Supplementary Information

Synthesis, Spectroscopic Characterizations and DFT Calculations of Two-Dimensional Monoclinic and Orthorhombic Phases of Metal–Organic Frameworks Based on BTC–2,2′-Bipyridine and Cu(II) Ions

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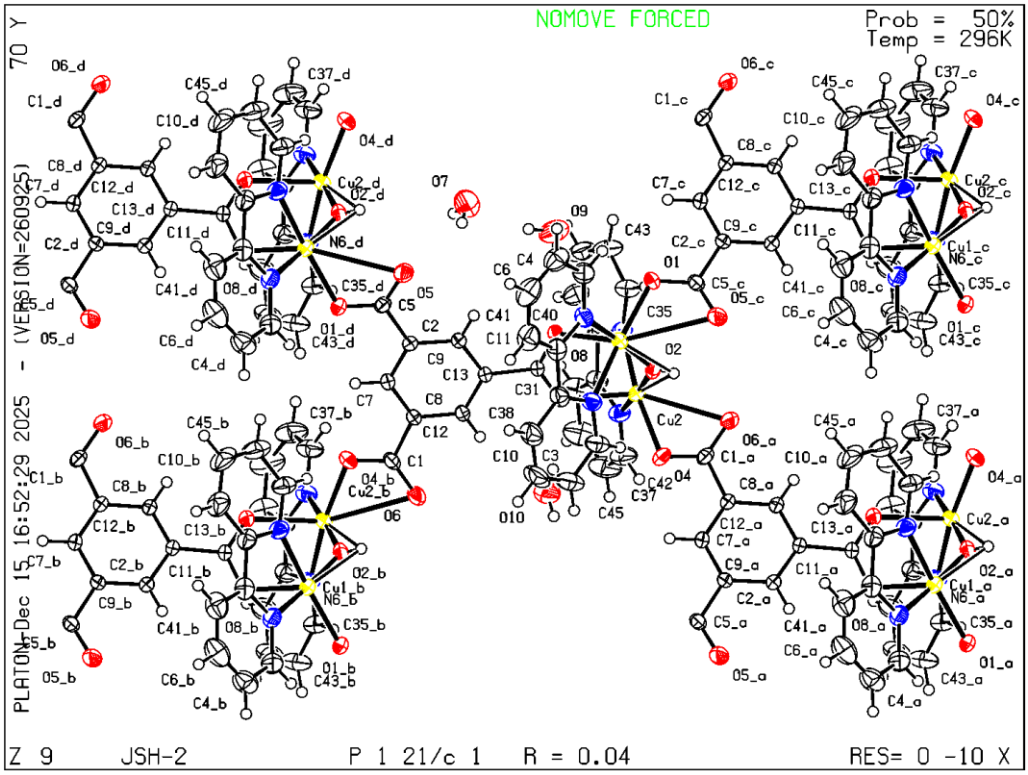

Figure S1. ORTEP diagram of system **1**.

