1.884 | 1.836 | 1.858 | 1.858 | 1.843 |
| Absorption coefficient [$mm^{-1}$] | 1.551 | 1.556 | 1.686 | 1.690 | 1.686 | 1.673 | 1.655 | 1.655 | 1.642 |
| F(000) | 880 | 440 | 582 | 1424 | 5824 | 1424 | 1464 | 1464 | 2928 |
| Crystal size [mm] | 1.69x0.35x0.22 | 1.39 x 0.76x 0.54 | 1.06x0.96x0.72 | 1.00x0.61x0.51 | 0.10x0.06x0.01 | 0.15x0.13x0.10 | 0.19 x0.10x0.07 | 0.12x 0.06x 0.03 | 0.12x0.05x0.03 |
| θ range for data collection [°] | 3.31 to 25.04 | 3.46 to 25.04 | 3.46 to 25.04 | 3.44 to 25.05 | 3.46 to 25.05 | 3.45 to 25.05 | 3.48 to 25.10 | 3.49 to 25.10 | 3.35 to 25.10 |
| Index ranges | $-9 \le h \le 10$<br>$-10 \le k \le 10$<br>$-24 \le l \le 26$ | $-10 \le h \le 10$<br>$-12 \le k \le 11$<br>$-12 \le l \le 12$ | $-16 \le h \le 21$<br>$-21 \le k \le 18$,<br>$-36 \le l \le 35$ | $-16 \le h \le 12$<br>$-11 \le k \le 15$<br>$-18 \le l \le 18$ | $-19 \le h \le 20$<br>$-22 \le k \le 21$,<br>$-36 \le l \le 31$ | $-13 \le h \le 16$<br>$-15 \le k \le 15$<br>$-19 \le l \le 15$ | $-14 \le h \le 16$<br>$-14 \le k \le 14$<br>$-19 \le l \le 19$ | $-13 \le h \le 15$<br>$-15 \le k \le 13$<br>$-17 \le l \le 19$ | $-14 \le h \le 14$<br>$-19 \le k \le 22$<br>$-26 \le l \le 22$ |
| Reflections collected | 5938 | 7106 | 12961 | 10617 | 13401 | 11587 | 13051 | 11503 | 17425 |
| Independent reflections | 2951 ($R_{int}$=0.0289) | 2968 ($R_{(int)}$=0.0579) | 2298 ($R_{(int)}$=0.0710) | 4578 ($R_{(int)}$=0.0340) | 2299 ($R_{(int)}$=0.1223) | 4626 ($R_{(int)}$=0.0561) | 4731 ($R_{int}$=0.0390) | 4731 ($R_{(int)}$=0.0661) | 4775 ($R_{(int)}$ = 0.0619) |
| Completeness to 2theta [%] | 99.7 | 99.7% | 99.7% | 99.8% | 99.7 % | 99.8 % | 99.8 | 99.7 | 99.8% |
| Max. and min. transmission | 1.000 and 0.654 | 1.000 and 0.838 | 1.000 and 0.656 | 1.000 and 0.855 | 1.000 and 0.375 | 1.000 and 0.647 | 1.000 and 0.125 | 1.000 and 0.552 | 1.000 and 0.559 |
| Data / restraints / parameters | 2951 / 0 / 210 | 2968 / 0 / 210 | 2298 / 0 / 182 | 4578 / 0 / 354 | 2299 / 0 / 182 | 4626 / 0 / 354 | 4731 / 0 / 363 | 4731 / 0 / 363 | 4775 / 0 / 363 |
| Goodness-of-fit on $F^2$ | 1.063 | 1.017 | 1.031 | 0.978 | 0.994 | 1.029 | 1.058 | 1.046 | 1.090 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0284<br>$wR_2$ = 0.0592 | R1 = 0.0426<br>wR2 = 0.0962 | R1 = 0.0384<br>wR2 = 0.0832 | R1 = 0.0303<br>wR2 = 0.0596 | R1 = 0.0579<br>wR2 = 0.1339 | R1 = 0.0561<br>wR2 = 0.1395 | $R_1$ = 0.0376<br>$wR_2$ = 0.0860 | R1 = 0.0592<br>wR2 = 0.1523 | R1 = 0.0571<br>wR2 = 0.0979 |
| R indices (all data) | $R_1$ = 0.0346<br>$wR_2$ = 0.0612 | R1 = 0.0558<br>wR2 = 0.1010 | R1 = 0.0717<br>wR2 = 0.0953 | R1 = 0.0513<br>wR2 = 0.0649 | R1 = 0.0838<br>wR2 = 0.1500 | R1 = 0.0838<br>wR2 = 0.1500 | $R_1$ = 0.0549<br>$wR_2$ = 0.0947 | R1 = 0.0773<br>wR2 = 0.1677 | R1 = 0.1019<br>wR2 = 0.1092 |
| Absolute structure parameter | -0.03(3) | | | | | | | | |
| Largest diff. peak and hole[$eÅ^{-3}$] | 0.442 and -0.319 | 0.488 and -0.593 | 0.739 and -0.966 | 0.495 and -0.380 | 1.395 and -0.788 | 1.395 and -0.788 | 0.686 and -0.648 | 1.546 and -1.565 | 1.924 and -0.844 |

**Table S2.** Crystallographic data and refinement details of **M** helical structure **1**.

| | **1a** | **1b** | **1c** | **1d** | **1e** | **1f** | **1g** |
|---|---|---|---|---|---|---|---|
| Empirical formula | $C_{14}H_{12}Cd\ N_4O_2S_2$ | $C_{14}H_{12}CdN_4O_2S_2$ | $C_{14}H_{12}CdN_4O_2S_2$ | $C_{14}H_{12}CdN_4O_2S_2$ | $C_{14}H_{12}CdN_4O_2S_2$ | $C_{14}H_{12}CdN_4O_2S_2$ | $C_{14}H_{12}CdN_4O_2S_2$ |
| Formula weight | 444.80 | 444.80 | 444.80 | 444.80 | 444.80 | 444.80 | 444.80 |
| Temperature [K] | 298.0(2) | 298.0(2) | 298.0(2) | 298.0(2) | 298.0(2) | 298.0(2) | 298.0(2) |
| Wavelength [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ |
| Unit cell dimensions [Å, °] | a = 8.5332(4) | a = 8.5164(6) | a = 8.5169(6) | a = 8.5034(5) | a = 8.5096(4) | a = 8.5129(5) | a = 8.4889(11) |
| | b = 8.9171(5) | b = 8.9025(8) | b = 8.9151(6) | b = 8.9150(6) | b = 8.9114(4) | b = 8.9041(6) | b = 8.8830(12) |
| | c = 22.3027(12) | c = 22.273(2) | c = 22.2586(19) | c = 22.2783(15) | c = 22.2113(10) | c = 22.2571(16) | c = 22.185(3) |
| Volume [$Å^3$] | 1697.05(15) | 1688.7(2) | 1690.1(2) | 1688.86(19) | 1684.35(13) | 1687.1(2) | 1672.9(4) |
| Z | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| Density (calculated) [$Mg/m^3$] | 1.741 | 1.750 | 1.748 | 1.749 | 1.754 | 1.751 | 1.766 |
| Absorption coefficient [$mm^{-1}$] | 1.545 | 1.553 | 1.552 | 1.553 | 1.557 | 1.554 | 1.568 |
| F(000) | 880 | 880 | 880 | 880 | 880 | 880 | 880 |
| Crystal size [mm] | 1.69x0.35x0.22 | 1.5x0.25x0.10 | 0.16x0.15x0.08 | 0.20x0.13x0.07 | 0.42x0.30x0.25 | 0.33x0.19x0.09 | 1.64x0.27x0.06 |
| θ range for data collection [°] | 3.43 to 25.05 | 3.43 to 25.04 | 3.43 to 25.05 | 3.43 to 25.03 | 3.65 to 25.05 | 3.44 to 25.04 | 3.58 to 25.04 |
| Index ranges | $-10 \le h \le 8$ | $-8 \le h \le 10$ | $-10 \le h \le 10$ | $-10 \le h \le 9$ | $-10 \le h \le 10$ | $-10 \le h \le 10$ | $-8 \le h \le 10$ |
| | $-10 \le k \le 9$ | $-10 \le k \le 10$ | $-10 \le k \le 10$ | $-10 \le k \le 10$ | $-10 \le k \le 10$ | $-10 \le k \le 8$ | $-8 \le k \le 10$ |
| | $-26 \le l \le 23$ | $-26 \le l \le 20$ | $-20 \le l \le 26$ | $-21 \le l \le 26$ | $-18 \le l \le 26$ | $-26 \le l \le 26$ | $-23 \le l \le 26$ |
| Reflections collected | 5441 | 5305 | 5508 | 5549 | 8516 | 9085 | 5771 |
| Independent reflections | 2971 ($R_{int}$=0.0325) | 2861 ($R_{int}$=0.0363) | 2862 ($R_{int}$=0.0366) | 2968 ($R_{int}$=0.0335) | 2977($R_{int}$ = 0.0325) | 2986 ($R_{int}$=0.0360) | 2921 ($R_{int}$=0.0405) |
| Completeness to $2\theta$=50º [%] | 99.4 | 99.7 | 99.7 | 99.7 | 99.5 | 99.7 | 99.6 |
| Max. and min. transmission | 1.000 and 0.798 | 1.000 and 0.783 | 1.000 and 0.733 | 1.000 and 0.638 | 1.000 and 0.478 | 1.000 and 0.644 | 1.000 and 0.583 |
| Data / restraints / parameters | 2971/ 0 / 210 | 2861 / 0 / 210 | 2862 / 0 / 210 | 2968 / 0 / 210 | 2977 / 0 / 210 | 2986 / 0 / 210 | 2921 / 0 / 210 |
| Goodness-of-fit on $F^2$ | 1.092 | 1.092 | 1.166 | 1.064 | 1.059 | 1.159 | 1.100 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0341 | $R_1$ = 0.0368 | $R_1$ = 0.0391 | $R_1$ = 0.0305 | $R_1$ = 0.0268 | $R_1$ = 0.0312 | $R_1$ = 0.0418 |
| | $wR_2$ = 0.0899 | $wR_2$ = 0.0797 | $wR_2$ = 0.0711 | $wR_2$ = 0.0613 | $wR_2$ = 0.0486 | $wR_2$ = 0.0729 | $wR_2$ = 0.1011 |
| R indices (all data) | $R_1$ = 0.0453 | $R_1$ = 0.0465 | $R_1$ = 0.0495 | $R_1$ = 0.0387 | $R_1$ = 0.0312 | $R_1$ = 0.0359 | $R_1$ = 0.0503 |
| | $wR_2$ = 0.1224 | $wR_2$ = 0.0833 | $wR_2$ = 0.0944 | $wR_2$ = 0.0647 | $wR_2$ = 0.0501 | $wR_2$ = 0.0747 | $wR_2$ = 0.1065 |
| Absolute structure parameter | -0.01(5) | -0.03(4) | 0.06(6) | -0.06(3) | -0.02(2) | 0.01(4) | 0.00(5) |
| Largest diff. peak and hole[e $Å^{-3}$] | 0.593 and -0.370 | 0.686 and -0.400 | 0.445 and -0.594 | 0.536 and -0.321 | 0.239 and -0.249 | 0.464 and -0.311 | 0.821 and -0.577 |

**Table S3**. Short intra- and intermolecular contacts detected in the structures **2-9**.

| D—H•••A | D—H [Å] | H•••A [Å] | D•••A [Å] | D—H•••A [°] |
|---|---|---|---|---|
| | | **2** | | |
| O(2)—H(1A)•••N(98)_#1 | 0.82 | 1.96 | 2.769(7) | 167.0 |
| C(12)—H(12C)•••O(2) | 0.96 | 2.45 | 2.791(7) | 100.0 |
| | | **4** | | |
| C(8)—H(8)•••N(97)_#2 | 0.93 | 2.61 | 3.533(9) | 172.0 |
| C(8)–H(8)•••O(2)_#3 | 0.93 | 2.36 | 2.674(7) | 100.0 |
| C(11)–H(11)•••N(98) | 0.93 | 2.61 | 3.317(9) | 133.0 |
| C(12)–H(12C)•••O(1) | 0.96 | 2.58 | 2.926(7) | 101.0 |
| C(12)–H(12C)•••N(99) | 0.96 | 2.57 | 3.291(8) | 132.0 |
| | | **5** | | |
| O(4)—H(4A)•••O(1)_#4 | 0.82 | 1.90 | 2.717(3) | 171.0 |
| C(2)—H(2)•••N(94)_#5 | 0.93 | 2.59 | 3.370(8) | 141.0 |
| C(14)—H(14)•••N(94)_#6 | 0.93 | 2.61 | 3.413(9) | 145.0 |
| C(20)—H(20)•••O(4) | 0.93 | 2.44 | 2.767(6) | 100.0 |
| | | **6** | | |
| C(4)—H(4)•••O(2) | 0.93 | 2.34 | 2.667(8) | 100.0 |
| C(12)—H(12B)•••O(1) | 0.96 | 2.58 | 2.916(10) | 101.0 |
| C(12)—H(12B)•••N(3)_#3 | 0.96 | 2.60 | 3.302(11) | 131.0 |
| | | **7** | | |
| O(4)—H(4A)•••O(1)_#7 | 0.82 | 1.92 | 2.738(7) | 171.0 |
| C(2)—H(2)••• O(96) _#5 | 0.93 | 2.46 | 3.204(16) | 137.0 |
| C(4)—H(4)••• O(2) | 0.93 | 2.47 | 2.788(10) | 100.0 |
| C(20)—H(20)••• O(4) | 0.93 | 2.45 | 2.761(9) | 100.0 |
| | | **8** | | |
| O(4)—H(4A)•••O(1)_#8 | 0.82 | 1.89 | 2.712(4) | 177.0 |
| C(2)—H(2)•••O(7) _#9 | 0.93 | 2.31 | 3.080(10) | 140.0 |
| C(4)—H(4)•••O(2) | 0.93 | 2.47 | 2.787(8) | 100.0 |
| C(14)—H(14)•••O(7)_#10 | 0.93 | 2.58 | 3.357(10) | 141.0 |
| C(20)—H(20)•••O(4) | 0.93 | 2.44 | 2.754(7) | 100.0 |
| C(20)—H(20)•••O(4) | 0.93 | 2.52 | 3.149(10) | 125.0 |
| | | **9a** | | |
| O(4)—H(4A)•••O(1)_#4 | 0.82 | 1.90 | 2.712(4) | 174.0 |
| C(2)—H(2)•••O(7)_#9 | 0.93 | 2.32 | 3.079(9) | 139.0 |
| C(4)—H(4)•••O(2) | 0.93 | 2.47 | 2.788(7) | 100.0 |
| C(20)—H(20)•••O(4) | 0.93 | 2.46 | 2.772(6) | 100.0 |
| C(23)—H(23)•••O(5) | 0.93 | 2.49 | 3.114(11) | 125.0 |
| | | **9b** | | |
| O(4)—H(4A)•••O(1) | 0.82 | 1.89 | 2.705(6) | 177.0 |
| C(1)—H(1)•••O(7)_#11 | 0.93 | 2.54 | 3.214(12) | 130.0 |
| C(8) —H(8)•••O(7)_#12 | 0.93 | 2.58 | 3.250(12) | 129.0 |
| C(14)—H(14)•••O(2) | 0.93 | 2.45 | 2.773(10) | 101.0 |
| C(15)—H(15)•••O(7)_#13 | 0.93 | 2.56 | 3.206(11) | 127.0 |
| C(15)—H(15)•••O(7)_#14 | 0.93 | 2.45 | 2.768(10) | 100.0 |
| C(23)—H(23)•••O(5) | 0.93 | 2.43 | 3.080(11) | 127.0 |

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**.

