Supporting Information for the article

Tuning Structures and Emissive Properties in a Series of Zn(II) and Cd(II) Coordination Polymers Containing Dicarboxylic Acids and Nicotinamide Pillars

Diana Chisca,[1,2] Lilia Croitor,[1] Oleg Petuhov,[3] Olga V. Kulikova,[1] Galina F. Volodina,[1] Eduard B. Coropceanu,[2,3] Artëm E. Masunov,[4,5,6,7*] Marina S. Fonari[1*]

[1]*Institute of Applied Physics Academy of Sciences of R. Moldova, Academy str., 5 MD2028, Chisinau, Moldova;*
[2]*Tiraspol State University, Iablocikin str. 5 MD2069, Chisinau, Moldova;*
[3]*Institute of Chemistry Academy of Sciences of R. Moldova, Academy str., 3 MD2028, Chisinau, Moldova;*
[4]*NanoScience Technology Center, Department of Chemistry, Department of Physics, and Florida Solar Energy Center, University of Central Florida, 12424 Research Parkway, Ste. 400, Orlando, Florida 32826, United States,*
[5]*South Ural State University, Lenin pr. 76, Chelyabinsk 454080, Russia*
[6]*Photochemistry Center RAS, ul. Novatorov 7a, Moscow 119421, Russia*
[7]*National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoye shosse 31, Moscow, 115409, Russia*

*Synthetic procedures for **1-12.***

$[Cd_2(suc)(Hsuc)_2(nia)_4]_n$ (1)

To $Cd(BF_4)_2 \cdot 6H_2O$ (0.039 g, 0.1 mmol) and nia (0.024 g, 0.2 mmol) in 15 mL solution CH_3OH:dmf (2:1), the succinic acid (0.012 g, 0.1 mmol) was added with continuous stirring lasted approximately for 10 min at 150 °C. Colorless crystals precipitated upon cooling were filtered, washed with CH_3OH:dmf (2:1), and dried in air. Yield: 55% (based on Cd). Anal. Calcd for $C_{18}H_{19}CdN_4O_8$: C, 40.61; H, 3.57; N, 10.53. Found: C, 40.64; H, 3.60; N, 10.49. IR (cm^{-1}): 3364 (m), 3321 (v.w.), 3164 (m), 2975 (v.w.), 2942 (v.w.), 1697 (v.s.), 1601 (m), 1550 (s), 1388 (v.s.), 1260 (m), 1144 (m), 1053 (m), 889 (m), 790 (s), 693 (m).

$\{[Cd(suc)(nia)_3]\cdot H_2O\cdot dmf\}_n$ (2)

To $Cd(BF_4)_2 \cdot 6H_2O$ (0.039 g, 0.1 mmol) and nia (0.024 g, 0.2 mmol) in 10 mL solution CH_3OH:dmf (3:1), the succinic acid (0.012 g, 0.1 mmol) was added with continuous stirring lasted approximately for 10 min at 150 °C. Colorless crystals precipitated upon cooling were filtered, washed with CH_3OH:dmf (3:1), and dried in air. Yield: 45 % (based on Cd). Anal. Calcd for $C_{25}H_{31}CdN_7O_9$: C, 43.73; H, 4.51; N, 14.28. Found: C, 43.69; H, 4.55; N, 14.30. IR (cm^{-1}): 3345 (m), 3177 (m), 2963 (v.w.), 2921 (v.w.), 1685 (v.s.), 1654 (m), 1534 (s), 1388 (v.s.), 1218 (w), 1207 (m), 1161 (w), 1048 (m), 884 (m), 820 (s), 674 (m).

$\{[Cd(adi)(iso\text{-}nia)_2]\cdot dmf\}_n$ (3)

To a hot solution of $Cd(BF_4)_2 \cdot 6H_2O$ (0.039 g, 0.1 mmol) and iso-nia (0.024 g, 0.2 mmol) dissolved in a 8 mL mixture of CH_3OH:dmf (5:3), H_2adi (0.015 g, 0.1 mmol) was added. The reaction mixture was heated in an open container for 10 min at 150 °C. Colorless crystals precipitated upon cooling were filtered, washed with CH_3OH:dmf (2:1), and dried in air. Yield: 65% (based on Cd). Anal. Calcd for $C_{21}H_{27}CdN_5O_7$: C, 43.91; H, 4.70; N, 12.21. Found: C, 43.87 ; H, 4.73; N, 12.21. IR (cm^{-1}): 3677 (w), 3182 (m), 2969 (v.w.), 2934 (w), 1678 (m), 1652

(s), 1581 (m), 1554 (m), 1416 (m), 1316 (s), 1274 (w), 1093 (m), 1058 (m), 856 (w), 807 (m), 772 (s).

$[Cd(adi)(iso\text{-}nia)_2]_n$ (4)

Compound **4** was obtained by SC-SC transformation by heating compound **3** in vacuum at 105 ˚for 4 hours.

$\{[Zn(mal)(iso\text{-}nia)(H_2O)]\cdot dmf\}_n$ (5)

To a hot solution of $Zn(BF_4)_2\cdot 6H_2O$ (0.034 g, 0.1 mmol) and iso-nia (0.024 g, 0.2 mmol) dissolved in a 9 mL mixture of CH_3OH:dmf (3:1), H_2mal (0.010 g, 0.1 mmol) was added. The reaction mixture was heated in an open container for 10 min at 150 °C. Colorless crystals precipitated upon cooling were filtered, washed with CH_3OH:dmf (2:1), and dried in air. Yield: 55 % (based on Zn). Anal. Calcd for $C_{12}H_{17}ZnN_3O_7$: C, 37.83; H, 4.46; N, 11.03. Found: C, 37.79 ; H, 4.41; N, 11.01. IR (cm^{-1}): 3677 (w), 2987 (v.w.), 2968 (w), 1673 (m), 1571 (m), 1552 (m), 1392 (m), 1346 (s), 1255 (m), 1225 (m), 1098 (m), 1067 (s), 978 (m), 856 (m), 697 (m).

$\{[Cd(mal)(iso\text{-}nia)(H_2O)]\cdot dmf\}_n$ (6)

To a hot solution of $Cd(BF_4)_2\cdot 6H_2O$ (0.039 g, 0.1 mmol) and iso-nia (0.024 g, 0.2 mmol) dissolved in a 8 mL mixture of CH_3OH:dmf (5:3), H_2mal (0.010 g, 0.1 mmol) was added. The reaction mixture was heated in an open container for 10 min at 150 °C. Colorless crystals precipitated upon cooling were filtered, washed with CH_3OH:dmf (2:1), and dried in air. Yield: 60 % (based on Cd). Anal. Calcd for $C_{12}H_{17}CdN_3O_7$: C, 33.67; H, 3.97; N, 9.82. Found: C, 33.65 ; H, 4.01; N, 9.81. IR (cm^{-1}): 3676 (m), 3199 (m), 2987 (w), 2972 (w), 1664 (s), 1559 (w), 1550 (m), 1394 (m), 1342 (s), 1254 (m), 1224 (m), 1066 (s), 976 (m), 861 (m), 697 (m).

$\{[Zn(mal)(nia)(H_2O)]\cdot dmf\}_n$ (7)

$Zn(BF_4)_2\cdot 6H_2O$ (0.034 g, 0.1 mmol) and nia (0.024 g, 0.2 mmol) were dissolved in a mixture (4 mL) CH_3OH:dmf (3:1) and continuous stirring approximately 5 min at 100°C. Then, H_2mal (0.010 g, 0.1 mmol) was added and the mixture was stirred for 5 min. The resulting solution was allowed for crystallization at room temperature. Colorless crystals precipitated were filtered, washed with CH_3OH:dmf (3:1), and dried in air. Yield: 55 % (based on Zn). Anal. Calcd for $C_{12}H_{17}ZnN_3O_7$: C, 37.83; H, 4.46; N, 11.03. Found: C, 37.79; H, 4.41; N, 11.01. IR (cm^{-1}): 3677 (w), 3158 (m), 2989 (v.w.), 2933 (w), 1692 (m), 1566 (s), 1477 (w), 1388 (m), 1350 (s), 1257 (m), 1051 (s), 947 (m), 787 (m), 700 (m).