Table S1. Bond distances (Å) for system **1.**

Bond	Value (Å)	Bond	Value (Å)	Bond	Value (Å)
Cu1-O1	1.9619(13)	N16-C24	1.352(3)	C10-H10	0.93
Cu1-O2	1.8987(15)	N16-C30	1.336(3)	C10-C38	1.375(4)
Cu1-O8	2.2589(14)	N23-C25	1.350(3)	C10-C45	1.355(4)
Cu1-N10	2.0269(16)	N23-C42	1.336(3)	C11-C13	1.514(2)
Cu1-N16	2.0101(17)	C1-C8	1.504(2)	C12-H12	0.93
Cu2-O2	1.9066(16)	C2-C5	1.502(2)	C12-C13	1.386(2)
Cu2-O3	2.3167(13)	C2-C7	1.395(2)	C21-C25	1.463(3)
Cu2-O4	1.9910(13)	C2-C9	1.396(2)	C21-C40	1.388(3)
Cu2-N6	2.0284(16)	C3-H3	0.93	C24-C27	1.465(3)
Cu2-N23	2.0077(18)	C3-C31	1.379(4)	C24-C41	1.388(3)
O1-C5	1.270(2)	C3-C37	1.370(4)	C25C31	1.384(3)
O2-H2	0.62(3)	C4-H4	0.93	C27-C38	1.394(3)
O3-C11	1.260(2)	C4-C6	1.371(4)	C30-H30	0.93
O4-C1	1.270(2)	C4-C30	1.384(3)	C31-H31	0.93
O5-C5	1.244(2)	C6-H6	0.93	C32-H32	0.93
O6-C1	1.232(2)	C6-C41	1.367(4)	C32-C45	1.384(3)
O8-C11	1.258(2)	C7-H7	0.93	C35-H35	0.93
N6-C21	1.345(3)	C7-C8	1.392(2)	C35-C43	1.377(3)
N6-C35	1.335(3)	C8-C12	1.397(2)	C37-H37	0.93
N10-C27	1.348(3)	C9-H9	0.93	C37-C42	1.389(4)
N10-C32	1.341(3)	C9-C13	1.391(2)	C38-H38	0.93

Table S2. Angles (°) for system **1.**

Angle	Value (°)	Angle	Value (°)	Angle	Value (°)
O2-Cu1-O1	93.22(6)	C35-N6-C21	119.22(18)	C8-C7-C2	120.11(16)
O8-Cu1-O1	104.07(6)	C27-N10-Cu1	114.12(14)	C8-C7-H7	119.95(10)
O8-Cu1-O2	91.31(6)	C32-N10-Cu1	125.85(15)	C7-C8-C1	122.45(16)
N10-Cu1-O1	166.19(7)	C32-N10-C27	119.17(19)	C12-C8-C1	118.05(15)
N10-Cu1-O2	94.58(7)	C24-N16-Cu1	114.96(14)	C12-C8-C7	119.49(15)
N10-Cu1-O8	87.14(6)	C30-N16-Cu1	125.78(15)	H9-C9-C2	119.57(10)
N16-Cu1-O1	91.47(6)	C30-N16-C24	119.20(19)	C13-C9-C2	120.86(15)
N16-Cu1-O2	174.45(7)	C25-N23-Cu2	113.92(13)	C13-C9-H9	119.57(10)
N16-Cu1-O8	90.42(6)	C42-N23-Cu2	126.69(16)	C38-C10-H10	120.16(16)
N16-Cu1-N10	80.24(7)	C42-N23-C25	119.0(2)	C45-C10-H10	120.16(15)
O3-Cu2-O2	90.49(6)	O6-C1-O4	123.55(17)	C45-C10-C38	119.7(2)
O4-Cu2-O2	93.02(7)	C8-C1-O4	117.33(16)	O8-C11-O3	125.85(15)
O4-Cu2-O3	102.45(5)	C8-C1-O6	119.12(17)	C13-C11-O3	117.50(15)
N6-Cu2-O2	94.87(7)	C7-C2-C5	121.31(15)	C13-C11-O8	116.65(15)
N6-Cu2-O3	88.95(6)	C9-C2-C5	119.25(15)	H12-C12-C8	119.52(10)
N6-Cu2-O4	166.07(7)	C9-C2-C7	119.41(15)	C13-C12-C8	120.97(15)
N23-Cu2-O2	174.67(7)	C31-C3-H3	120.11(18)	C13-C12-H12	119.52(10)
N23-Cu2-O3	90.22(6)	C37-C3-H3	120.11(16)	C11-C13-C9	120.04(14)
N23-Cu2-O4	91.99(7)	C37-C3-C31	119.8(3)	C12-C13-C9	119.00(15)
N23-Cu2-N6	79.86(7)	C6-C4-H4	120.70(15)	C12-C13-C11	120.95(15)
C5-O1-Cu1	114.70(12)	C30-C4-H4	120.70(15)	C25-C21-N6	114.63(18)
Cu2-O2-Cu1	135.04(8)	C30-C4-C6	118.6(2)	C40-C21-N6	121.3(2)
H2-O2-Cu1	113(3)	O5-C5-O1	124.02(16)	C40-C21-C25	124.1(2)
H2-O2-Cu2	111(3)	C2-C5-O1	115.95(16)	C27-C24-N16	114.72(18)
C11-O3-Cu2	124.79(11)	C2-C5-O5	120.03(16)	C41-C24-N16	120.8(2)
C1-O4-Cu2	112.41(12)	H6-C6-C4	120.03(15)	C41-C24-C27	124.4(2)
C11-O8-Cu1	119.98(11)	C41-C6-C4	119.9(2)	C21-C25-N23	114.83(19)
C21-N6-Cu2	113.28(13)	C41-C6-H6	120.03(16)	C31-C25-N23	122.0(2)
C35-N6-Cu2	126.42(15)	H7-C7-C2	119.95(10)	C31-C25-C21	123.1(2)