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.402(3) | N(1)–Cd(1)–N(2) | 82.44(11) |
| Cd(1)–N(2) | 2.322(3) | N(1)–Cd(1)–O(1) | 65.67(10) |
| Cd(1)–O(1) | 2.603(3) | N(2)–Cd(1)–O(1) | 64.62(10) |
| Cd(1)–N(98) | 2.273(4) | N(1)–Cd(1)–N(99) | 85.21(13) |
| Cd(1)–N(99) | 2.287(4) | N(1)–Cd(1)–N(98) | 169.88(14) |
| Cd(1)–S(99) | 2.5756(12) | N(1)–Cd(1)–S(99) | 101.67(9) |
| N(98)–C(98) | 1.129(6) | N(2)–Cd(1)–N(99) | 100.15(13) |
| C(98)–S(98) | 1.639(5) | N(2)–Cd(1)–N(98) | 88.22(13) |
| C(99)–N(99) | 1.138(6) | N(2)–Cd(1)–S(99) | 155.35(9) |
| C(99)–S(99)#1 | 1.642(5) | O(1)–Cd(1)–N(99) | 148.02(12) |
| S(99)-C(99)#2 | 1.642(5) | O(1)–Cd(1)–N(98) | 113.65(14) |
| | | O(1)–Cd(1)–S(99) | 94.64(7) |
| | | N(98)–Cd(1)–N(99) | 92.64(16) |
| | | N(98)–Cd(1)–S(99) | 88.44(12) |
| | | N(99)–Cd(1)–S(99) | 104.39(11) |
| | | C(99)–N(99)–Cd(1) | 165.9(4) |
| | | C(98)–N(98)–Cd(1) | 164.7(4) |
| | | C(99)#2–S(99)–Cd(1) | 101.84(16) |
| | | N(98)–C(98)–S(98) | 179.0(5) |
| | | N(99)–C(99)–S(99)#1 | 177.3(4) |

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**.

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.383(3) | N(1)–Cd(1)–N(2) | 78.58(12) |
| Cd(1)–N(2) | 2.370(4) | N(1)–Cd(1)–O(1) | 66.67(12) |
| Cd(1)–O(1) | 2.498(3) | N(2)–Cd(1)–O(1) | 68.00(11) |
| Cd(1)–N(99)#1 | 2.265(4) | N(99)#1–Cd(1)–N(1) | 84.19(15) |
| Cd(1)–S(99) | 2.6336(14) | N(1)–Cd(1)–S(98) | 168.73(11) |
| Cd(1)–S(98) | 2.5953(15) | N(1)–Cd(1)–S(99) | 92.45(11) |
| C(98)–N(98) | 1.142(7) | N(2)–Cd(1)–S(98) | 97.78(9) |
| C(98)–S(98) | 1.663(6) | N(2)–Cd(1)–S(99) | 96.92(10) |
| C(99)–N(99) | 1.148(6) | N(99)#1–Cd(1)–N(2) | 154.69(15) |
| C(99)–S(99) | 1.641(5) | N(99)#1–Cd(1)–S(98) | 95.54(13) |
| | | N(99)#1–Cd(1)–S(99) | 102.25(12) |
| | | S(98)–Cd(1)–S(99) | 98.60(6) |
| | | O(1)–Cd(1)–S(98) | 102.06(8) |
| | | O(1)–Cd(1)–S(99) | 155.80(8) |
| | | N(99)#1–Cd(1)–O(1) | 88.22(13) |
| | | C(98)–S(98)–Cd(1) | 99.45(18) |
| | | C(99)–S(99)–Cd(1) | 92.58(17) |
| | | C(99)–N(99)–Cd(1)#1 | 159.9(4) |
| | | N(98)–C(98)–S(98) | 177.9(6) |
| | | N(99)–C(99)–S(99) | 178.4(4) |

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

**Table S6**. The experimental and calculated bond lengths [Å] and angles [°] for **4**.

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.301(5) | N(1)–Cd(1)–N(2) | 99.51(18) |
| Cd(1)–N(2) | 2.373(5) | N(99)–Cd(1)–N(1) | 87.87(19) |
| Cd(1)–N(99) | 2.247(5) | N(99)–Cd(1)–N(2) | 92.64(19) |
| Cd(1)–O(1) | 2.392(3) | N(1)–Cd(1)–O(1) | 68.98(14) |
| Cd(1)–O(1)#1 | 2.449(4) | N(2)–Cd(1)–O(1) | 145.16(14) |
| O(1)–Cd(1)#1 | 2.449(4) | N(99)–Cd(1)–O(1) | 118.63(17) |
| O(1)–Cd(1)#2 | 2.246(4) | N(1)–Cd(1)–O(1)#1 | 101.74(14) |
| Cd(1)–O(1)#3 | 2.246(4) | N(2)–Cd(1)–O(1)#1 | 70.78(14) |
| N(97)–N(98) | 1.146(8) | N(99)–Cd(1)–O(1)#1 | 161.88(16) |
| N(98)–N(99) | 1.167(7) | O(1)–Cd(1)–O(1)#1 | 79.37(13) |
| | | O(1)#3–Cd(1)–O(1) | 76.33(14) |
| | | O(1)#3–Cd(1)–O(1)#1 | 75.17(13) |
| | | O(1)#3–Cd(1)–N(1) | 145.06(14) |
| | | O(1)#3–Cd(1)–N(2) | 111.59(16) |
| | | O(1)#3–Cd(1)–N(99) | 105.6(2) |
| | | Cd(1)–O(1)–Cd(1)#1 | 97.90(13) |
| | | Cd(1)#2–O(1)–Cd(1) | 104.31(14) |
| | | Cd(1)#2–O(1)–Cd(1)#1 | 102.49(14) |
| | | N(98)–N(99)–Cd(1) | 131.6(5) |
| | | N(97)–N(98)–N(99) | 177.5(8) |

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**.

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.291(3) | N(1)–Cd(1)–N(3) | 107.48(11) |
| Cd(1)–N(3) | 2.345(3) | N(99)–Cd(1)–N(1) | 102.49(12) |
| Cd(1)–O(1) | 2.367(2) | N(99)–Cd(1)–N(3) | 95.02(11) |
| Cd(1)–O(3) | 2.242(2) | N(1)–Cd(1)–O(1) | 71.05(10) |
| Cd(1)-O(3)#1 | 2.319(2) | N(1)–Cd(1)–O(3) | 149.08(10) |
| Cd(1)–N(99) | 2.269(3) | N(1)–Cd(1)–O(3)#1 | 105.78(9) |
| Cd(2)–N(2) | 2.376(3) | N(3)–Cd(1)–O(1) | 102.99(9) |
| Cd(2)–N(4) | 2.373(3) | N(3)–Cd(1)–O(3) | 71.63(10) |
| Cd(2)–O(1) | 2.285(2) | N(3)–Cd(1)–O(3)#1 | 146.56(9) |
| Cd(2)–O(3) | 2.393(2) | N(99)–Cd(1)–O(1) | 161.94(10) |
| Cd(2)–N(96) | 2.211(4) | N(99)–Cd(1)–O(3) | 108.39(11) |
| Cd(2)–N(99)#1 | 2.322(3) | N(99)–Cd(1)–O(3)#1 | 81.02(10) |
| N(94)–N(95) | 1.146(6) | O(3)–Cd(1)–O(1) | 78.98(8) |
| N(95)–N(96) | 1.156(5) | O(3)#1–Cd(1)–O(1) | 84.57(8) |
| N(97)–N(98) | 1.133(5) | O(3)–Cd(1)–O(3)#1 | 78.16(8) |
| N(98)–N(99) | 1.170(5) | N(98)–N(99)–Cd(1) | 123.1(3) |
| | | Cd(1)–N(99)–Cd(2)#1 | 101.37(13) |
| | | N(4)–Cd(2)–N(2) | 101.11(11) |
| | | N(96)–Cd(2)–N(2) | 92.54(14) |
| | | N(99)#1–Cd(2)–N(2) | 164.96(13) |
| | | N(96)–Cd(2)–N(4) | 95.97(14) |
| | | N(99)#1–Cd(2)–N(4) | 92.01(12) |
| | | N(96)–Cd(2)–N(99)#1 | 93.39(14) |
| | | N(2)–Cd(2)–O(1) | 69.85(10) |
| | | N(2)–Cd(2)–O(3) | 99.31(9) |
| | | N(4)–Cd(2)–O(1) | 143.68(10) |
| | | N(4)–Cd(2)–O(3) | 69.08(9) |
| | | N(96)–Cd(2)–O(1) | 118.99(13) |
| | | N(96)–Cd(2)–O(3) | 162.38(13) |
| | | O(1)–Cd(2)–N(99)#1 | 95.21(11) |
| | | N(99)#1–Cd(2)–O(3) | 78.40(9) |
| | | O(1)–Cd(2)–O(3) | 77.61(7) |
| | | N(95)–N(96)–Cd(2) | 122.2(3) |
| | | N(98)–N(99)–Cd(2)#1 | 130.8(3) |
| | | N(94)–N(95)–N(96) | 177.7(6) |
| | | N(97)–N(98)–N(99) | 178.1(5) |

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**.

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.360(6) | N(1)–Cd(1)–N(2) | 98.3(2) |
| Cd(1)–N(2) | 2.324(6) | N(99)–Cd(1)–N(1) | 92.2(3) |
| Cd(1)–N(99) | 2.205(7) | N(99)–Cd(1)–N(2) | 90.9(2) |
| Cd(1)–O(1) | 2.481(5) | N(1)–Cd(1)–O(1) | 70.40(19) |
| Cd(1)–O(1)#1 | 2.363(5) | N(2)–Cd(1)–O(1) | 100.65(19) |
| O(1)–Cd(1)#1 | 2.363(5) | N(99)–Cd(1)–O(1) | 160.2(2) |
| O(1)–Cd(1)#2 | 2.248(5) | N(1)–Cd(1)–O(1)#1 | 144.73(19) |
| Cd(1)–O(1)#3 | 2.248(5) | N(2)–Cd(1)–O(1)#1 | 69.21(19) |
| C(99)–N(99) | 1.120(11) | N(99)–Cd(1)–O(1)#1 | 119.9(2) |
| C(99)–O(99) | 1.200(11) | O(1)–Cd(1)–O(1)#1 | 79.50(18) |
| | | O(1)#3–Cd(1)–O(1) | 75.11(18) |
| | | O(1)#3–Cd(1)–O(1)#1 | 77.52(19) |
| | | O(1)#3–Cd(1)–N(1) | 110.7(2) |
| | | O(1)#3–Cd(1)–N(2) | 146.63(19) |
| | | O(1)#3–Cd(1)–N(99) | 103.7(2) |
| | | Cd(1)–O(1)–Cd(1)#1 | 98.12(17) |
| | | Cd(1)#2–O(1)–Cd(1) | 100.98(19) |
| | | Cd(1)#2–O(1)–Cd(1)#1 | 104.69(19) |
| | | C(99)–N(99)–Cd(1) | 145.5(8) |
| | | N(99)–C(99)–O(99) | 179.3(14) |

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**.

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.299(6) | N(1)–Cd(1)–N(3) | 107.5(2) |
| Cd(1)–N(3) | 2.366(6) | N(99)–Cd(1)–N(1) | 101.0(2) |
| Cd(1)–O(1) | 2.381(5) | N(99)–Cd(1)–N(3) | 95.2(2) |
| Cd(1)–O(3) | 2.241(4) | N(1)–Cd(1)–O(1) | 71.16(19) |
| Cd(1)–O(3)#1 | 2.310(5) | N(1)–Cd(1)–O(3) | 148.53(19) |
| Cd(1)–N(99) | 2.258(6) | N(1)–Cd(1)–O(3)#1 | 105.28(18) |
| Cd(2)–N(2) | 2.415(7) | N(3)–Cd(1)–O(1) | 102.01(19) |
| Cd(2)–N(4) | 2.385(6) | N(3)–Cd(1)–O(3) | 71.37(18) |
| Cd(2)–O(1) | 2.287(5) | N(3)–Cd(1)–O(3)#1 | 146.86(18) |
| Cd(2)–O(3) | 2.408(4) | N(99)–Cd(1)–O(1) | 162.5(2) |
| Cd(2)–N(96) | 2.184(7) | N(99)–Cd(1)–O(3) | 110.5(2) |
| Cd(2)–N(99)#1 | 2.341(7) | N(99)–Cd(1)–O(3)#1 | 82.8(2) |
| C(96)–N(96) | 1.135(12) | O(3)–Cd(1)–O(1) | 78.25(15) |
| C(96)–O(96) | 1.161(14) | O(3)#1–Cd(1)–O(1) | 84.34(15) |
| C(99)–N(99) | 1.159(11) | O(3)–Cd(1)–O(3)#1 | 78.37(16) |
| C(99)–O(99) | 1.197(12) | C(99)–N(99)–Cd(1) | 128.0(7) |
| | | Cd(1)–N(99)–Cd(2)#1 | 100.0(3) |
| | | N(4)–Cd(2)–N(2) | 100.0(2) |
| | | N(96)–Cd(2)–N(2) | 90.7(3) |
| | | N(99)#1–Cd(2)–N(2) | 165.7(2) |
| | | N(96)–Cd(2)–N(4) | 98.2(3) |
| | | N(99)#1–Cd(2)–N(4) | 91.9(2) |
| | | N(96)–Cd(2)–N(99)#1 | 95.6(3) |
| | | N(2)–Cd(2)–O(1) | 69.1(2) |
| | | N(2)–Cd(2)–O(3) | 97.71(18) |
| | | N(4)–Cd(2)–O(1) | 142.16(19) |
| | | N(4)–Cd(2)–O(3) | 68.70(17) |
| | | N(96)–Cd(2)–O(1) | 117.5(3) |
| | | N(96)–Cd(2)–O(3) | 165.4(3) |
| | | O(1)–Cd(2)–N(99)#1 | 96.6(2) |
| | | N(99)#1–Cd(2)–O(3) | 79.01(19) |
| | | O(1)–Cd(2)–O(3) | 76.83(15) |
| | | C(96)–N(96)–Cd(2) | 132.7(8) |
| | | C(99)–N(99)–Cd(2)#1 | 129.4(6) |
| | | N(96)–C(96)–O(96) | 175.8(13) |
| | | N(99)–C(99)–O(99) | 177.6(12) |