$\{[Cd(mal)(nia)(H_2O)]\cdot dmf\}_n$ (8)

$Cd(BF_4)_2\cdot 6H_2O$ (0.039 g, 0.1 mmol) and nia (0.024 g, 0.2 mmol) were dissolved in a mixture (8 mL) CH_3OH:dmf (5:3) and continuous stirring approximately 5 min at 150°C. Then, H_2mal (0.010 g, 0.1 mmol) was added and the mixture was stirred for 5 min. The resulting solution was allowed for crystallization at room temperature. Colorless crystals precipitated were filtered, washed with CH_3OH:dmf (5:3), and dried in air. Yield: 53 % yield (based on Cd). Anal. Calcd for $C_{12}H_{17}CdN_3O_7$: C, 33.67; H, 3.97; N, 9.82. Found: C, 33.65; H, 4.01; N, 9.81. IR (cm^{-1}): 3677 (w), 2989 (w), 1696 (s), 1552 (s), 1479 (w), 1380 (m), 1342 (s), 1198 (m), 1051 (s), 945 (m), 742 (m), 699 (m).

$\{[Zn(mal)(S\text{-}nia)(H_2O)]\cdot dmf\}_n$ (9)

To a hot solution of $Zn(BF_4)_2\cdot 6H_2O$ (0.034 g, 0.1 mmol) and S-nia (0.014 g, 0.1 mmol) dissolved in a 5 mL mixture of CH_3OH:dmf:H_2O (3:1:1), H_2mal (0.010 g, 0.1 mmol) was added. The reaction mixture was heated in an open container for 5 min at 100 °C. Yellow crystals precipitated upon cooling were filtered and dried in air. Yield: 45 % (based on Zn). Anal. Calcd for $C_{12}H_{17}ZnN_3O_6S$: C, 36.29; H, 4.28; N, 10.58. Found: C, 36.31; H, 4.25; N, 10.60. IR (cm^{-1}):

3737 (w), 3138 (w), 2989 (w), 2909 (m), 1582 (w), 1555 (s), 1475 (w), 1440 (s), 1357 (s), 1187 (m), 1053 (m), 949 (m), 806 (m), 687 (m).

{[Zn(bdc)(nia)$_2$)]·dmf}$_n$ (10)

$Zn(BF_4)_2 \cdot 6H_2O$ (0.034 g, 0.1 mmol) and nia (0.024 g, 0.2 mmol) were dissolved in a mixture (11 mL) CH_3OH:dmf:H_2O (5:5:1) and continuous stirring approximately 5 min at 200°C. Then, H_2bdc (0.016 g, 0.1mmol) was added and the mixture was stirred for 5 min. The resulting solution was allowed for crystallization at room temperature. Colorless crystals precipitated were filtered, washed with CH_3OH:dmf (1:1), and dried in air. Yield: 55 % (based on Zn). Anal. Calcd for $C_{23}H_{23}ZnN_5O_7$: C, 50.47; H, 4.20; N, 12.80. Found: C, 50.44.79; H, 4.23; N, 12.77. IR (cm^{-1}): 3658 (m), 1671 (s), 1601 (w), 1577 (m), 1473 (w), 1392 (s), 1286 (w), 1265 (w), 1040 (w), 1018 (s), 826 (m), 748 (m), 689 (m).

{[Cd(bdc)(nia)$_2$)]·dmf}$_n$ (11)

$Cd(BF_4)_2 \cdot 6H_2O$ (0.039 g, 0.1 mmol) and nia (0.024 g, 0.2 mmol) were dissolved in a mixture (8 mL) CH_3OH:dmf (1:1) and continuous stirring approximately 5 min at 200°C. Then, H_2bdc (0.016 g, 0.1mmol) was added and the mixture was stirred for 5 min. The resulting solution was allowed for crystallization at room temperature. Colorless crystals precipitated were filtered, washed with CH_3OH:dmf (1:1), and dried in air. Yield: 52 % (based on Cd). Anal. Calcd for $C_{23}H_{23}CdN_5O_7$: C, 46.47; H, 3.87; N, 11.78. Found: C, 46.50; H, 3.85; N, 11.77. IR (cm^{-1}): 3667 (m), 2987 (v.w.), 2971 (w), 1667 (s), 1612 (m), 1578 (s), 1384 (s), 1256 (m), 1150 (w), 1066(w), 1057 (w), 831(m), 748 (m), 697 (w).

{[Cd(bdc)(H_2O)$_2$(dmf)]·dmf}$_n$ (12)

To a hot solution of $Cd(BF_4)_2 \cdot 6H_2O$ (0.039 g, 0.1 mmol) and iso-nia (0.024 g, 0.2 mmol) dissolved in a 8 mL mixture of CH_3OH:dmf (1:1), H_2bdc (0.016 g, 0.1 mmol) was added. The reaction mixture was heated in an open container for 10 min at 150 °C. Colorless crystals precipitated were filtered and dried in air. Yield: 57 % (based on Cd). Anal. Calcd for $C_{14}H_{22}CdN_2O_8$: C, 36.62; H, 4.79; N, 6.10. Found: C, 36.59; H, 4.82; N, 6.07. IR (cm^{-1}): 3677 (w), 2989 (m), 1657 (m), 1560 (m), 1500 (m), 1438 (w), 1372 (s), 1295 (m), 1147 (m), 1112 (w), 838 (m), 746 (s).

Table S1. Selected bond distances (Å) and angles (deg) in **1**-**12**.