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

**Table S10**. The selected bond lengths [Å] and angles [°] for **8**.

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.293(4) | N(1)–Cd(1)–N(3) | 107.31(14) |
| Cd(1)–N(3) | 2.347(4) | N(99)–Cd(1)–N(1) | 100.49(16) |
| Cd(1)–O(1) | 2.386(3) | N(99)–Cd(1)–N(3) | 96.38(15) |
| Cd(1)–O(3) | 2.243(3) | N(1)–Cd(1)–O(1) | 70.96(12) |
| Cd(1)–O(3)#1 | 2.314(3) | N(1)–Cd(1)–O(3) | 148.25(12) |
| Cd(1)–N(99) | 2.268(4) | N(1)–Cd(1)–O(3)#1 | 105.49(12) |
| Cd(2)–N(2) | 2.385(4) | N(3)–Cd(1)–O(1) | 103.49(12) |
| Cd(2)–N(4) | 2.381(4) | N(3)–Cd(1)–O(3) | 71.43(13) |
| Cd(2)–O(1) | 2.293(3) | N(3)–Cd(1)–O(3)#1 | 147.05(13) |
| Cd(2)–O(3) | 2.404(3) | N(99)–Cd(1)–O(1) | 159.91(14) |
| Cd(2)–O(5) | 2.427(5) | N(99)–Cd(1)–O(3) | 111.23(14) |
| Cd(2)–O(6) | 2.491(6) | N(99)–Cd(1)–O(3)#1 | 80.61(13) |
| Cd(2)–N(99)#1 | 2.313(4) | O(3)–Cd(1)–O(1) | 78.44(10) |
| N(97)–N(98) | 1.151(7) | O(3)#1–Cd(1)–O(1) | 84.24(9) |
| N(98)–N(99) | 1.174(6) | O(3)–Cd(1)–O(3)#1 | 79.09(10) |
| | | N(98)–N(99)–Cd(1) | 124.8(4) |
| | | Cd(1)–N(99)–Cd(2)#1 | 101.69(17) |
| | | Cd(2)–O(1)–Cd(1) | 100.04(11) |
| | | Cd(1)–O(3)–Cd(1)#1 | 100.91(10) |
| | | Cd(1)–O(3)–Cd(2) | 100.95(10) |
| | | Cd(1)#1–O(3)–Cd(2) | 97.66(10) |
| | | N(4)–Cd(2)–N(2) | 103.22(15) |
| | | N(2)–Cd(2)–O(1) | 69.26(14) |
| | | N(2)–Cd(2)–O(3) | 98.57(12) |
| | | N(2)–Cd(2)–O(5) | 82.98(19) |
| | | N(2)–Cd(2)–O(6) | 94.52(18) |
| | | N(4)–Cd(2)–O(1) | 143.48(13) |
| | | N(4)–Cd(2)–O(3) | 68.57(12) |
| | | N(4)–Cd(2)–O(5) | 82.20(18) |
| | | N(4)–Cd(2)–O(6) | 125.0(2) |
| | | O(1)–Cd(2)–O(3) | 77.13(10) |
| | | O(1)–Cd(2)–O(5) | 129.64(17) |
| | | O(1)–Cd(2)–O(6) | 91.52(18) |
| | | O(3)–Cd(2)–O(5) | 150.36(17) |
| | | O(3)–Cd(2)–O(6) | 158.25(17) |
| | | O(5)–Cd(2)–O(6) | 48.6(2) |
| | | O(1)–Cd(2)–N(99)#1 | 96.14(13) |
| | | N(99)#1–Cd(2)–N(2) | 165.39(16) |
| | | N(99)#1–Cd(2)–O(3) | 77.82(12) |
| | | N(99)#1–Cd(2)–O(5) | 107.24(19) |
| | | N(99)#1–Cd(2)–O(6) | 85.14(18) |
| | | N(99)#1–Cd(2)–N(4) | 88.75(15) |
| | | N(98)–N(99)–Cd(2)#1 | 130.7(4) |
| | | N(97)–N(98)–N(99) | 179.5(6) |

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

**Table S11**. The selected bond lengths [Å] and angles [°] for **9a.**

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.291(5) | N(1)–Cd(1)–N(3) | 106.86(18) |
| Cd(1)–N(3) | 2.361(4) | N(99)–Cd(1)–N(1) | 101.26(17) |
| Cd(1)–O(1) | 2.404(3) | N(99)–Cd(1)–N(3) | 95.99(15) |
| Cd(1)–O(3) | 2.244(3) | N(1)–Cd(1)–O(1) | 70.56(14) |
| Cd(1)–O(3)#1 | 2.312(3) | N(1)–Cd(1)–O(3) | 147.18(13) |
| Cd(1)–N(99) | 2.269(4) | N(1)–Cd(1)–O(3)#1 | 105.08(13) |
| Cd(2)–N(2) | 2.363(6) | N(3)–Cd(1)–O(1) | 102.44(13) |
| Cd(2)–N(4) | 2.371(4) | N(3)–Cd(1)–O(3) | 71.39(15) |
| Cd(2)–O(1) | 2.300(3) | N(3)–Cd(1)–O(3)#1 | 147.66(17) |
| Cd(2)–O(3) | 2.397(3) | N(99)–Cd(1)–O(1) | 161.31(13) |
| Cd(2)–O(5) | 2.435(6) | N(99)–Cd(1)–O(3) | 111.54(17) |
| Cd(2)–O(6) | 2.491(6) | N(99)–Cd(1)–O(3)#1 | 82.57(15) |
| Cd(2)–N(99)#1 | 2.334(5) | O(3)–Cd(1)–O(1) | 77.78(12) |
| C(99)–N(99) | 1.155(6) | O(3)#1–Cd(1)–O(1) | 83.49(12) |
| C(99)–O(99) | 1.189(7) | O(3)–Cd(1)–O(3)#1 | 79.10(10) |
| | | C(99)–N(99)–Cd(1) | 129.4(5) |
| | | Cd(1)–N(99)–Cd(2)#1 | 99.61(16) |
| | | Cd(2)–O(1)–Cd(1) | 100.09(14) |
| | | Cd(1)–O(3)–Cd(1)#1 | 100.90(10) |
| | | Cd(1)–O(3)–Cd(2) | 101.96(14) |
| | | Cd(1)#1–O(3)–Cd(2) | 96.60(9) |
| | | N(4)–Cd(2)–N(2) | 103.33(17) |
| | | N(2)–Cd(2)–O(1) | 69.36(14) |
| | | N(2)–Cd(2)–O(3) | 98.54(14) |
| | | N(2)–Cd(2)–O(5) | 82.7(2) |
| | | N(2)–Cd(2)–O(6) | 92.5(2) |
| | | N(4)–Cd(2)–O(1) | 143.47(13) |
| | | N(4)–Cd(2)–O(3) | 68.73(12) |
| | | N(4)–Cd(2)–O(5) | 80.65(19) |
| | | N(4)–Cd(2)–O(6) | 123.67(19) |
| | | O(1)–Cd(2)–O(3) | 76.89(12) |
| | | O(1)–Cd(2)–O(5) | 131.0(2) |
| | | O(1)–Cd(2)–O(6) | 92.77(19) |
| | | O(3)–Cd(2)–O(5) | 148.86(17) |
| | | O(3)–Cd(2)–O(6) | 160.96(18) |
| | | O(5)–Cd(2)–O(6) | 47.88(19) |
| | | O(1)–Cd(2)–N(99)#1 | 95.55(14) |
| | | N(99)#1–Cd(2)–N(2) | 164.74(15) |
| | | N(99)#1–Cd(2)–O(3) | 79.42(13) |
| | | N(99)#1–Cd(2)–O(5) | 106.9(2) |
| | | N(99)#1–Cd(2)–O(6) | 85.8(2) |
| | | N(99)#1–Cd(2)–N(4) | 90.11(18) |
| | | C(99)–N(99)–Cd(2)#1 | 130.9(5) |
| | | N(99)–C(99)–O(99) | 179.2(8) |

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

**Table S12**. The selected bond lengths [Å] and angles [°] for **9b**.

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Cd(1)–N(1) | 2.278(6) | N(1)–Cd(1)–N(3) | 106.5(2) |
| Cd(1)–N(3) | 2.354(6) | N(99)–Cd(1)–N(1) | 101.4(2) |
| Cd(1)–O(1)#1 | 2.394(4) | N(99)–Cd(1)–N(3) | 94.4(2) |
| Cd(1)–O(3) | 2.259(4) | N(1)–Cd(1)–O(1)#1 | 71.46(18) |
| Cd(1)–O(3)#1 | 2.297(4) | N(1)–Cd(1)–O(3) | 147.65(19) |
| Cd(1)–N(99) | 2.274(6) | N(1)–Cd(1)–O(3)#1 | 106.29(18) |
| Cd(2)–N(2) | 2.380(6) | N(3)–Cd(1)–O(1)#1 | 102.75(18) |
| Cd(2)–N(4) | 2.349(6) | N(3)–Cd(1)–O(3) | 70.52(19) |
| Cd(2)–O(1) | 2.286(4) | N(3)–Cd(1)–O(3)#1 | 147.00(18) |
| Cd(2)–O(3)#1 | 2.426(4) | N(99)–Cd(1)–O(1)#1 | 162.70(19) |
| Cd(2)–O(5) | 2.435(8) | N(99)–Cd(1)–O(3) | 110.88(19) |
| Cd(2)–O(6) | 2.500(7) | N(99)–Cd(1)–O(3)#1 | 82.41(19) |
| Cd(2)–N(99) | 2.324(6) | O(3)–Cd(1)–O(1)#1 | 77.76(15) |
| C(99)–N(99) | 1.168(10) | O(3)#1–Cd(1)–O(1)#1 | 84.53(15) |
| C(99)–O(99) | 1.186(10) | O(3)–Cd(1)–O(3)#1 | 79.96(16) |
| | | C(99)–N(99)–Cd(1) | 127.3(6) |
| | | Cd(1)–N(99)–Cd(2) | 100.4(2) |
| | | Cd(2)–O(1)–Cd(1)#1 | 101.50(16) |
| | | Cd(1)–O(3)–Cd(1)#1 | 100.04(16) |
| | | Cd(1)#1–O(3)–Cd(2)#1 | 96.74(15) |
| | | Cd(1)–O(3)–Cd(2)#1 | 101.28(16) |
| | | N(4)–Cd(2)–N(2) | 98.5(2) |
| | | N(2)–Cd(2)–O(1) | 70.04(19) |
| | | N(2)–Cd(2)–O(3)#1 | 96.93(18) |
| | | N(2)–Cd(2)–O(5) | 82.6(3) |
| | | N(2)–Cd(2)–O(6) | 97.1(2) |
| | | N(4)–Cd(2)–O(1) | 142.39(19) |
| | | N(4)–Cd(2)–O(3)#1 | 69.19(18) |
| | | N(4)–Cd(2)–O(5) | 80.9(2) |
| | | N(4)–Cd(2)–O(6) | 124.9(3) |
| | | O(1)–Cd(2)–O(3)#1 | 76.62(15) |
| | | O(1)–Cd(2)–O(5) | 130.0(2) |
| | | O(1)–Cd(2)–O(6) | 92.5(2) |
| | | O(3)#1–Cd(2)–O(5) | 149.7(2) |
| | | O(3)#1–Cd(2)–O(6) | 158.1(2) |
| | | O(5)–Cd(2)–O(6) | 49.4(2) |
| | | O(1)–Cd(2)–N(99) | 95.50(19) |
| | | N(99)–Cd(2)–N(2) | 165.5(2) |
| | | N(99)–Cd(2)–O(3)#1 | 78.66(18) |
| | | N(99)–Cd(2)–O(5) | 108.2(3) |
| | | N(99)–Cd(2)–O(6) | 83.6(2) |
| | | N(99)–Cd(2)–N(4) | 92.8(2) |
| | | C(99)–N(99)–Cd(2) | 132.1(6) |
| | | N(99)–C(99)–O(99) | 178.4(11) |

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

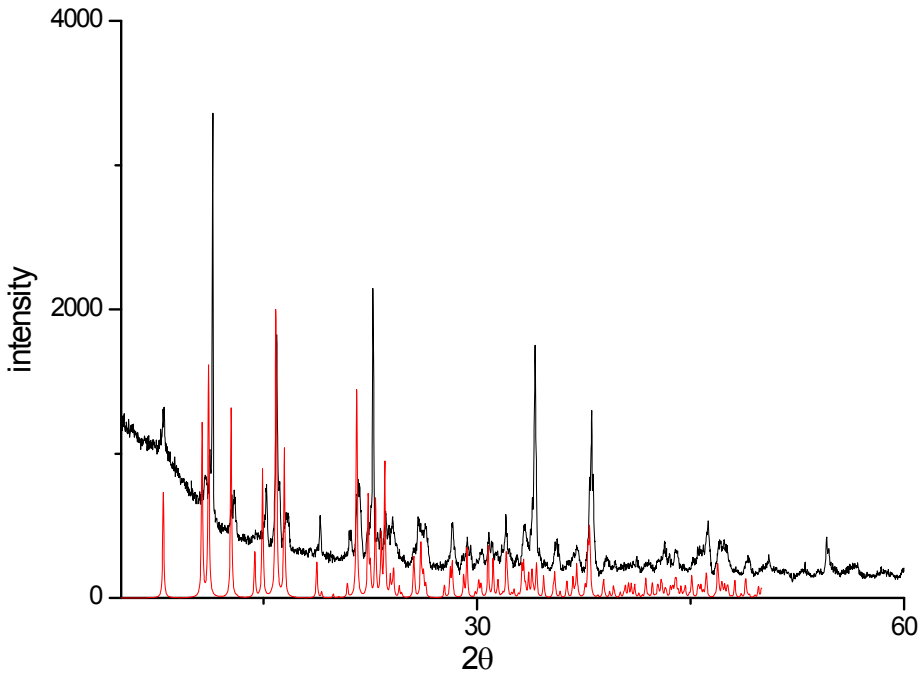



**Figure S1.** The XRPD spectrum (Cu−Kα radiation) of **1** (black), together with the calculated pattern from the single crystal data (red).

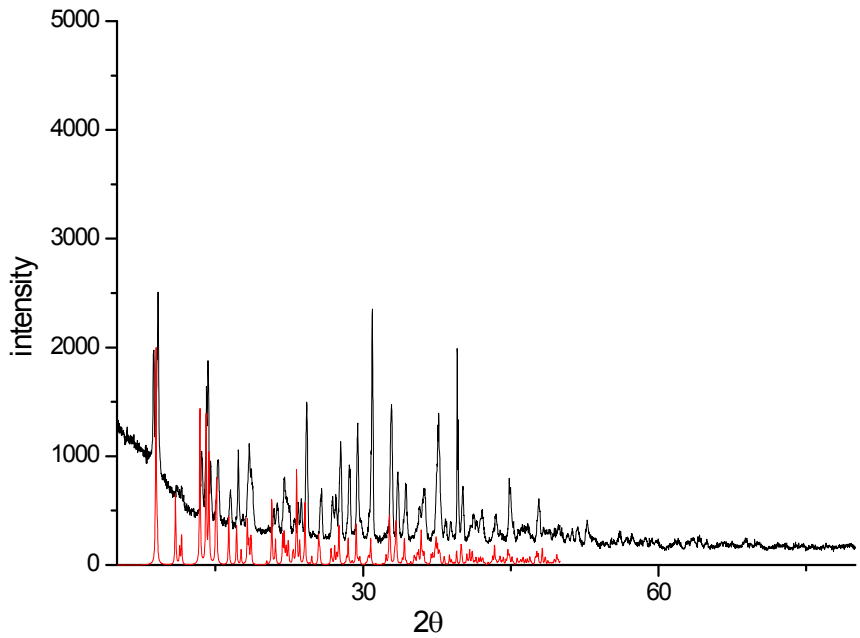



**Figure S2.** The XRPD spectrum (Cu−Kα radiation) of **2** (black), together with the calculated pattern from the single crystal data (red).

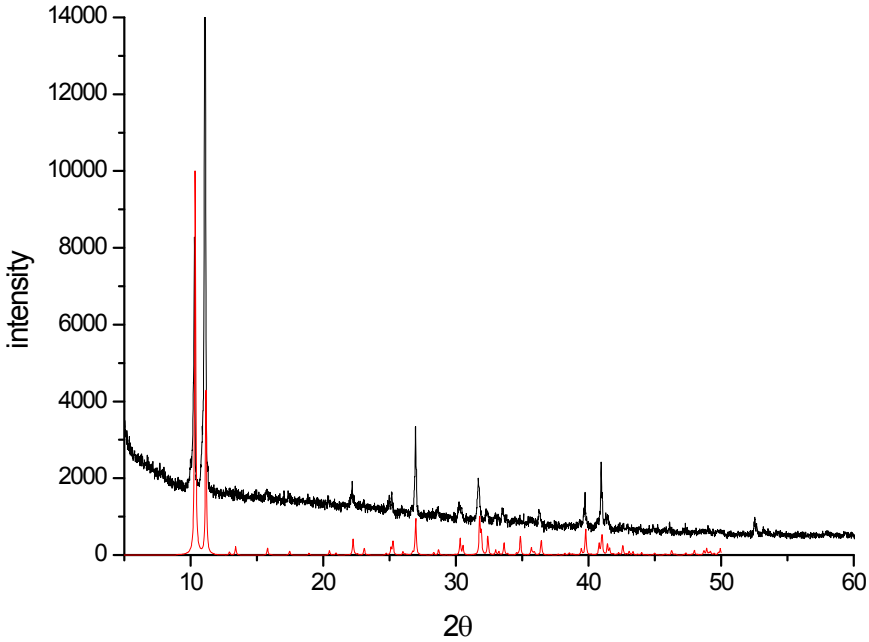



**Figure S3.** The XRPD spectrum (Co−Kα radiation) of **4** (black), together with the calculated pattern from the single crystal data (red).

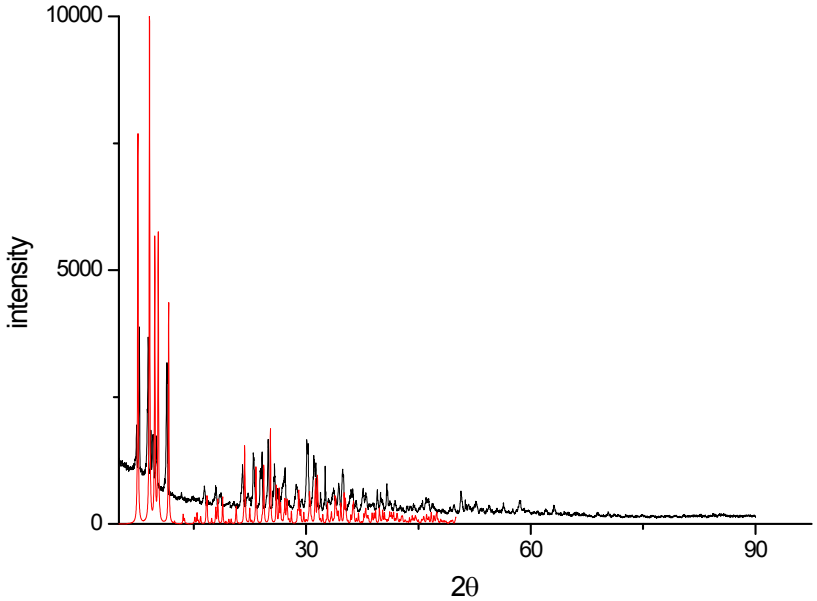



**Figure S4.** The XRPD spectrum (Cu−Kα radiation) of **5** (black), together with the calculated pattern from the single crystal data (red).

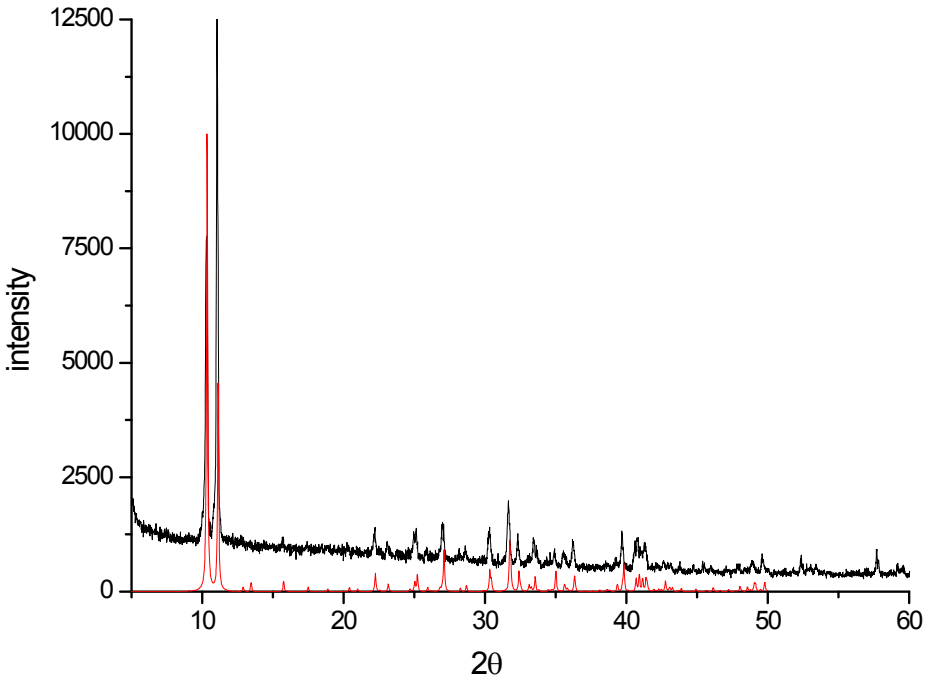



**Figure S5.** The XRPD spectrum (Co−Kα radiation) of **6** (black), together with the calculated pattern from the single crystal data (red).

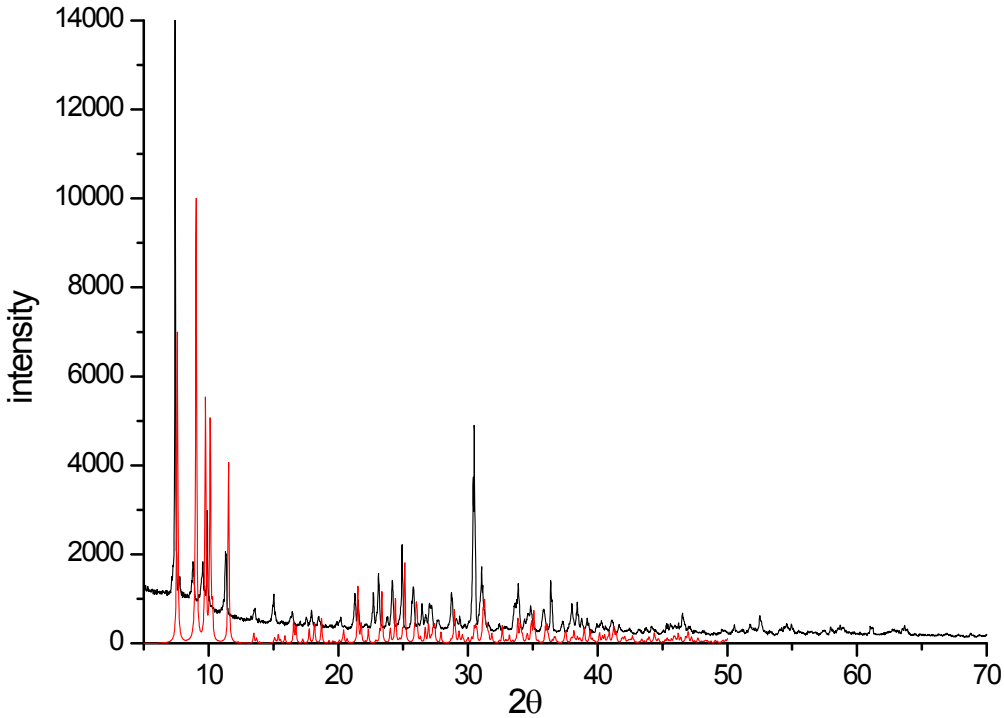



**Figure S6.** The XRPD spectrum (Cu−Kα radiation) of **7** (black), together with the calculated pattern from the single crystal data (red).

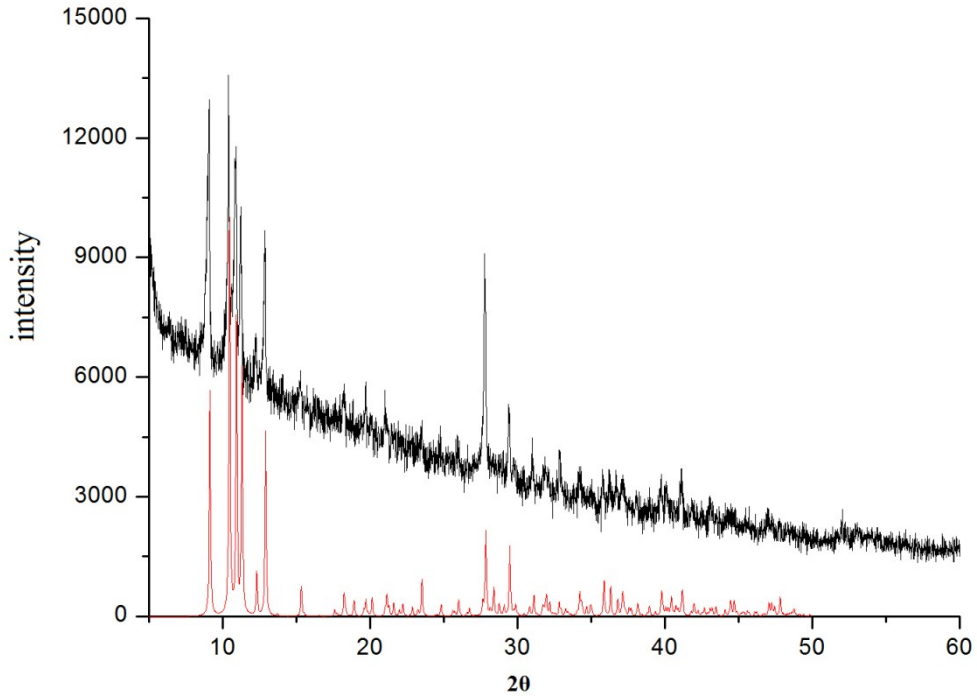



**Figure S7.** The XRPD spectrum (Co−Kα radiation) of **8** (black), together with the calculated pattern from the single crystal data (red).

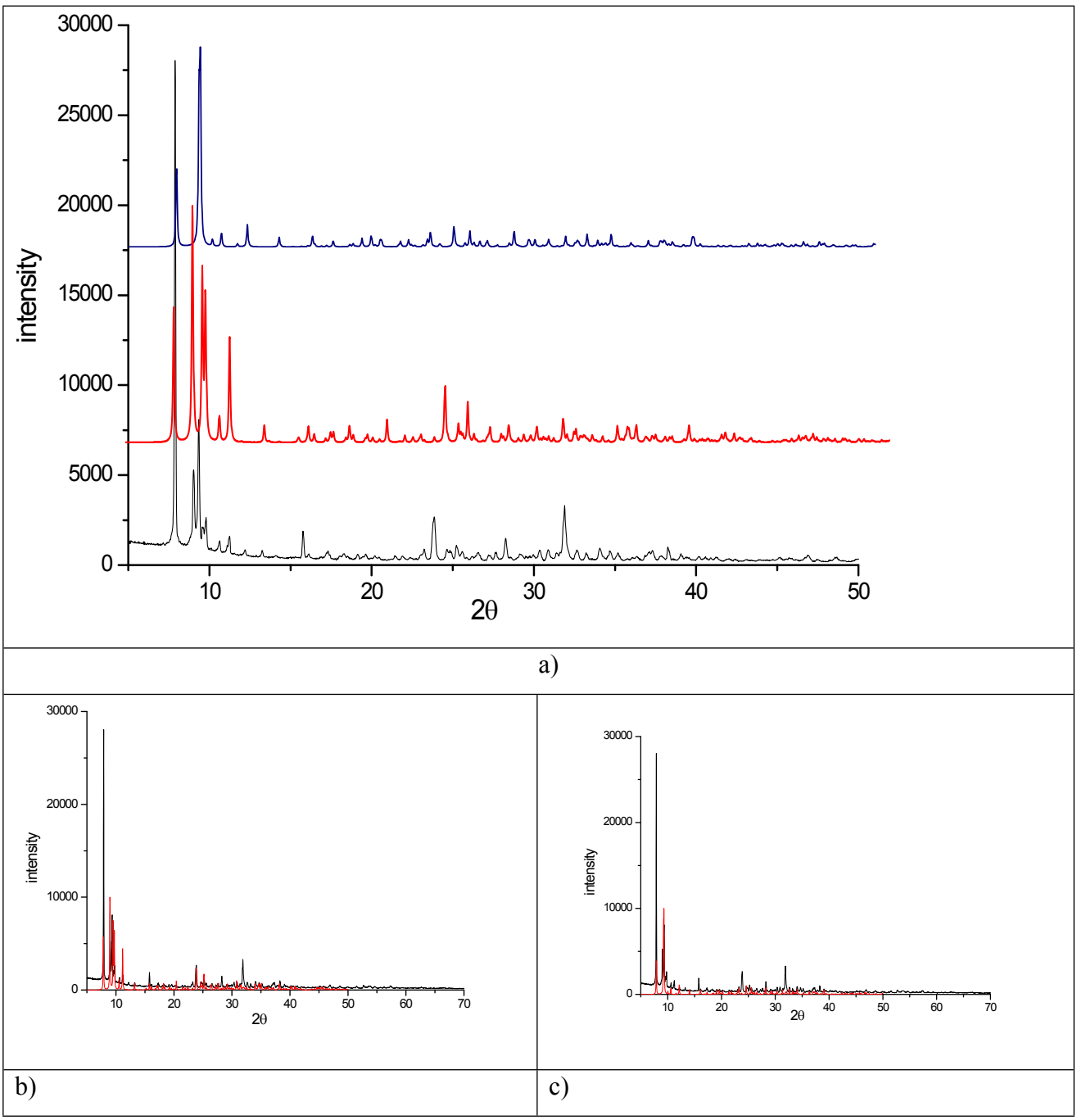



**Figure S8.** a) The XRPD spectra (Cu−Kα radiation) of **9** (**a+b**) (black), together with the calculated pattern from the single crystal data (red for **9a** and blue for **9b**), b) The powder XRD pattern of compound **9**(**a+b**) (black), together with the calculated pattern from the single crystal 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).