1			
Cd(1)-O(4)[a]	2.277(4)	Cd(1)-N(1)	2.326(3)
Cd(1)-O(3)	2.299(3)	Cd(1)-O(8)	2.353(3)
Cd(1)-N(3)	2.321(3)	Cd(1)-O(7)	2.455(3)
O(4)[a]-Cd(1)-O(3)	126.57(16)	N(3)-Cd(1)-O(8)	91.24(12)
O(4)[a]-Cd(1)-N(3)	86.97(12)	N(1)-Cd(1)-O(8)	89.25(12)
O(3)-Cd(1)-N(3)	90.99(12)	O(4)[a]-Cd(1)-O(7)	149.78(15)
O(4)[a]-Cd(1)-N(1)	92.50(12)	O(3)-Cd(1)-O(7)	82.47(12)
O(3)-Cd(1)-N(1)	88.99(12)	N(3)-Cd(1)-O(7)	84.05(12)
N(3)-Cd(1)-N(1)	179.32(13)	N(1)-Cd(1)-O(7)	96.61(12)
O(4)[a]-Cd(1)-O(8)	97.30(15)	O(8)-Cd(1)-O(7)	54.25(10)
O(3)-Cd(1)-O(8)	136.12(12)		
[a] 1-x, 2-y, -z			
2			
Cd(1)-O(4)	2.328(2)	Cd(1)-O(7)[a]	2.407(2)
Cd(1)-N(3)	2.356(2)	Cd(1)-O(6) [a]	2.476(2)
Cd(1)-N(1)	2.384(3)	Cd(1)-O(5)	2.504(2)
Cd(1)-N(5)	2.392(3)		
O(4)-Cd(1)-N(3)	136.20(9)	N(3)-Cd(1)-O(7)[a]	133.91(8)
O(4)-Cd(1)-N(1)	93.63(9)	N(1)-Cd(1)-O(7)[a]	89.77(8)
N(3)-Cd(1)-N(1)	94.62(9)	N(5)-Cd(1)-O(7)[a]	85.77(8)
O(4)-Cd(1)-N(5)	85.36(9)	O(4)-Cd(1)-O(6)[a]	142.56(8)
N(3)-Cd(1)-N(5)	89.16(9)	N(3)-Cd(1)-O(6)[a]	80.90(8)
N(1)-Cd(1)-N(5)	175.44(9)	O(7)[a]-Cd(1)-O(5)	142.41(7)
O(4)-Cd(1)-O(7)[a]	89.01(8)	O(6)[a]-Cd(1)-O(5)	162.56(7)
[a] 1-x, y-1/2, 1/2-z			
3			
Cd(1)-O(5)[a]	2.235(3)	Cd(1)-N(3)	2.345(3)
Cd(1)-O(6)[b]	2.241(3)	Cd(1)-O(4)	2.362(3)
Cd(1)-N(1)	2.336(3)	Cd(1)-O(3)	2.393(3)
O(5)[a]-Cd(1)-O(6)[b]	128.74(12)	N(1)-Cd(1)-O(4)	84.55(10)
O(5)[a]-Cd(1)-N(1)	87.42(10)	N(3)-Cd(1)-O(4)	99.27(11)
O(6)[b]-Cd(1)-N(1)	86.60(11)	O(5)[a]-Cd(1)-O(3)	145.23(10)
O(5)[a]-Cd(1)-N(3)	89.08(10)	O(6)[b]-Cd(1)-O(3)	85.14(11)
O(6)[b]-Cd(1)-N(3)	92.65(11)	N(1)-Cd(1)-O(3)	87.16(10)
N(1)-Cd(1)-N(3)	174.84(11)	N(3)-Cd(1)-O(3)	97.86(10)
O(5)[a]-Cd(1)-O(4)	90.50(10)	O(4)-Cd(1)-O(3)	54.79(9)
O(6)[b]-Cd(1)-O(4)	139.26(11)		
[a] -x, -y, -z [b] x, y+1, z			
4			
Cd(1)-O(5)[a]	2.283(12)	Cd(1)-N(3)	2.353(11)
Cd(1)-O(6)[b]	2.283(12)	Cd(1)-N(1)	2.392(14)
Cd(1)-O(4)	2.341(10)	Cd(1)-O(3)	2.435(11)
O(5)[a]-Cd(1)-O(6)[b]	125.0(5)	N(1)-Cd(1)-O(4)	89.2(4)
O(5)[a]-Cd(1)-N(1)	83.0(5)	N(3)-Cd(1)-O(4)	93.6(4)
O(6)[b]-Cd(1)-N(1)	90.2(5)	O(5)[a]-Cd(1)-O(3)	150.9(5)

O(5)[a]-Cd(1)-N(3)	84.4(4)	O(6)[b]-Cd(1)-O(3)	82.4(4)
O(6)[b]-Cd(1)-N(3)	96.4(5)	N(1)-Cd(1)-O(3)	87.7(5)
N(1)-Cd(1)-N(3)	167.4(4)	N(3)-Cd(1)-O(3)	103.9(4)
O(5)[a]-Cd(1)-O(4)	98.9(5)	O(4)-Cd(1)-O(3)	53.3(4)
O(6)[b]-Cd(1)-O(4)	135.6(4)		
[a] 1-x, 2-y, -z [b] x, y-1, z			
5			
Zn(1)-O(5)	2.096(4)	Zn(1)-O(4)	2.106(4)
Zn(1)-O(2)	2.099(4)	Zn(1)-O(6)	2.140(4)
Zn(1)-O(3)	2.105(4)	Zn(1)-N(1)	2.148(4)
O(5)-Zn(1)-O(2)	172.89(15)	O(3)-Zn(1)-O(6)	91.44(14)
O(5)-Zn(1)-O(3)	88.84(15)	O(4)-Zn(1)-O(6)	90.76(15)
O(2)-Zn(1)-O(3)	97.80(15)	O(5)-Zn(1)-N(1)	91.12(17)
O(5)-Zn(1)-O(4)	85.24(15)	O(2)-Zn(1)-N(1)	86.79(16)
O(2)-Zn(1)-O(4)	88.02(15)	O(3)-Zn(1)-N(1)	86.33(16)
O(3)-Zn(1)-O(4)	173.68(16)	O(4)-Zn(1)-N(1)	91.57(16)
O(5)-Zn(1)-O(6)	89.94(15)	O(6)-Zn(1)-N(1)	177.51(16)
O(2)-Zn(1)-O(6)	92.43(15)		
6			
Cd(1)-O(5)	2.255(2)	Cd(1)-O(4)	2.292(2)
Cd(1)-O(2)	2.271(3)	Cd(1)-O(6)	2.339(3)
Cd(1)-O(3)	2.289(2)	Cd(1)-N(1)	2.341(3)
O(5)-Cd(1)-O(2)	168.09(10)	O(3)-Cd(1)-O(6)	93.53(9)
O(5)-Cd(1)-O(3)	87.82(9)	O(4)-Cd(1)-O(6)	88.43(9)
O(2)-Cd(1)-O(3)	81.12(9)	O(5)-Cd(1)-N(1)	88.40(10)
O(5)-Cd(1)-O(4)	103.87(10)	O(2)-Cd(1)-N(1)	87.57(10)
O(2)-Cd(1)-O(4)	86.92(10)	O(3)-Cd(1)-N(1)	91.90(10)
O(3)-Cd(1)-O(4)	167.73(9)	O(4)-Cd(1)-N(1)	84.79(10)
O(5)-Cd(1)-O(6)	98.80(9)	O(6)-Cd(1)-N(1)	171.13(10)
O(2)-Cd(1)-O(6)	86.36(10)		
7			
Zn(1)-O(1)	2.059(13)	Zn(1)-N(1)	2.137(16)
Zn(1)-O(3)	2.112(12)	Zn(1)-O(5)	2.156(4)
Zn(1)-O(4)	2.065(13)	Zn(1)-N(1A)	2.17(2)
Zn(1)-O(2)	2.130(12)		
O(1)-Zn(1)-O(3)	173.3(5)	O(1)-Zn(1)-O(5)	91.5(5)
O(1)-Zn(1)-O(4)	88.1(5)	O(3)-Zn(1)-O(5)	89.6(4)
O(3)-Zn(1)-O(4)	85.3(2)	O(4)-Zn(1)-O(5)	90.4(5)
O(1)-Zn(1)-O(2)	97.28(19)	O(2)-Zn(1)-O(5)	91.4(5)
O(3)-Zn(1)-O(2)	89.3(5)	N(1)-Zn(1)-O(5)	177.5(6)
O(4)-Zn(1)-O(2)	174.3(5)	O(1)-Zn(1)-N(1A)	89.7(10)
O(1)-Zn(1)-N(1)	85.9(7)	O(3)-Zn(1)-N(1A)	89.7(9)
O(3)-Zn(1)-N(1)	92.9(6)	O(4)-Zn(1)-N(1A)	94.6(9)
O(4)-Zn(1)-N(1)	89.7(7)	O(2)-Zn(1)-N(1A)	83.5(9)
O(2)-Zn(1)-N(1)	88.8(7)	O(5)-Zn(1)-N(1A)	174.9(10)
8			
Cd(1)-O(3)	2.26(2)	Cd(1)-N(1A)	2.35(3)
Cd(1)-O(1)	2.22(2)	Cd(1)-O(5)	2.361(7)
Cd(1)-O(4)	2.27(2)	Cd(1)-N(1)	2.334(19)
Cd(1)-O(2)	2.32(2)		
O(3)-Cd(1)-O(1)	171.5(9)	O(3)-Cd(1)-O(5)	88.0(7)

O(3)-Cd(1)-O(4)	81.3(2)	O(1)-Cd(1)-O(5)	93.2(7)
O(1)-Cd(1)-O(4)	90.3(8)	O(4)-Cd(1)-O(5)	90.6(7)
O(3)-Cd(1)-O(2)	89.0(8)	O(2)-Cd(1)-O(5)	91.7(7)
O(1)-Cd(1)-O(2)	99.4(2)	N(1A)-Cd(1)-O(5)	175.1(13)
O(4)-Cd(1)-O(2)	169.9(9)	O(3)-Cd(1)-N(1)	95.3(8)
O(3)-Cd(1)-N(1A)	92.1(13)	O(1)-Cd(1)-N(1)	83.5(8)
O(1)-Cd(1)-N(1A)	87.4(13)	O(4)-Cd(1)-N(1)	90.0(9)
O(4)-Cd(1)-N(1A)	94.2(13)	O(2)-Cd(1)-N(1)	88.2(9)
O(2)-Cd(1)-N(1A)	83.4(14)	O(5)-Cd(1)-N(1)	176.7(7)
9			
Zn(1)-O(4)	2.080(10)	Zn(1)-N(1A)	2.093(16)
Zn(1)-O(3)	2.088(10)	Zn(1)-O(5)	2.153(4)
Zn(1)-O(2)	2.090(11)	Zn(1)-N(1)	2.221(16)
Zn(1)-O(1)	2.122(11)		
O(4)-Zn(1)-O(3)	86.15(16)	O(4)-Zn(1)-O(5)	90.5(5)
O(4)-Zn(1)-O(2)	174.6(5)	O(3)-Zn(1)-O(5)	90.0(5)
O(3)-Zn(1)-O(2)	88.8(5)	O(2)-Zn(1)-O(5)	91.3(5)
O(4)-Zn(1)-N(1A)	92.8(9)	N(1A)-Zn(1)-O(5)	176.4(7)
O(3)-Zn(1)-N(1A)	91.7(8)	O(1)-Zn(1)-O(5)	93.7(5)
O(2)-Zn(1)-N(1A)	85.5(10)	O(4)-Zn(1)-N(1)	91.2(8)
O(4)-Zn(1)-O(1)	88.0(5)	O(3)-Zn(1)-N(1)	89.5(6)
O(3)-Zn(1)-O(1)	173.1(5)	O(2)-Zn(1)-N(1)	86.9(8)
O(2)-Zn(1)-O(1)	96.94(16)	O(1)-Zn(1)-N(1)	86.9(7)
N(1A)-Zn(1)-O(1)	84.9(9)	O(5)-Zn(1)-N(1)	178.1(9)
10			
Zn(1)-O(3)	1.987(3)	Zn(1)-N(3)	2.186(4)
Zn(1)-O(4)[a]	2.037(3)	Zn(1)-N(1)	2.188(4)
Zn(1)-O(6)[b]	2.088(3)		
O(3)-Zn(1)-O(4)[a]	123.41(11)	O(6)[b]-Zn(1)-N(3)	92.42(13)
O(3)-Zn(1)-O(6)[b]	93.96(12)	O(3)-Zn(1)-N(1)	94.40(13)
O(4)[a]-Zn(1)-O(6)[b]	142.60(12)	O(4)[a]-Zn(1)-N(1)	85.47(13)
O(3)-Zn(1)-N(3)	94.65(13)	O(6)[b]-Zn(1)-N(1)	93.79(13)
O(4)[a]-Zn(1)-N(3)	83.83(12)	N(3)-Zn(1)-N(1)	168.65(13)
[a] -x, -y, z [b] x+1/2, 1/2-y, z			
11			
Cd(1)-O(3)	2.167(5)	Cd(1)-N(3)	2.358(10)
Cd(1)-O(4)[a]	2.224(5)	Cd(1)-N(1)	2.348(8)
Cd(1)-O(6)[b]	2.297(5)	Cd(1)-O(5)[b]	2.465(5)
O(3)-Cd(1)-O(4)[a]	128.7(2)	O(6)[b]-Cd(1)-N(3)	92.2(2)
O(3)-Cd(1)-O(6)[b]	88.0(2)	N(1)-Cd(1)-N(3)	169.8(3)
O(4)[a]-Cd(1)-O(6)[b]	143.3(2)	O(3)-Cd(1)-O(5)[b]	142.9(2)
O(3)-Cd(1)-N(1)	92.1(3)	O(4)[a]-Cd(1)-O(5)[b]	88.4(2)
O(4)[a]-Cd(1)-N(1)	87.0(2)	O(6)[b]-Cd(1)-O(5)[b]	54.91(19)
O(6)[b]-Cd(1)-N(1)	94.8(2)	N(1)-Cd(1)-O(5)[b]	90.3(2)
O(3)-Cd(1)-N(3)	95.6(2)	N(3)-Cd(1)-O(5)[b]	87.6(2)
O(4)[a]-Cd(1)-N(3)	82.9(2)		
[a] 2-x, -y, z [b] x+1/2, 1/2-y, z			
12			
Cd(1)-O(2)	2.279(2)	Cd(2)-O(3W)	2.296(3)
Cd(1)-O(1W)	2.308(2)	Cd(2)-O(4W)	2.302(2)
Cd(1)-O(5)	2.331(2)	Cd(2)-O(10)	2.339(3)
Cd(1)-O(9)	2.339(2)	Cd(2)-O(7)	2.365(2)

Cd(1)-O(2W)	2.347(3)	Cd(2)-O(8)	2.380(2)
Cd(1)-O(6)	2.432(2)	Cd(2)-O(3)	2.384(2)
Cd(1)-O(1)	2.530(2)	Cd(2)-O(4)	2.433(2)
O(2)-Cd(1)-O(1W)	84.13(9)	O(3W)-Cd(2)-O(4W)	83.21(11)
O(2)-Cd(1)-O(5)	135.28(9)	O(3W)-Cd(2)-O(10)	170.90(11)
O(1W)-Cd(1)-O(5)	140.58(9)	O(4W)-Cd(2)-O(10)	93.13(11)
O(2)-Cd(1)-O(9)	97.32(10)	O(3W)-Cd(2)-O(7)	96.35(10)
O(1W)-Cd(1)-O(9)	88.46(9)	O(4W)-Cd(2)-O(7)	81.87(9)
O(5)-Cd(1)-O(9)	87.22(9)	O(10)-Cd(2)-O(7)	91.35(10)
O(2)-Cd(1)-O(2W)	89.73(9)	O(3W)-Cd(2)-O(8)	84.55(11)
O(1W)-Cd(1)-O(2W)	88.98(9)	O(4W)-Cd(2)-O(8)	133.04(9)
O(5)-Cd(1)-O(2W)	90.09(9)	O(10)-Cd(2)-O(8)	103.92(10)
O(9)-Cd(1)-O(2W)	172.22(9)	O(7)-Cd(2)-O(8)	54.77(8)
O(2)-Cd(1)-O(6)	169.57(9)	O(3W)-Cd(2)-O(3)	89.71(10)
O(1W)-Cd(1)-O(6)	85.51(9)	O(4W)-Cd(2)-O(3)	84.21(9)
O(5)-Cd(1)-O(6)	55.06(8)	O(10)-Cd(2)-O(3)	81.61(10)
O(9)-Cd(1)-O(6)	83.55(9)	O(7)-Cd(2)-O(3)	164.04(8)
O(2W)-Cd(1)-O(6)	88.92(9)	O(8)-Cd(2)-O(3)	140.86(8)
O(2)-Cd(1)-O(1)	54.22(8)	O(3W)-Cd(2)-O(4)	92.95(9)
O(1W)-Cd(1)-O(1)	138.03(9)	O(4W)-Cd(2)-O(4)	138.67(9)
O(5)-Cd(1)-O(1)	81.16(8)	O(10)-Cd(2)-O(4)	84.28(10)
O(9)-Cd(1)-O(1)	100.56(9)	O(7)-Cd(2)-O(4)	139.31(8)
O(2W)-Cd(1)-O(1)	86.22(9)	O(8)-Cd(2)-O(4)	87.05(8)
O(6)-Cd(1)-O(1)	135.95(8)	O(3)-Cd(2)-O(4)	54.55(8)

Table S2. Selected hydrogen bonds in **1-12** [Å and °]