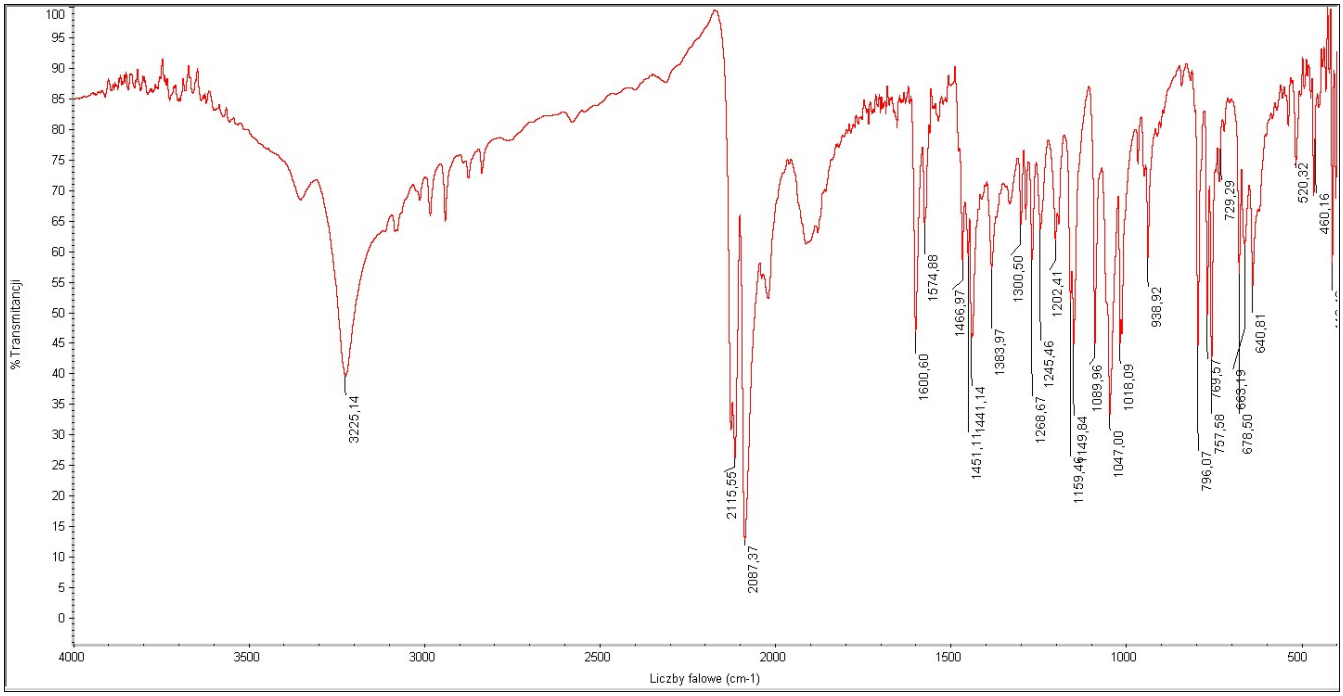



**Figure S9**. IR spectrum of **1.**

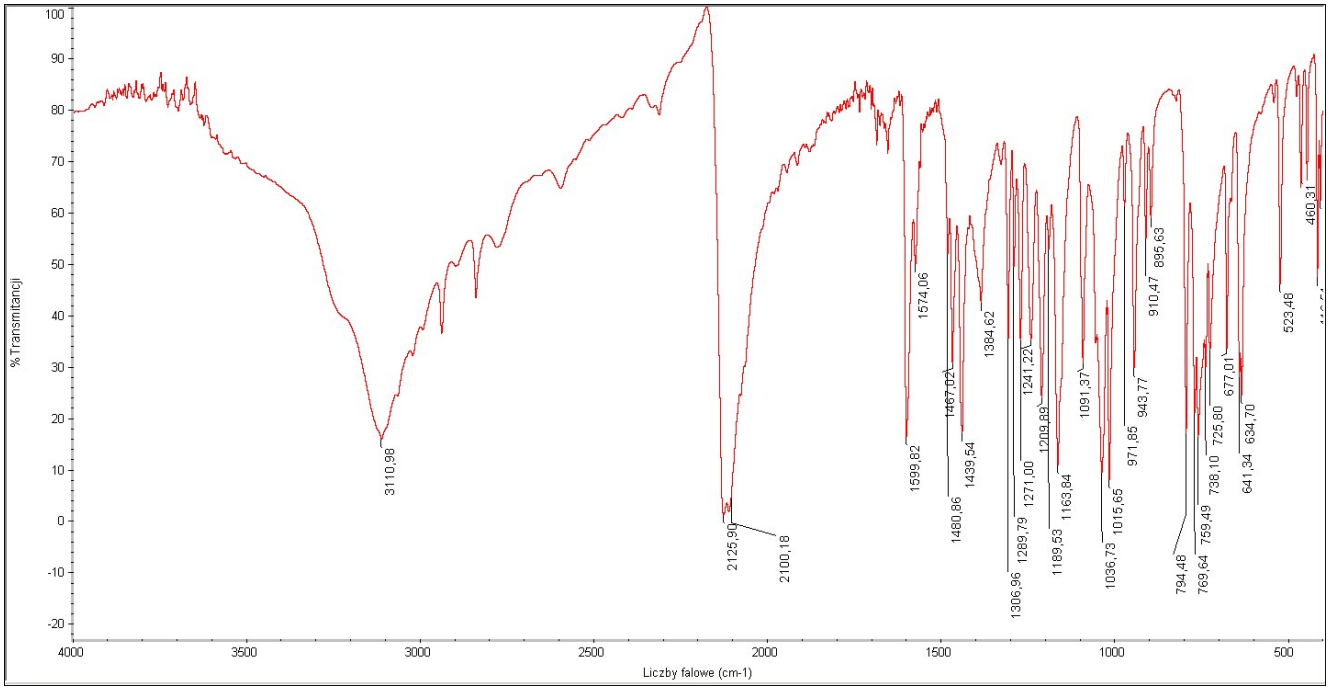



**Figure S10**. IR spectrum of **2.**

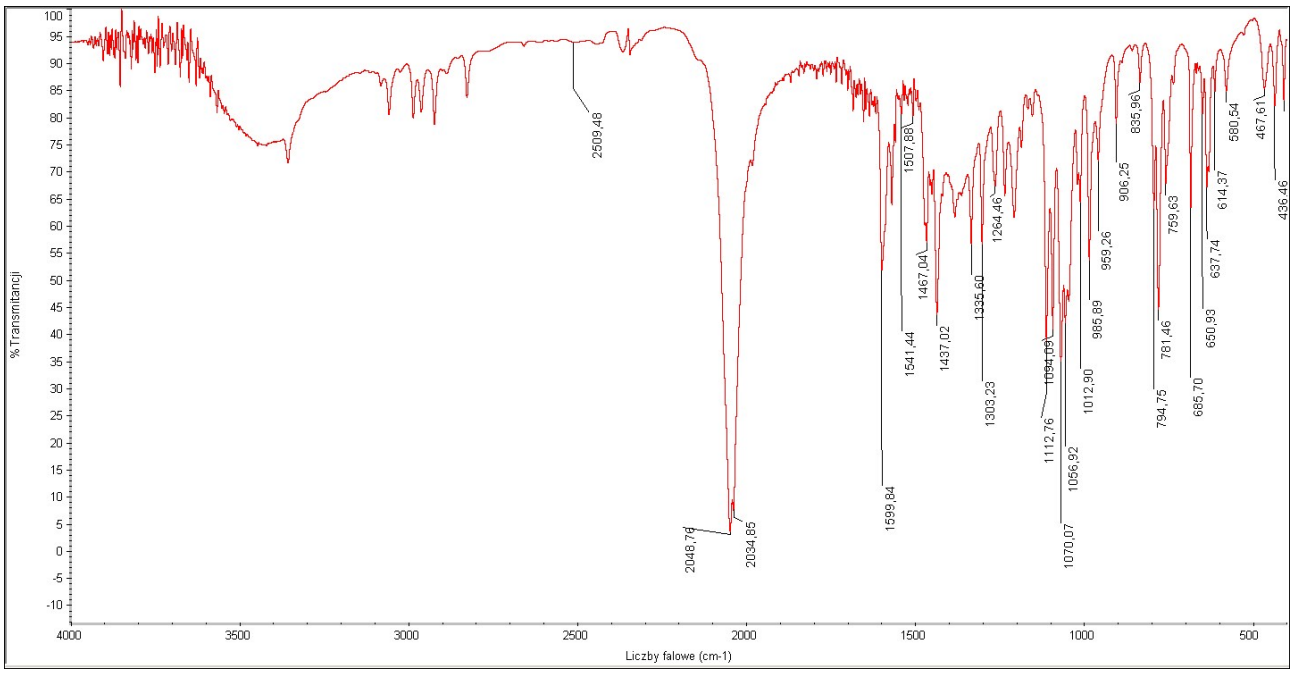



**Figure S11**. IR spectrum of **4.**

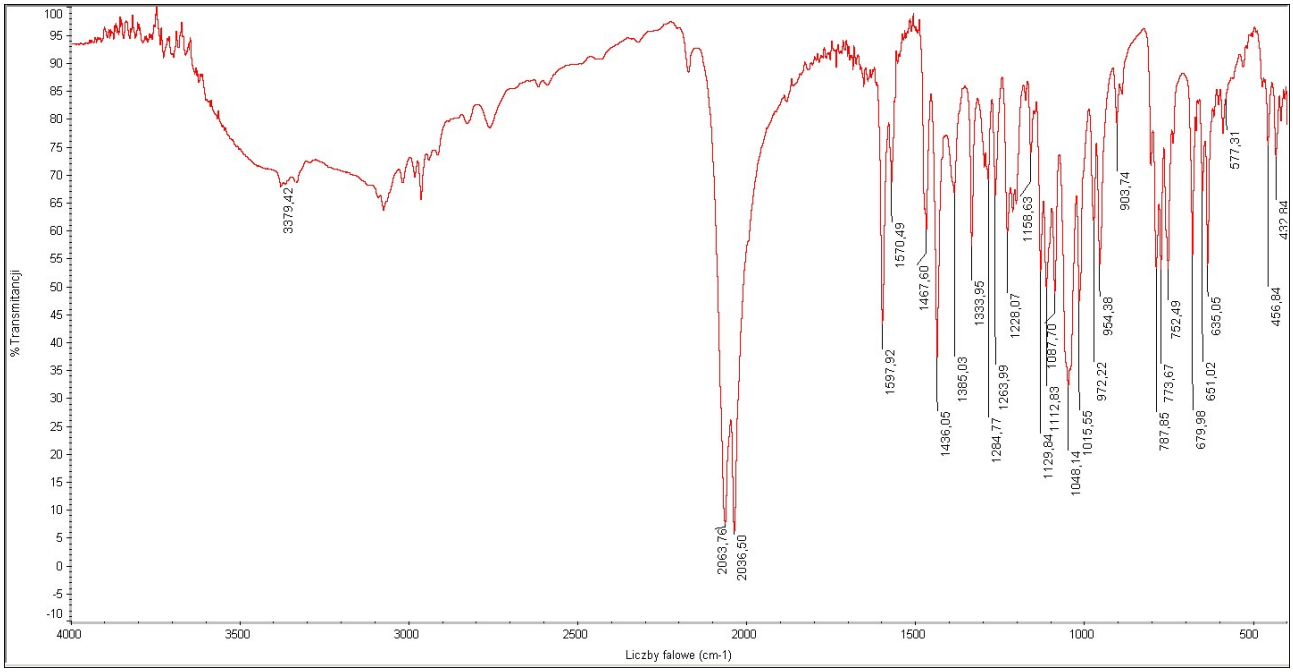



**Figure S12**. IR spectrum of **5.**

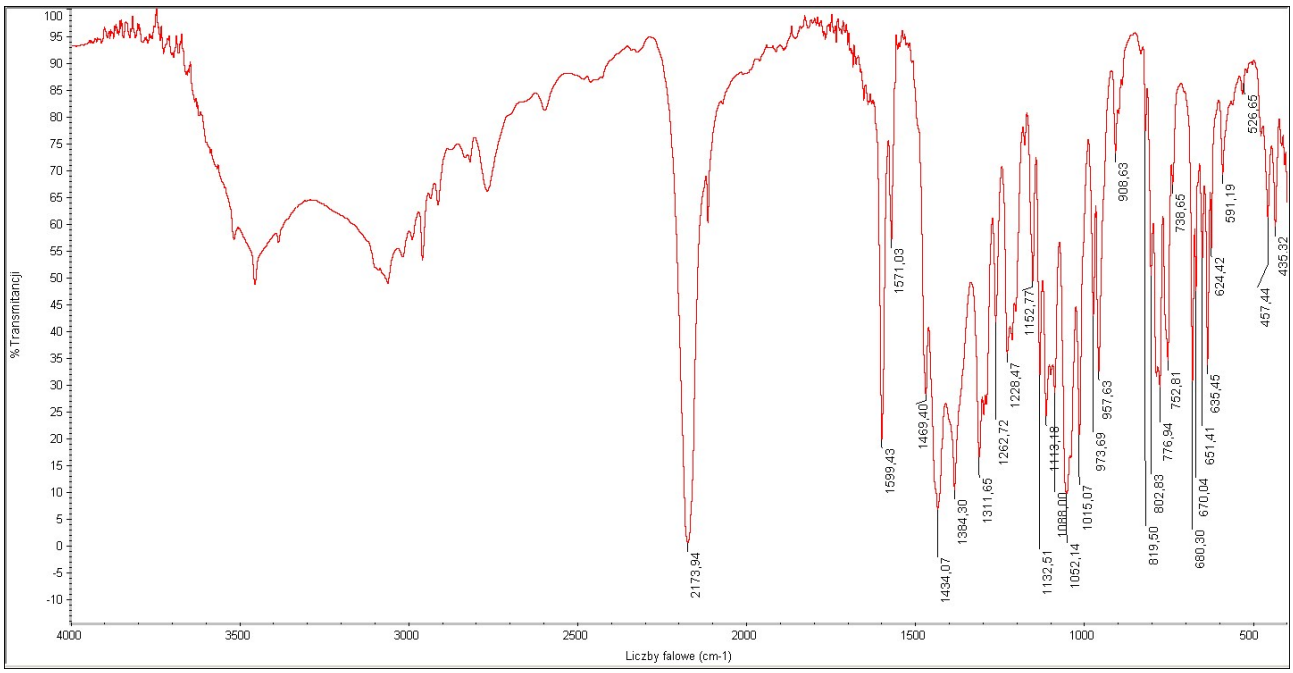



**Figure S13**. IR spectrum of **6.**

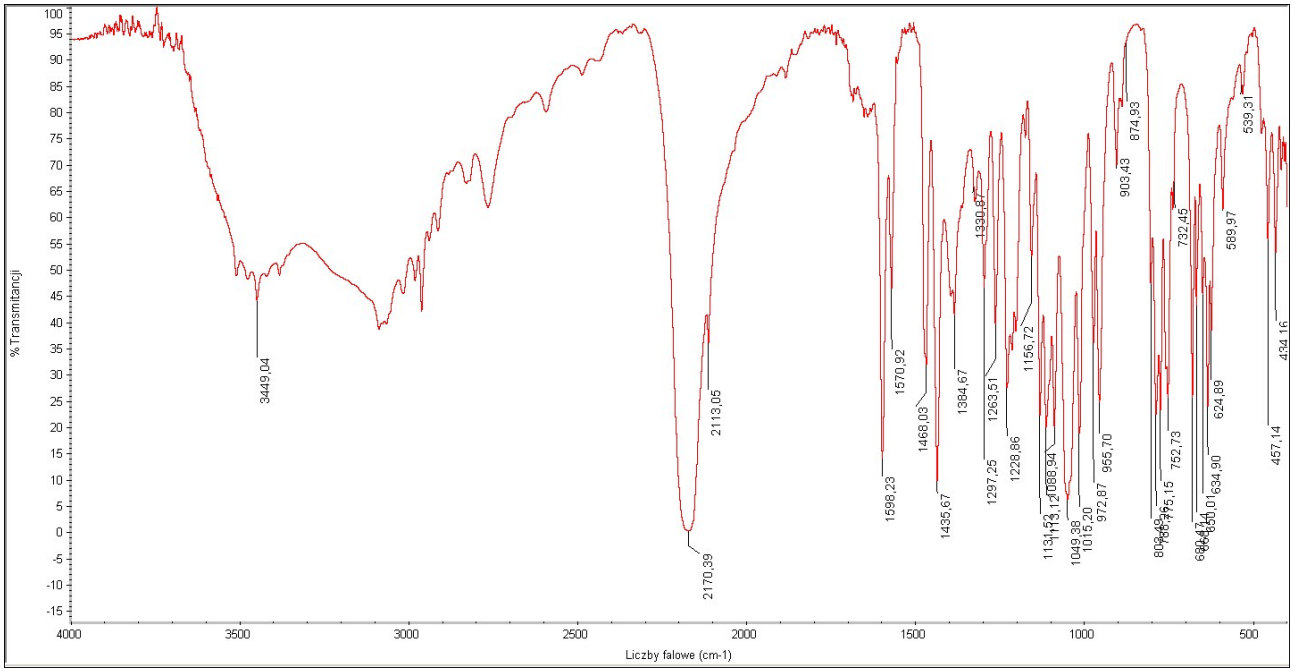



**Figure S14**. IR spectrum of **7.**

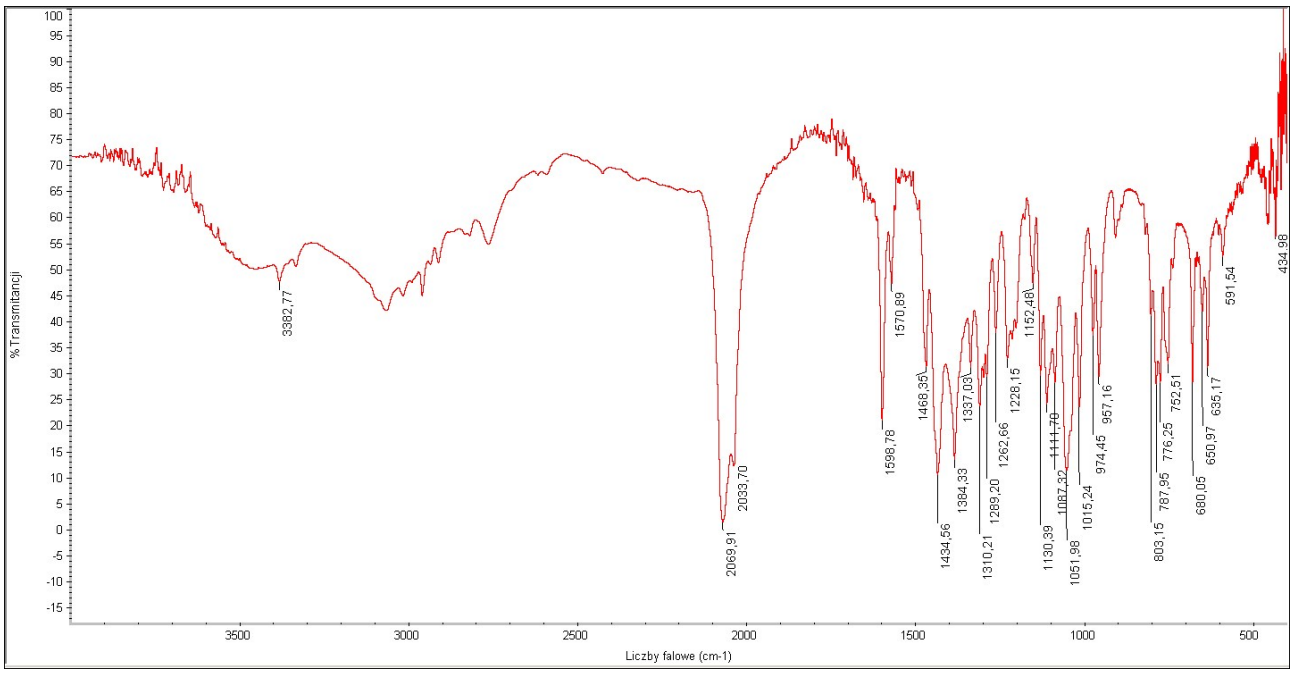