D-H···A	***d*(D-H)**	***d*(H···A), Å**	***d*(D···A), Å**	**∠DHA,°**	**symmetry operation for acceptor**
1					
O(6)-H(1O6)…O(5)	1.42(1)	1.20(1)	2.618(8)	177(5)	-x, 2-y, -z
N(4)-H(4N)...O(1)	0.84(2)	2.13(2)	2.964(5)	171(5)	x, y+1, z
N(4)-H(3N)...O(7)	0.85(2)	2.30(2)	3.138(5)	173(4)	1/2-x, y+1/2, 1/2-z
N(2)-H(2N)...O(2)	0.84(2)	2.04(2)	2.881(5)	177(5)	x, y-1, z
N(2)-H(1N)...O(8)	0.84(2)	2.18(2)	3.005(5)	167(4)	3/2-x, y-1/2, 1/2-z
2					
N(4)-H(3N)...O(1S)	0.85(2)	2.06(2)	2.904(4)	173(4)	x, y+1, z
N(2)-H(2N)...O(1W)	0.86(2)	2.11(2)	2.928(4)	158(3)	1-x, y+1/2, 1/2-z
N(6)-H(6N)...O(1S)	0.86(2)	2.14(2)	2.969(4)	164(4)	1-x, 1-y, -z
N(6)-H(5N)...O(5)	0.86(2)	2.12(2)	2.925(4)	155(3)	1-x, 2-y, -z
N(2)-H(1N)...O(1)	0.84(2)	2.19(2)	3.027(4)	170(4)	2-x, 2-y, 1-z
N(4)-H(4N)...O(1)	0.86(2)	2.10(2)	2.945(4)	171(3)	x, 5/2-y, z-1/2
O(1W)-H(1W)...O(6)	0.85(2)	1.90(2)	2.750(4)	172(4)	x, y-1, z
O(1W)-H(2W)...O(2)	0.84(2)	2.07(2)	2.889(3)	166(3)	1-x, 1-y, -z
3					
N(2)-H(1N2)…O(1S)	0.86(2)	2.21(3)	2.982(4)	151(4)	x-1, y, z
N(2)-H(2N2)…O(2)	0.89(2)	1.98(2)	2.855(4)	167(4)	x-1, y-1, z+1
N(4)-H(1N4)…O(1S)	0.86(2)	2.19(2)	3.035(4)	168(3)	x, y+1, z-1
N(4)-H(2N4)…O(3)	0.87(2)	1.99(2)	2.852(4)	171(3)	1-x, 1-y,-z
4					
N(2)-H(2A)...O(3)	0.86	2.51	3.24(2)	142.1	1-x, 2-y, 1-z

N(2)-H(2B)...O(2)	0.86	2.13	2.943(19)	157.0	1-x, 1-y,-z
N(4)-H(4A)...O(1)	0.86	2.08	2.936(18)	171.3	x+1, y-1, z-1
N(4)-H(4B)...O(6)	0.86	2.08	2.893(18)	157.4	2-x, 2-y, -z
5					
N(2)-H(2N)…O(1)	0.86(2)	2.06(2)	2.924(8)	174(10)	3–x, -y, 1-z
N(2)-H(1N)…O(1S)	0.86(2)	2.00(5)	2.82(2)	160(11)	x, y-1, z
O(6)-H(1O6)…O(4)	0.87(2)	1.85(3)	2.693(5)	163(6)	x-1/2, 1/2-y, z+1/2
O(6)-H(2O6)…O(5)	0.86(2)	1.91(4)	2.684(5)	149(6)	x-1/2, 1/2-y, z-1/2
6					
N(2)-H(1N2)…O(1S)	0.87(2)	1.99(2)	2.843(5)	166(4)	x, y, z+1
N(2)-H(2N2)…O(1)	0.87(2)	2.10(2)	2.958(4)	173(5)	2–x, -y, 2-z
O(6)-H(1O6)…O(3)	0.86(2)	1.90(2)	2.732(3)	163(4)	x-1/2, 1/2-y, z+1/2
O(6)-H(2O6)…O(2)	0.86(2)	1.92(2)	2.750(4)	160(4)	x-1/2, 1/2-y, z-1/2
7					
O(5)-H(2O5)…O(1)	0.88(2)	2.48(7)	3.021(16)	120(6)	x, y, z
O(5)-H(2O5)…O(3)	0.88(2)	1.94(6)	2.69(2)	142(7)	1/2–x, y-1/2, z+1/2
N(2)-H(2D)…O(1P)	0.86	2.05	2.88(3)	161.9	–x, 1-y, z+1/2
N(2A)-H(2A2)…O(1S)	0.86	2.01	2.84(4)	160.5	–x, 1-y, z-1/2
8					
O(5)-H(2O5)…O(3)	0.89(3)	1.95(6)	2.75(3)	149(8)	1/2–x, y-1/2, z+1/2
C(2)-H(2B)…O(5)	0.97	2.55	3.274(9)	131.8	1/2–x, y-1/2, z+1/2
N(2)-H(2D)…O(1P)	0.86	2.04	2.86(4)	159.4	–x, 1-y, z+1/2
N(2A)-H(2A2)…O(1S)	0.86	2.18	2.97(6)	152.4	–x, 1-y, z-1/2
9					
O(5)-H(2O5)…O(2)	0.87(2)	2.62(8)	3.034(16)	110(7)	x, y, z
O(5)-H(2O5)…O(4)	0.87(2)	1.85(4)	2.66(2)	153(8)	-x-1/2, y+1/2, z+1/2
O(5)-H(1O5)…O(3)	0.87(2)	2.05(7)	2.71(2)	132(7)	-x-1/2, y+1/2, z-1/2
N(2)-H(2C)…O(1P)	0.86	2.17	2.94(3)	147.8	-x, -y-1, z-1/2
N(2A)-H(2A1)…O(1S)	0.86	1.98	2.75(3)	148.7	-x, -y-1, z+1/2
10					
N(2)-H(1N)…O(2)	0.87(2)	2.00(3)	2.865(5)	177(5)	–y, 1/2-x, z-1/4
N(2)-H(2N)…O(5)	0.87(2)	2.23(3)	3.069(5)	161(4)	y-1/2, -x, z-1/4
N(4)-H(3N)…O(6)	0.85(2)	2.25(2)	3.094(5)	175(4)	y, -x-1/2, z+1/4
N(4)-H(4N)…O(1)	0.86(2)	2.16(3)	3.002(5)	167(4)	x, -y, z+1/2
11					
N(4)-H(4N)…O(6)	0.86(3)	2.15(3)	3.004(9)	174(11)	y+1, 1/2-x, z+1/4
N(2)-H(1N)…O(5)	0.85(3)	2.41(5)	3.215(9)	158(10)	y+1/2, 1-x, z-1/4
N(4)-H(3N)…O(1)	0.85(3)	2.26(4)	3.095(9)	167(10)	x, -y, z+1/2
N(2)-H(2N)…O(2)	0.86(3)	2.05(4)	2.893(9)	165(13)	1–y, 3/2-x, z-1/4
12					
O(1W)-H(1W)...O(5)	0.84(2)	2.39(3)	3.009(3)	131(3)	x-1, y, z
O(1W)-H(1W)...O(1S)	0.84(2)	2.26(4)	2.90(3)	133(3)	x-1, y, z
O(1W)-H(1W)...O(1S')	0.84(2)	2.58(4)	3.22(2)	134(3)	x-1, y, z
O(1W)-H(2W)...O(1)	0.85(2)	2.00(2)	2.778(3)	151(3)	x-1, y, z
O(2W)-H(3W)...O(1S)	0.85(2)	2.05(3)	2.90(2)	175(3)	x, y, z
O(2W)-H(3W)...O(1S')	0.85(2)	1.78(3)	2.62(2)	170(4)	x, y, z
O(2W)-H(4W)...O(1X)	0.87(2)	1.82(2)	2.674(4)	171(3)	2-x, 2-y, 1-z
O(3W)-H(5W)...O(2W)	0.87(2)	1.92(2)	2.783(4)	173(4)	x+1, y+1, z
O(3W)-H(6W)...O(1S)	0.85(2)	1.82(3)	2.65(2)	166(4)	x, y+1, z
O(3W)-H(6W)...O(1S')	0.85(2)	2.08(3)	2.92(2)	171(5)	x, y+1, z
O(4W)-H(8W)...O(4)	0.87(2)	1.99(2)	2.781(3)	153(3)	x+1, y, z
O(4W)-H(7W)...O(8)	0.86(2)	1.95(2)	2.741(3)	153(3)	x+1, y, z

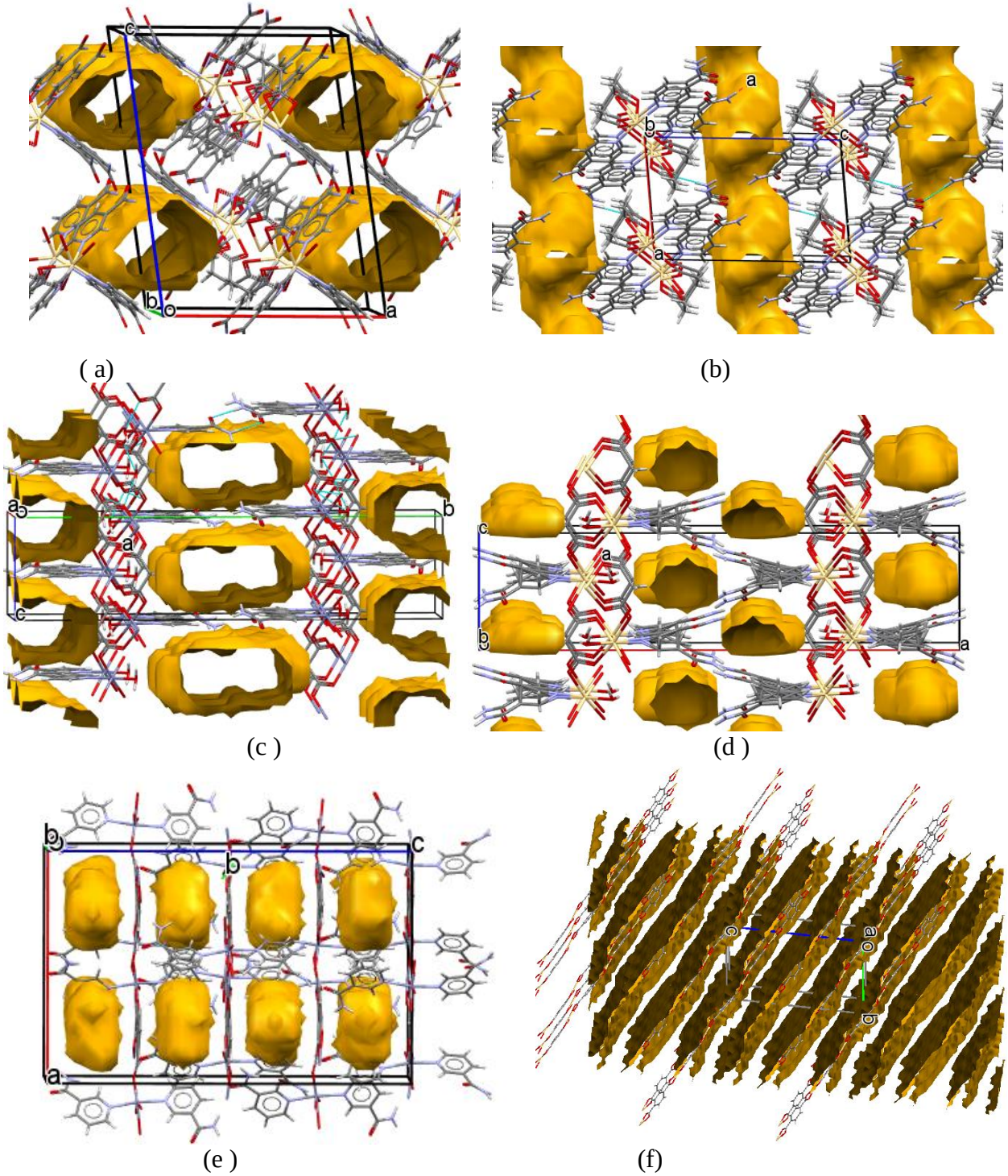


Figure S1. View of solvent accessible voids shown by yellow color in **2** (a), **3** (b), **5** (c), **8** (d), **10** (e), **12** (f).

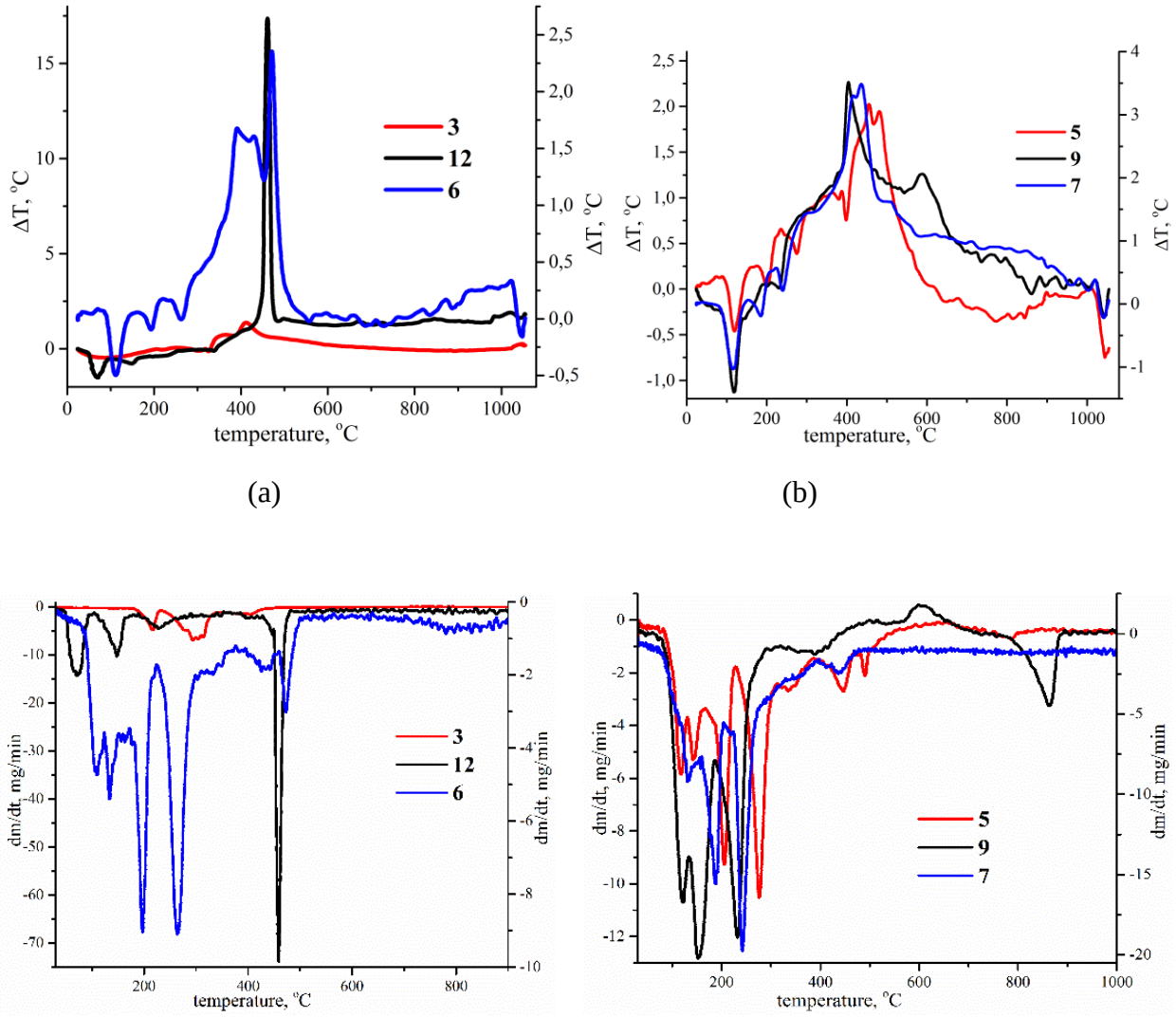
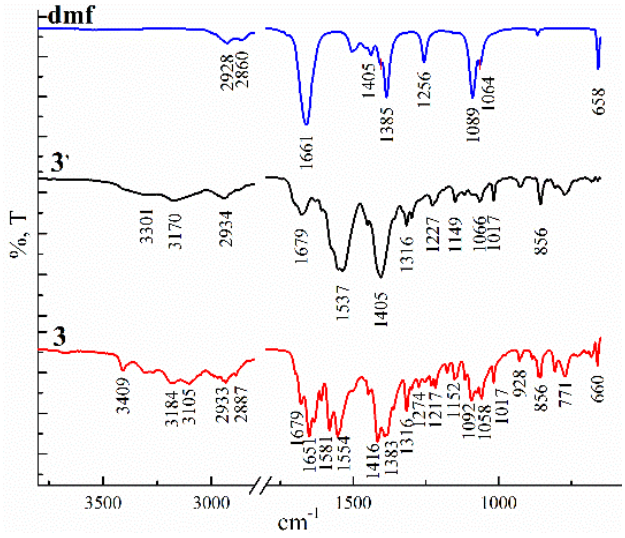