**Figure S15**. IR spectrum of **8.**

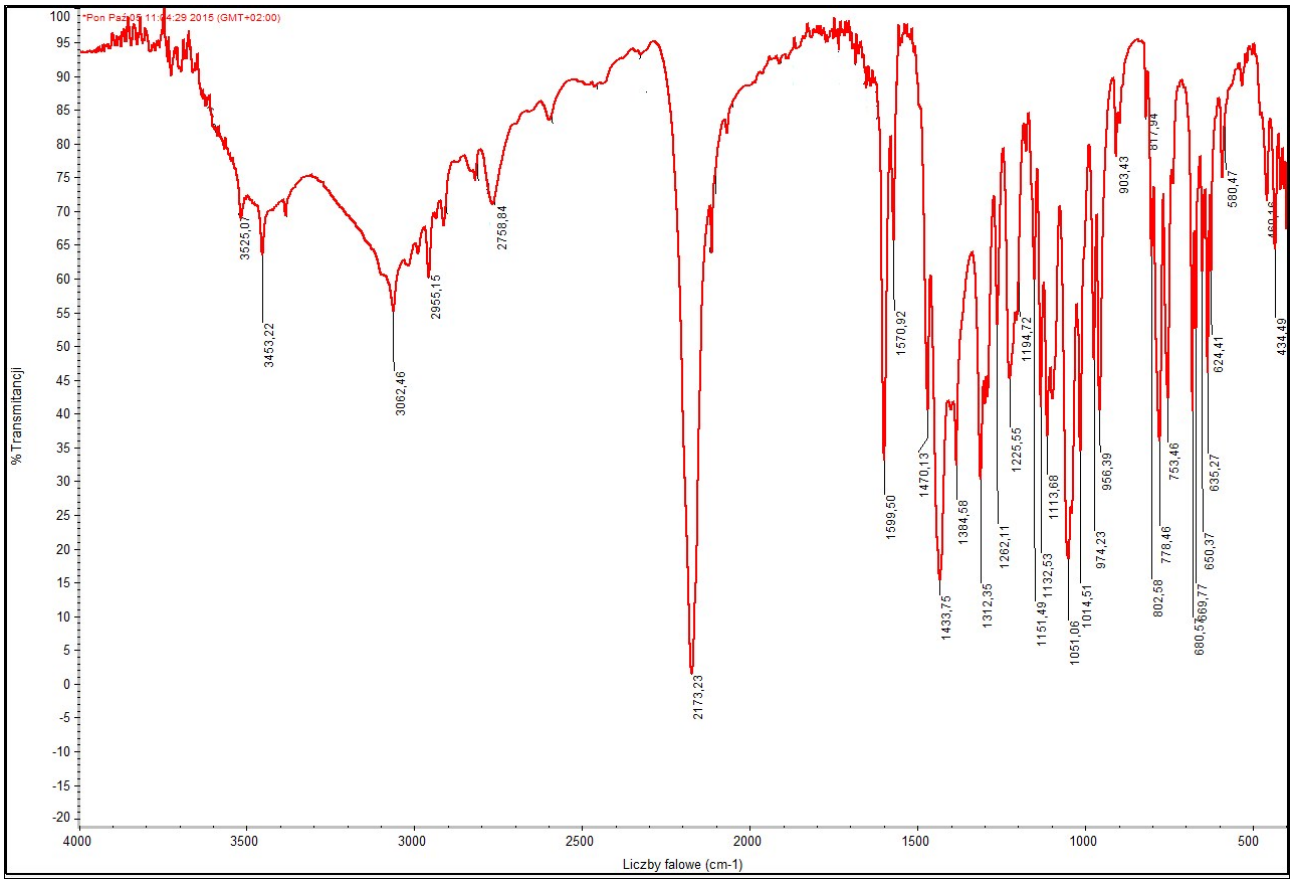



**Figure S16**. IR spectrum of **9**(**a**+**b**).

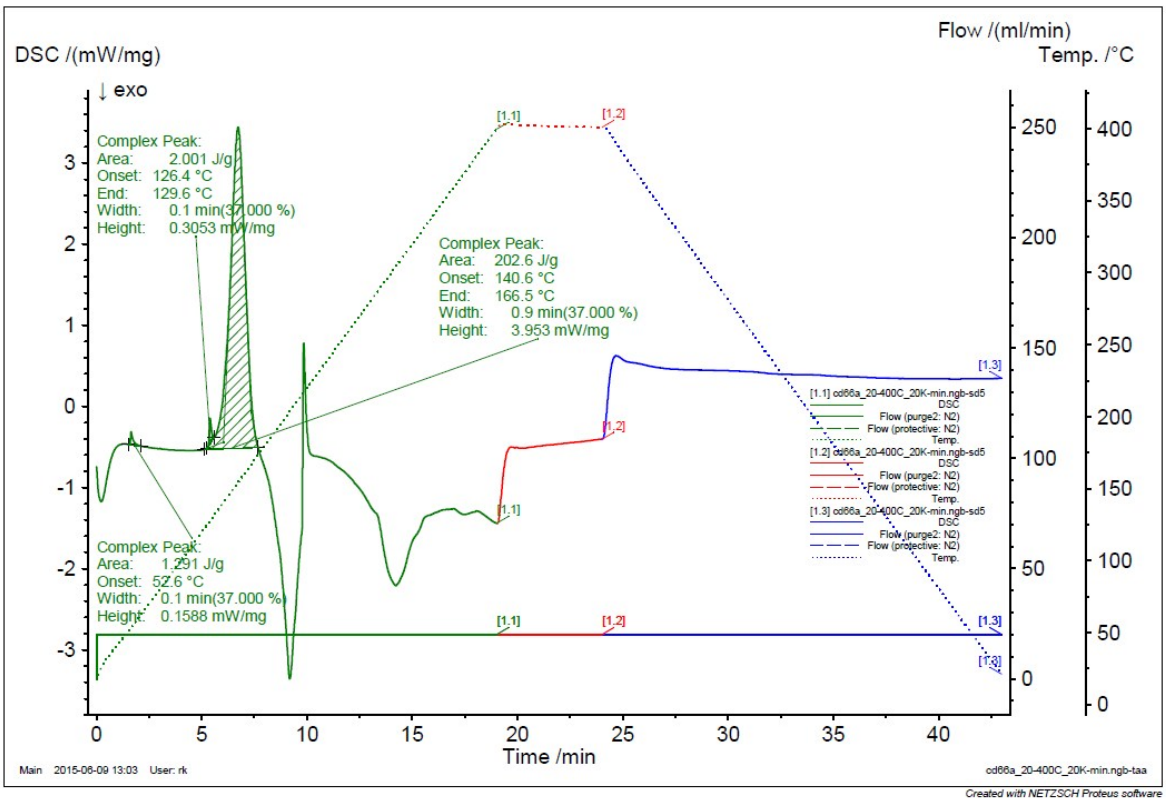



**Figure S17.** DSC curve of **1**.

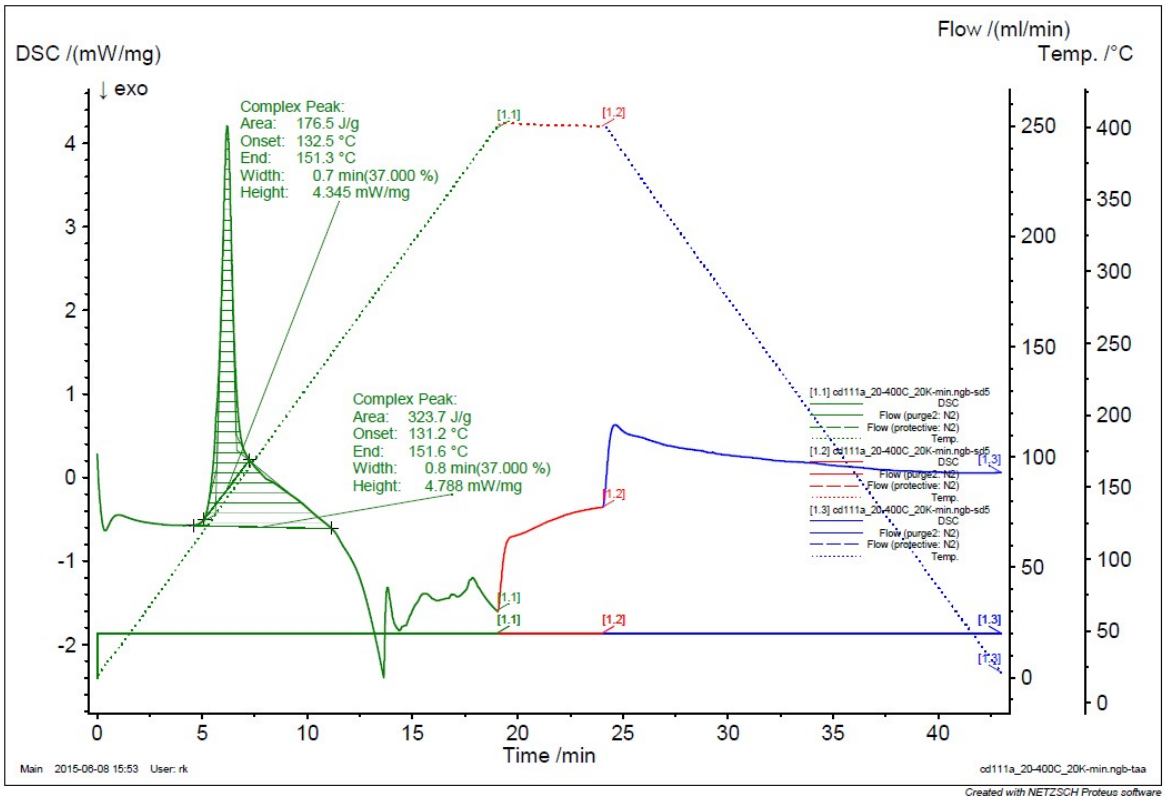



**Figure S18.** DSC curve of **2**.

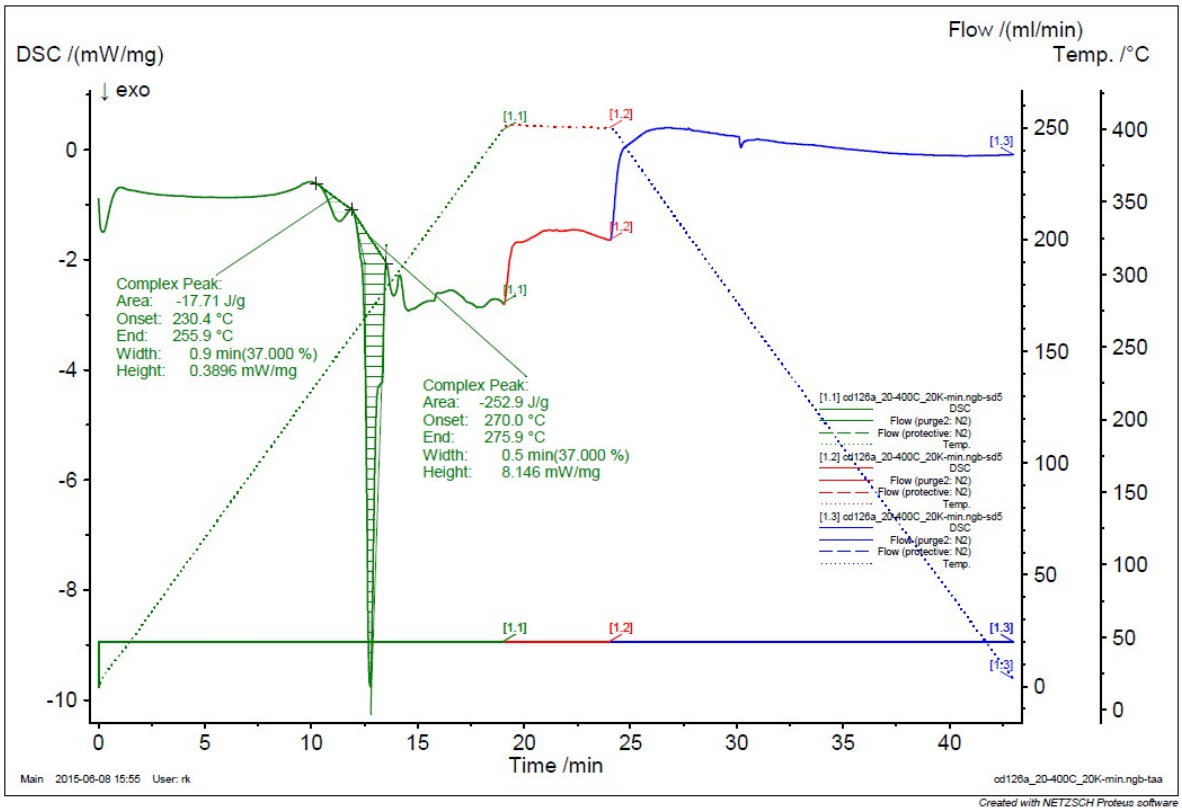



**Figure S19.** DSC curve of **4**.

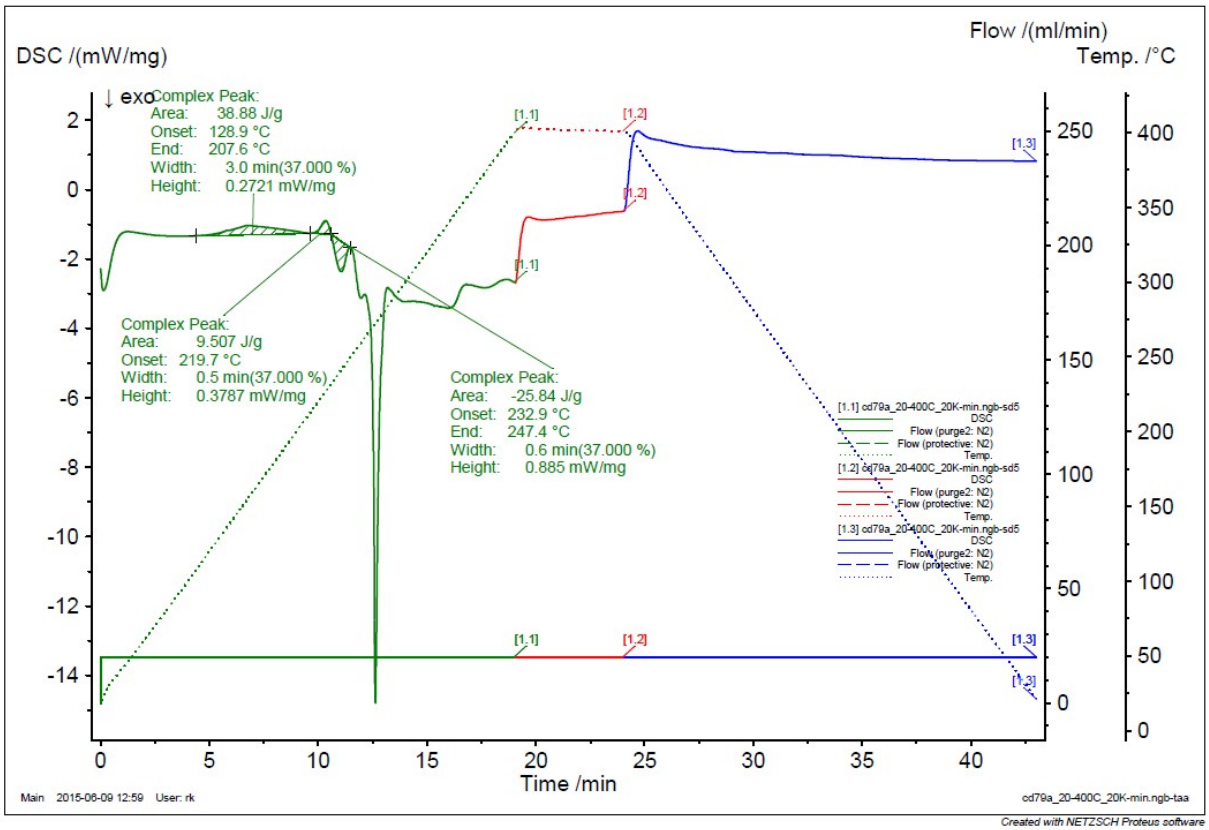



**Figure S20.** DSC curve of **5**.

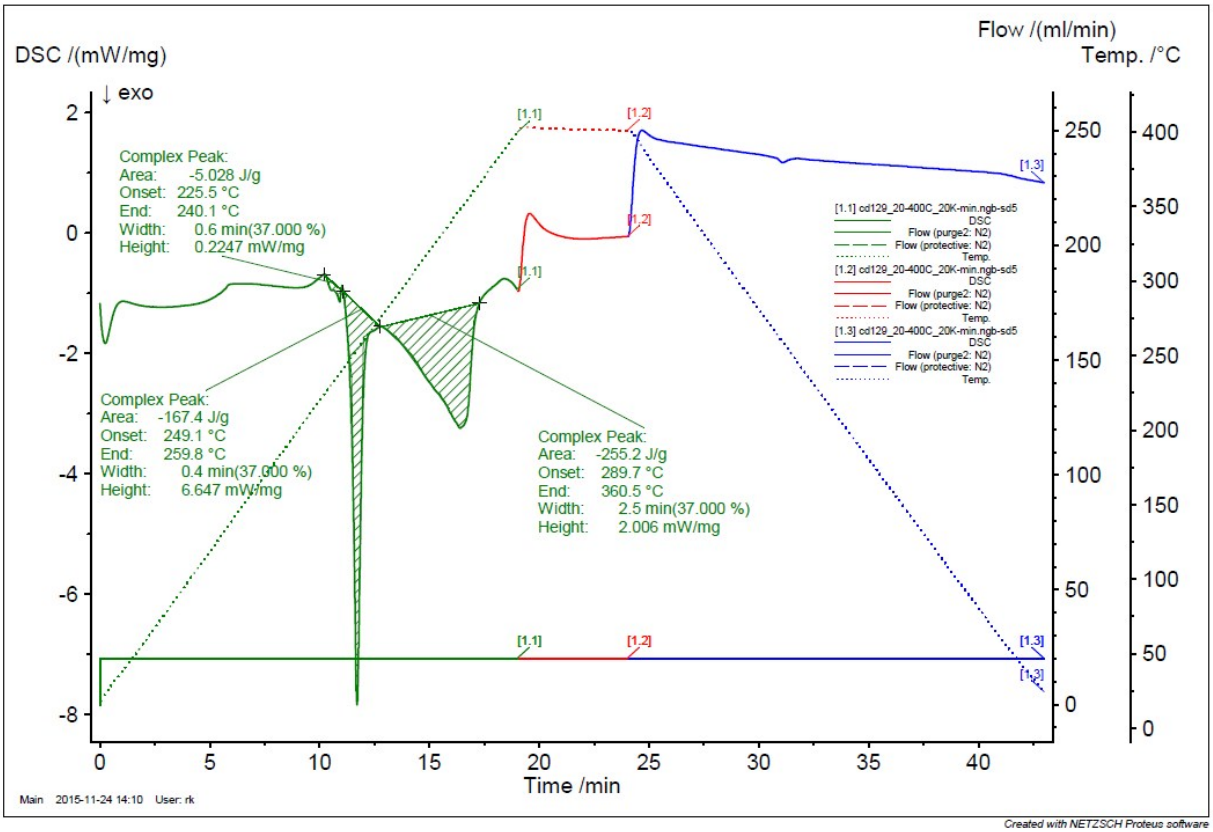