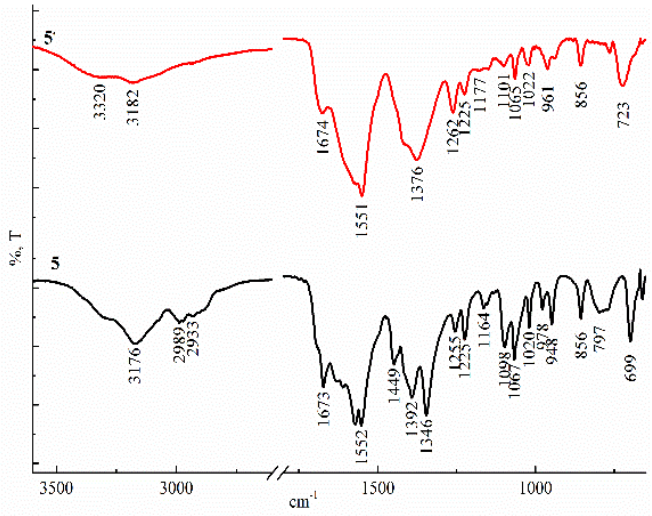
Figure S2. DTA (a, b)/DTG(c, d) curves for **3, 5-7, 9, 12.**

Table S3. Thermal decomposition details for **3, 5, 6, 7, 9,12.**

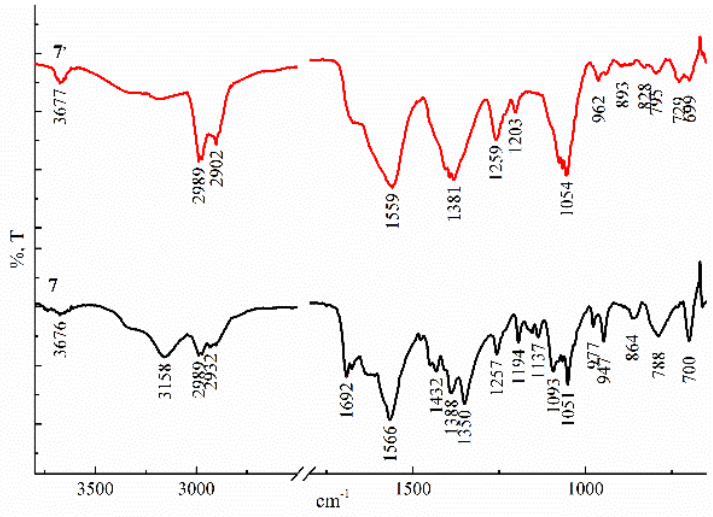
Coordination compound	Temperature interval, °C	DTG max, °C	DTA max, °C	Thermal effect	Weight loss found/calc., %	Removed group
3	167-225	214	219	*endo*	14.02/12.72	-2*dmf*
	225-278	-			15.32/15.30	$-2CO_2$
	278-497	-	410	*exo*	48.61/49.48	oxidation
5	80-196	123	123	*endo*	22.14/23.88	$-H_2O$,
	196-233	150	-	-	12.02/11.81	$-HCONH_2$
	233-324	278	278	*endo*	23.26/23.10	$-2CO_2$
	324-650	471	454	*exo*	20.98/19.95	oxidation
6	82-172	116, 144	120	*endo*	21.14/21.26	$-H_2O$, -*dmf*
	191-217	205	201	*endo*	11.96/10.52	$-HCONH_2$
	232-290	271	271	*endo*	20.63/20.57	$-2CO_2$
	290-500	466	466	*exo*	21.83/21.31	oxidation
7	70-129	128	128	*endo*	4.57/4.72	$-H_2O$
	129-191	147	-	-	19.62/19.16	-*dmf*
	195-222	204	201	*endo*	12.30/11.84	$-HCONH_2$
	223-290	258	258	*endo*	23.94/23.10	$-2CO_2$
	290-491	445	445	*exo*	16.87/18.48	oxidation
9	80-142	126	122	*endo*	18.01/18.39	-*dmf*
	142-205	163	-	-	27.65/26.70	$-H_2O$, $-2CO_2$
	205-455	236	398	*exo*	28.41/30.30	oxidation
12	45-115	70	70	*endo*	18.87/19.82	$-H_2O$, *dmf*
	115-145	-	-	*endo*	4.06/3.92	$-H_2O$
	145-370	227	-	-	15.60/15.93	-*dmf*
	370-480	454	456	*exo*	32.57/32.42	oxidation



(a)



(b)



(c)

Figure S3. IR spectra for dmf, **3** and **3'** (a); **5** and **5'** (b); **7** and **7'** (c).

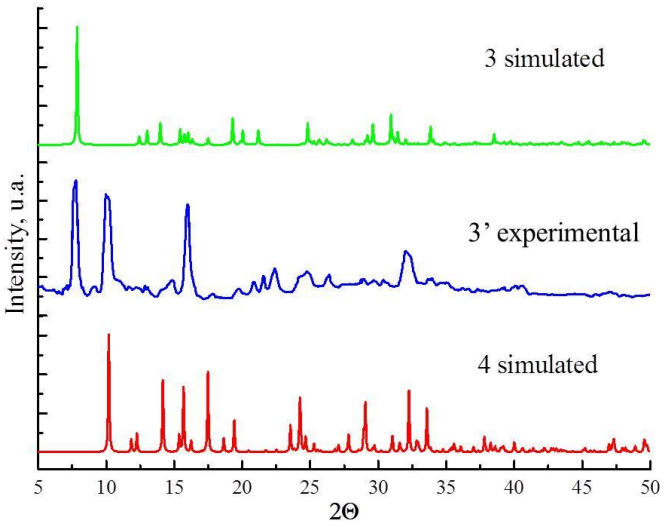


Figure S4. XRPD patterns for **3** (simulated), **3'** (experimental) and **4** (simulated).

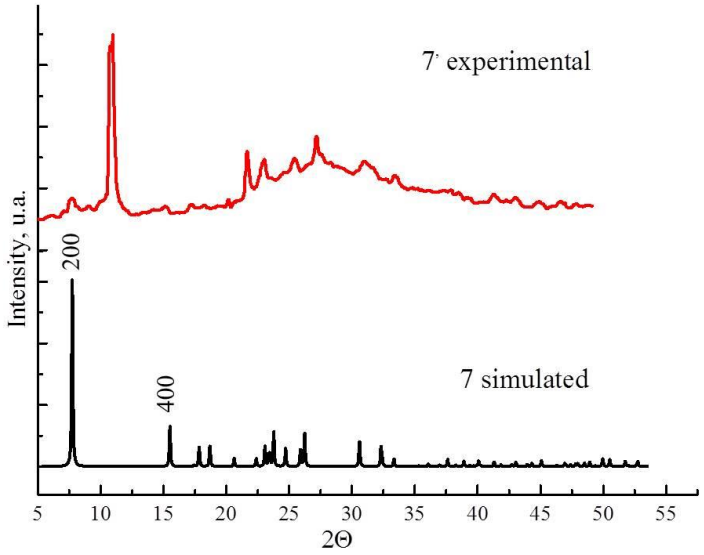


Figure S5. XRPD patterns for **7** (simulated), and **7'** (experimental).

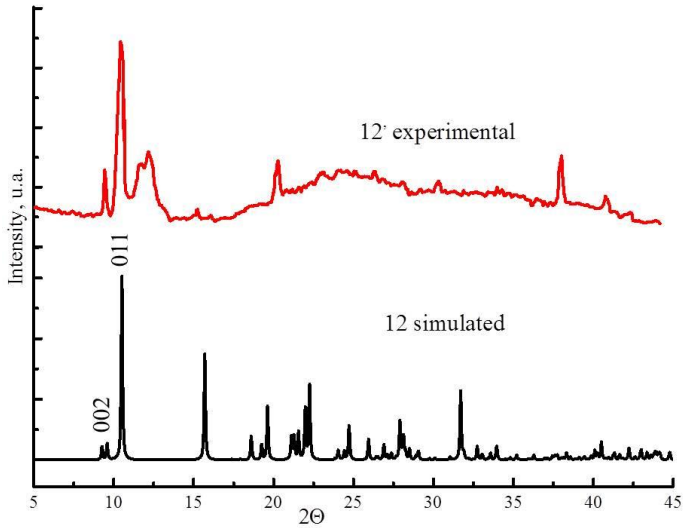
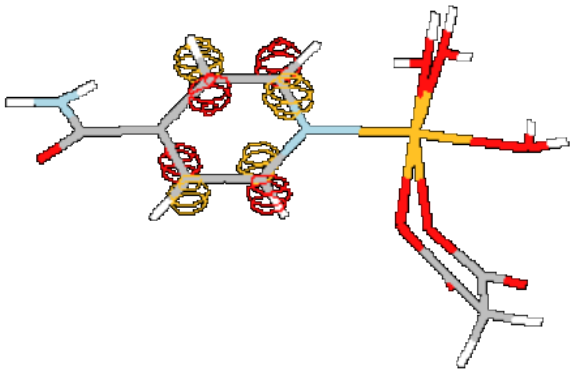
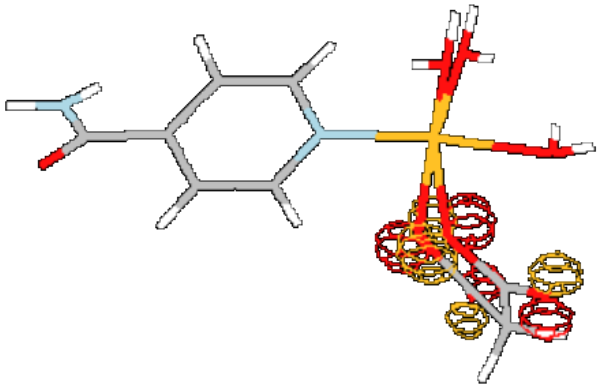


Figure S6. XRPD patterns for **12** (simulated), and **12'** (experimental).



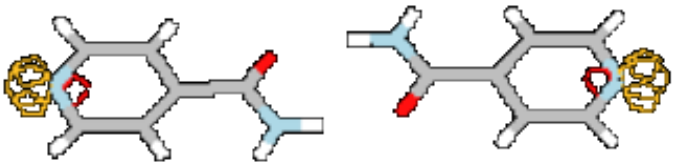
LUMO+3



HOMO-1

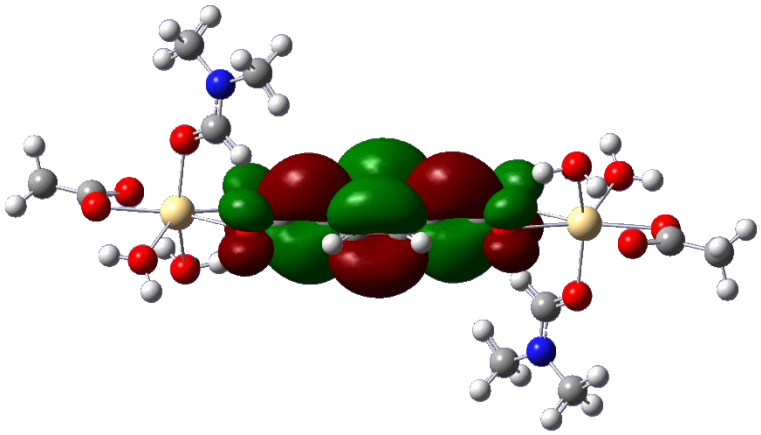
Figure S7. Emitting state in compound **5** representing ligand to ligand charge transfer (oscillator strength: 0.0011)

LUMO

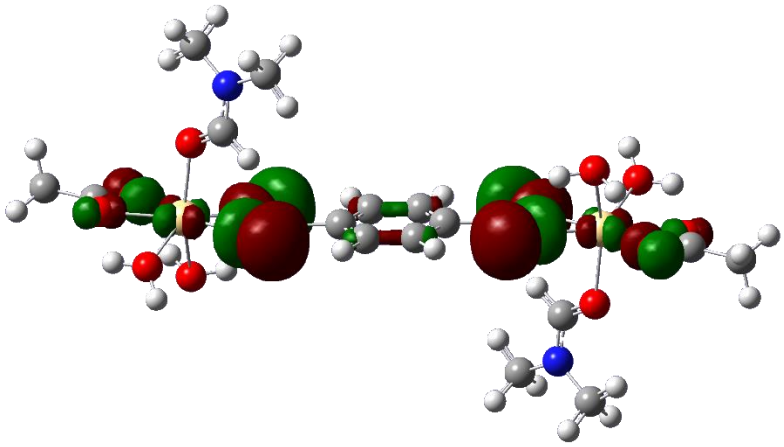


HOMO-4

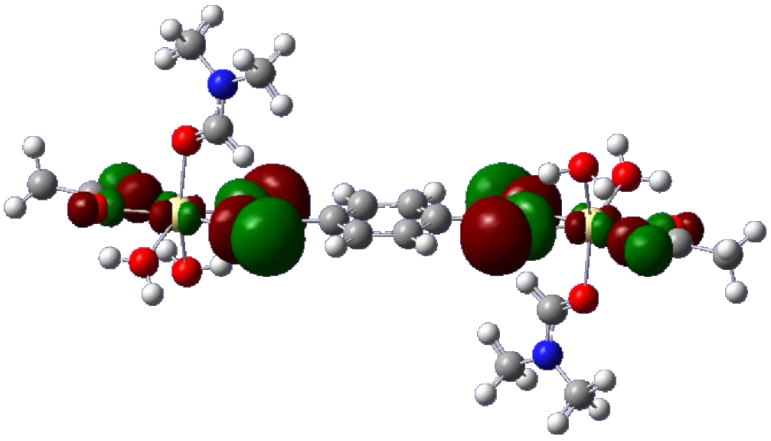
Figure S8. Emitting state in iso-nia dimer (n-π* character, oscillator strength: 0.006)



LUMO



HOMO



HOMO-1

Figure S9. Emitting state in compound **12** representing local excitation of COO- to Phenyl charge transfer nature (oscillator strength: 0.0002).