**Figure S21.** DSC curve of **6**.

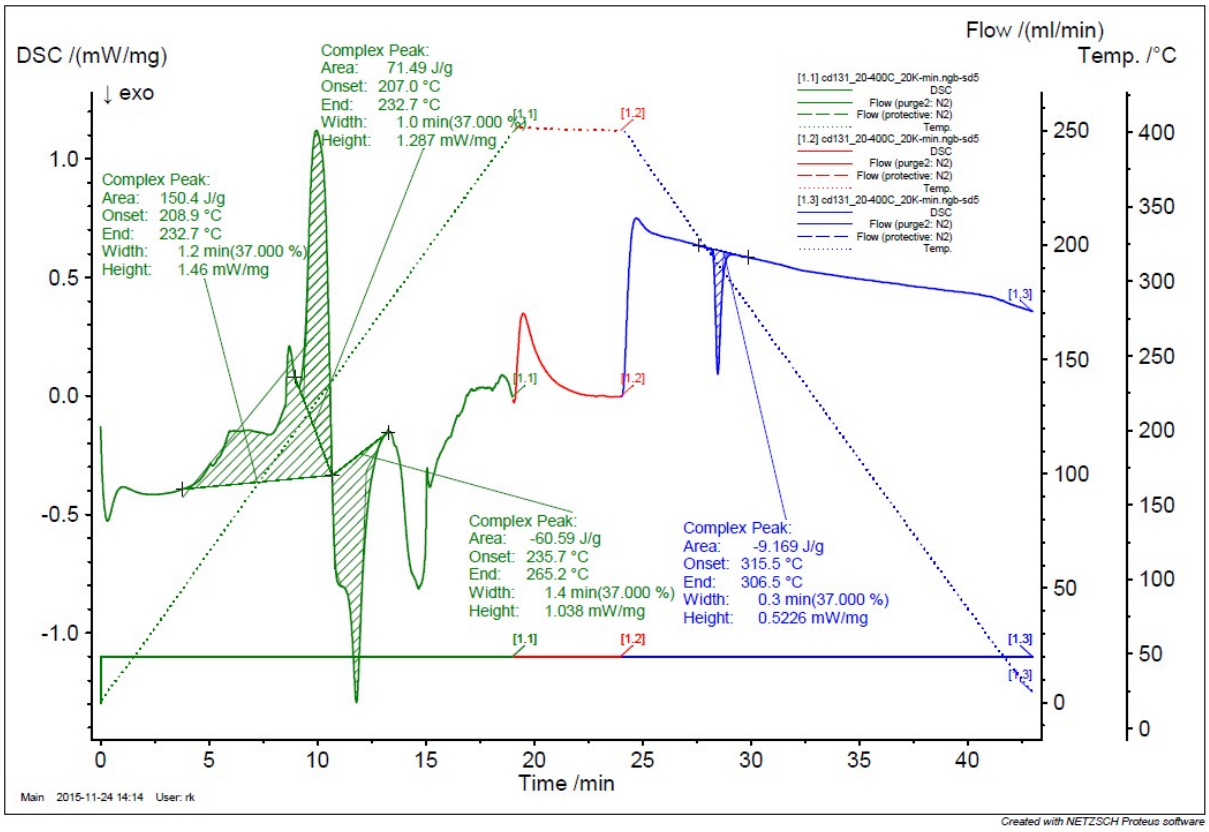



**Figure S22.** DSC curve of **7**.

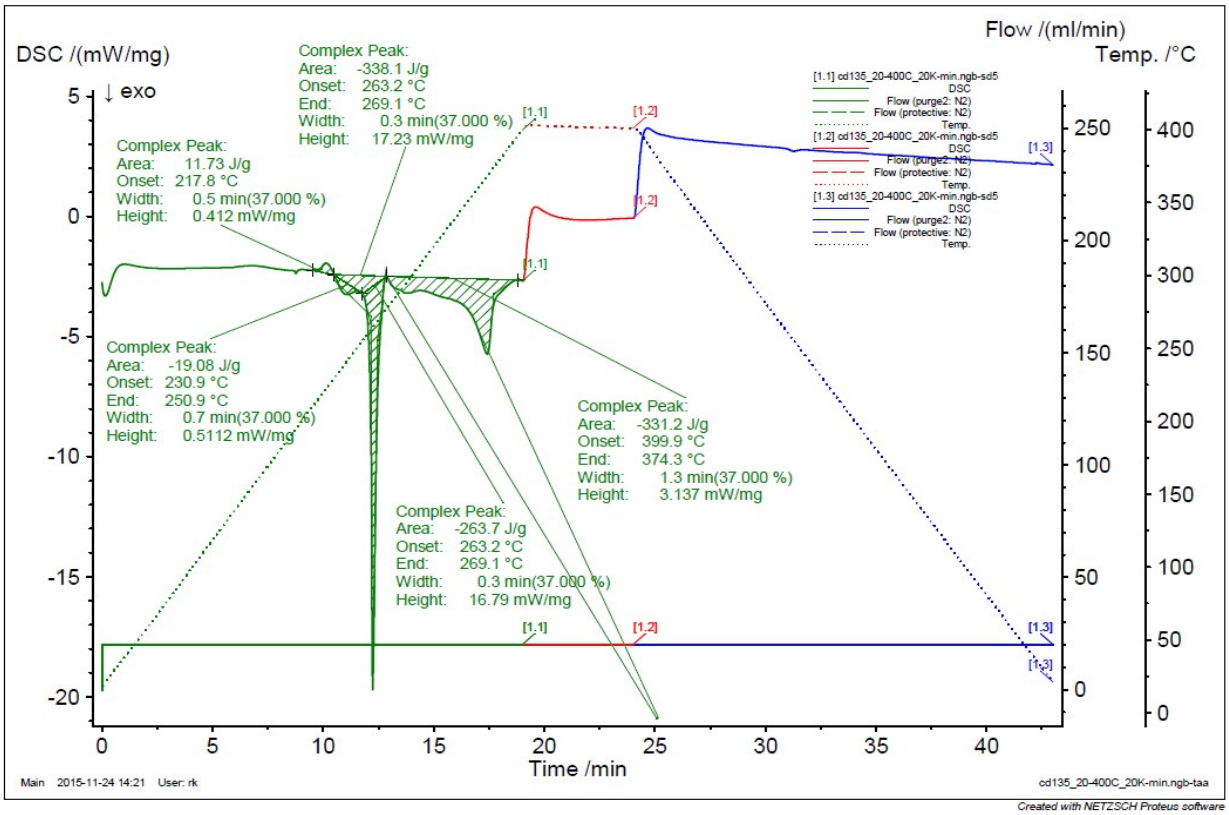



**Figure S23.** DSC curve of **8**.

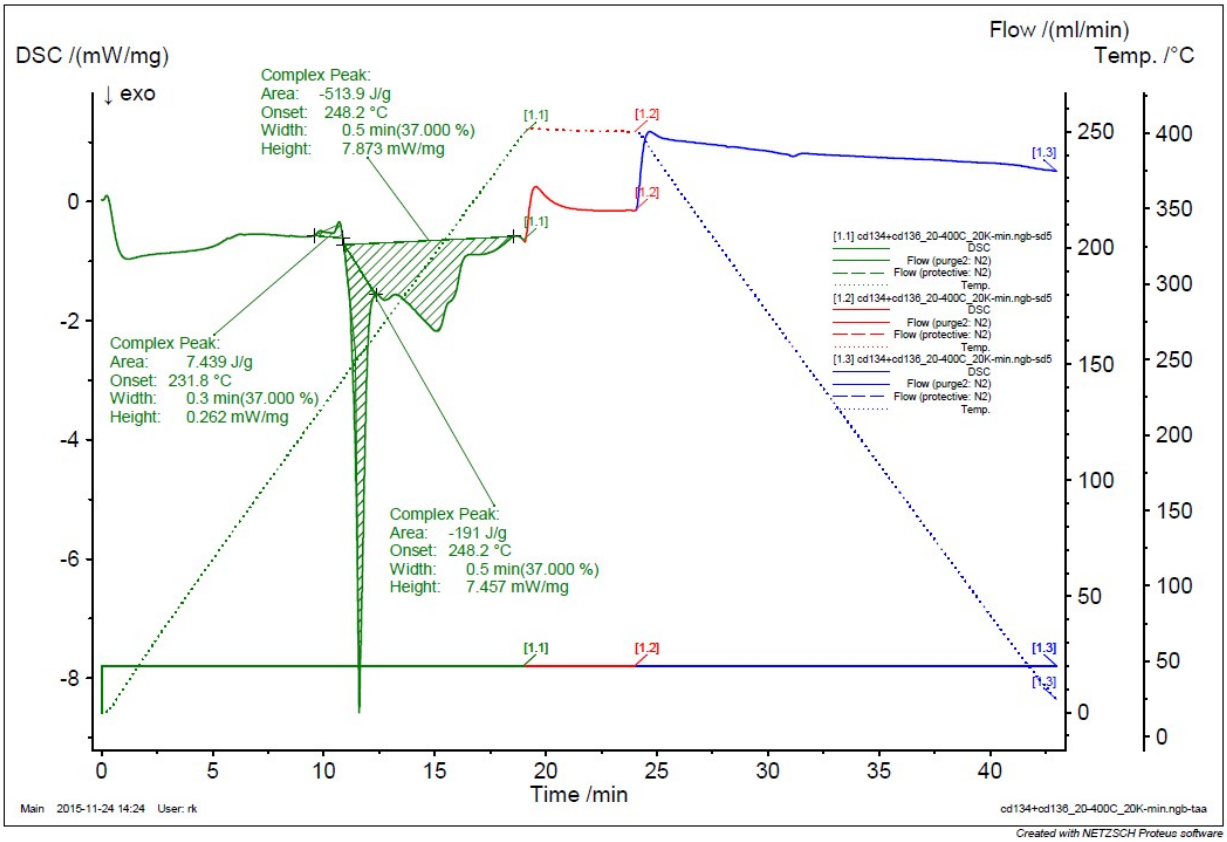
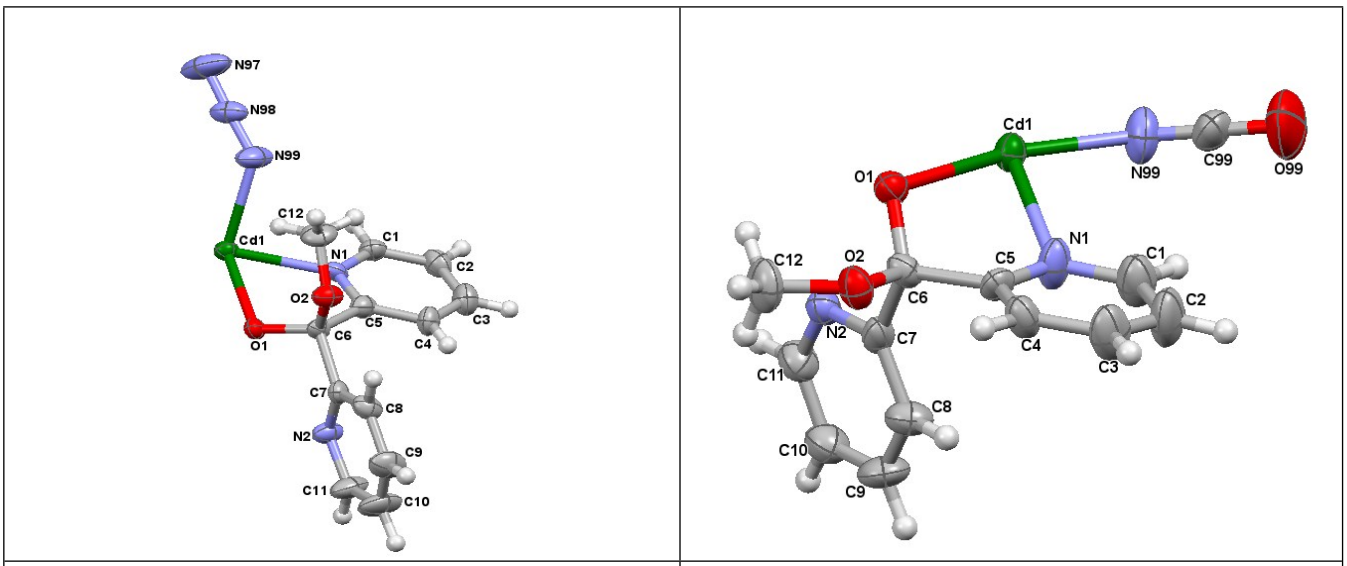
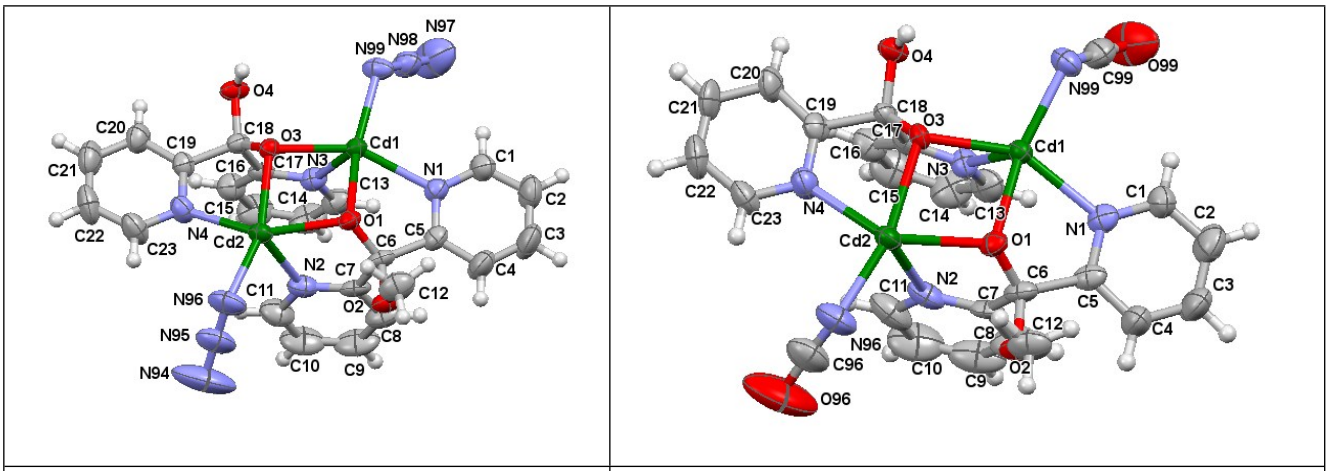



**Figure S24.** DSC curve of **9**(**a**+**b**).




**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.




**a)** **b)**

**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.

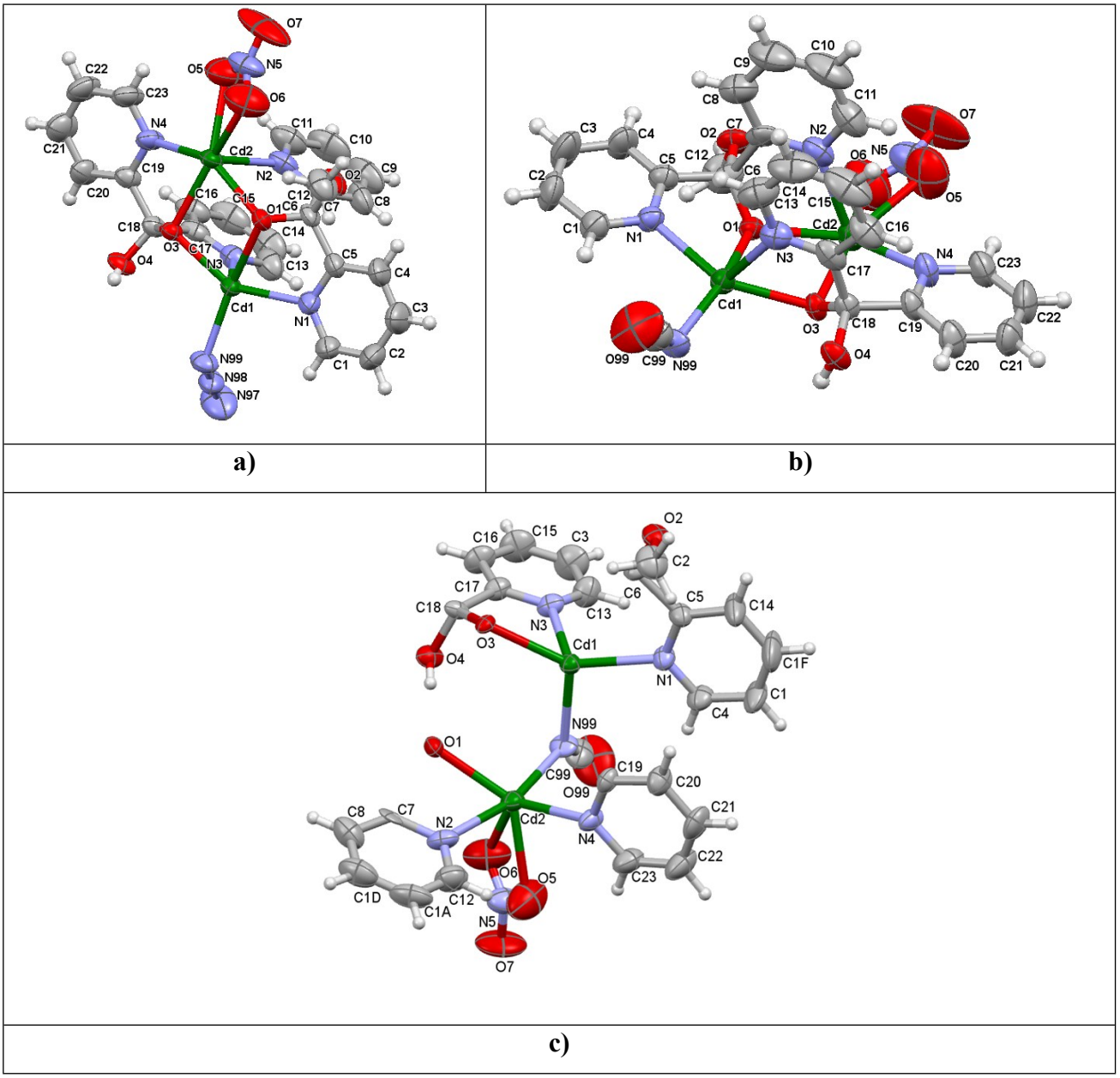



**Figure S27.** Perspective views of the asymmetric unit of **8** (**a**), **9a** (**b**) and **9b** (**c**) showing the atom numbering. Displacement ellipsoids are drawn at 50% probability

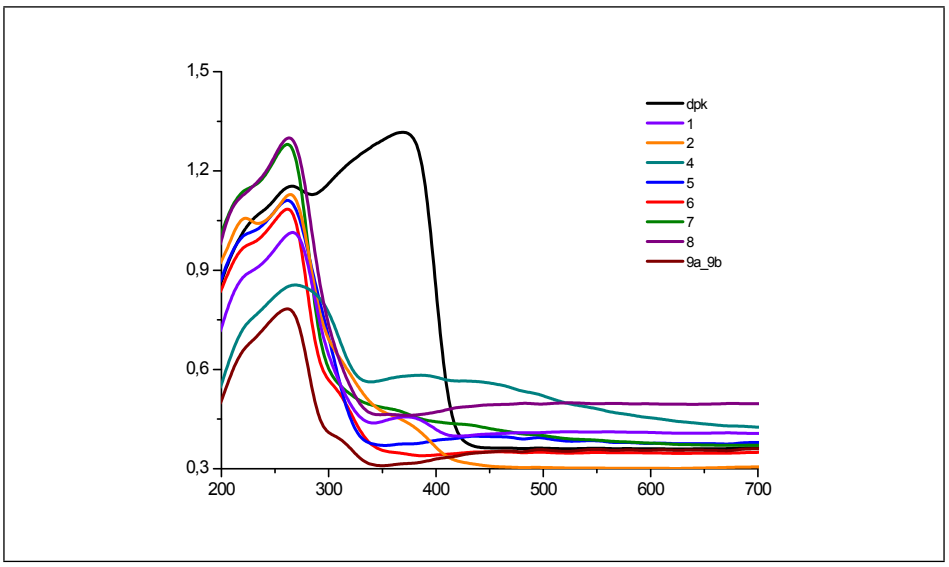



**Figure S28.** The solid state absorption electronic spectra of $(py)_2CO$ and the Cd(II) coordination compounds.

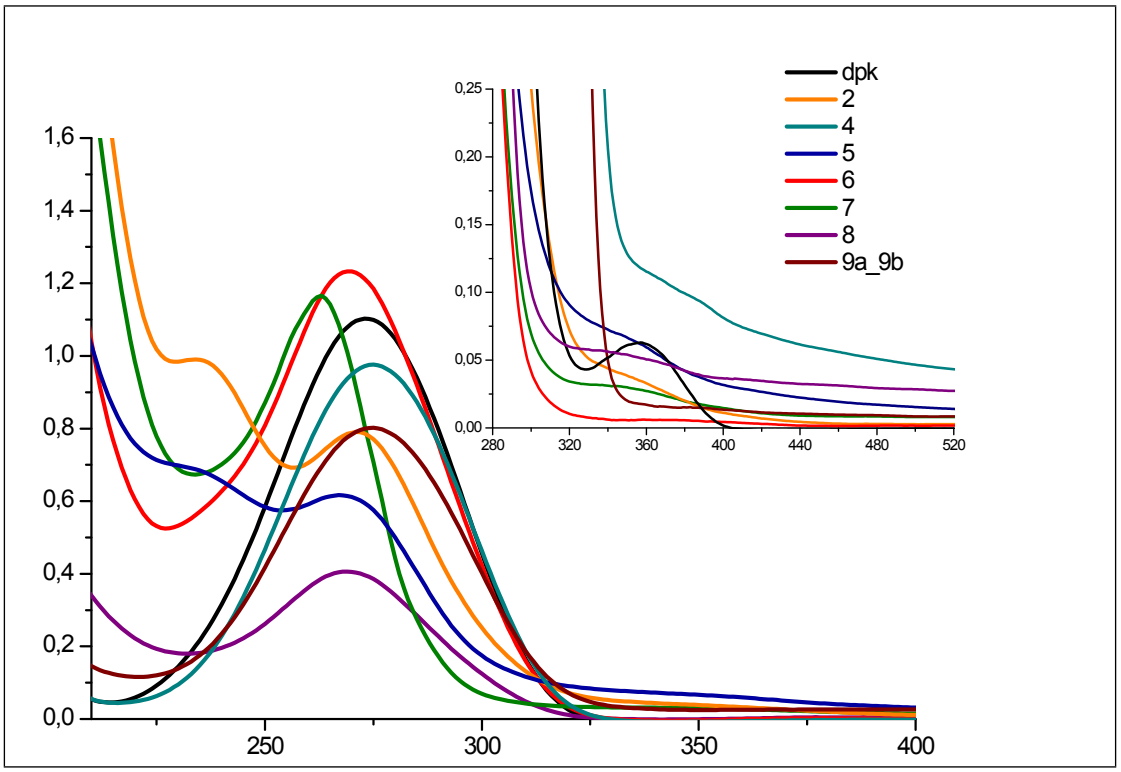



**Figure S29**. The UV-Vis spectra of the free ligand and Cd(II) compounds in acetonitrile solution ($10^{-4}$ M).