Table S3. Dihedral angles (°) for system **1.**

Angle	Value (°)	Angle	Value (°)	Angle	Value (°)
Cu1-O1-C5-O5	-15.18(15)	O1-C5-C2-C7	-6.4(2)	N16-C24-C27-C38	-173.6(2)
Cu1-O1-C5-C2	164.00(11)	O1-C5-C2-C9	171.61(16)	N16-C24-C41-C6	0.1(3)
Cu1-O8-C11-O3	-48.06(15)	O3-C11-C13-C9	-176.88(16)	N16-C30-C4-C6	-0.6(3)
Cu1-O8-C11-C13	131.71(12)	O3-C11-C13-C12	1.8(2)	N23-C25-C21-C40	-178.6(2)
Cu1-N10-C27-C24	-10.42(15)	O4-C1-C8-C7	17.6(2)	N23-C25-C31-C3	-2.2(3)
Cu1-N10-C27-C38	168.43(16)	O4-C1-C8-C12	-163.69(18)	N23-C42-C37-C3	-2.8(3)
Cu1-N10-C32-C45	-167.0(2)	O5-C5-C2-C7	174.35(18)	C1-C8-C7-C2	175.24(18)
Cu1-N16-C24-C27	2.72(15)	O5-C5-C2-C9	-7.6(2)	C1-C8-C12-C13	-177.74(17)
Cu1-N16-C24-C41	-177.32(17)	O6-C1-C8-C7	-161.7(2)	C2-C7-C8-C12	-3.4(2)
Cu1-N16-C30-C4	177.22(19)	O6-C1-C8-C12	17.0(2)	C2-C9-C13-C11	174.66(16)
Cu2-O3-C11-O8	-9.76(17)	O8-C11-C13-C9	3.3(2)	C2-C9-C13-C12	-4.0(2)
Cu2-O3-C11-C13	170.47(13)	O8-C11-C13-C12	-178.01(16)	C3-C31-C25-C21	175.2(2)
Cu2-O4-C1-O6	-1.59(18)	N6-C21-C25-N23	2.2(2)	C4-C6-C41-C24	-0.3(3)
Cu2-O4-C1-C8	177.67(12)	N6-C21-C25-C31	-175.4(2)	C6-C41-C24-C27	-179.9(2)
Cu2-N6-C21-C25	-15.02(15)	N6-C21-C40-C39	2.2(3)	C7-C8-C12-C13	1.0(2)
Cu2-N6-C21-C40	165.75(16)	N6-C35-C43-C39	2.0(3)	C8-C12-C13-C9	2.7(2)
Cu2-N6-C35-C43	-166.3(2)	N10-C27-C24-N16	5.2(2)	C8-C12-C13-C11	-175.95(17)
Cu2-N23-C25-C21	11.84(16)	N10-C27-C24-C41	-174.8(2)	C10-C38-C27-C24	178.9(2)
Cu2-N23-C25-C31	-170.49(17)	N10-C27-C38-C10	0.1(3)	C21-C40-C39-C43	0.9(3)
Cu2-N23-C42-C37	172.1(2)	N10-C32-C45-C10	-0.4(3)	C35-C43-C39-C40	-2.9(3)

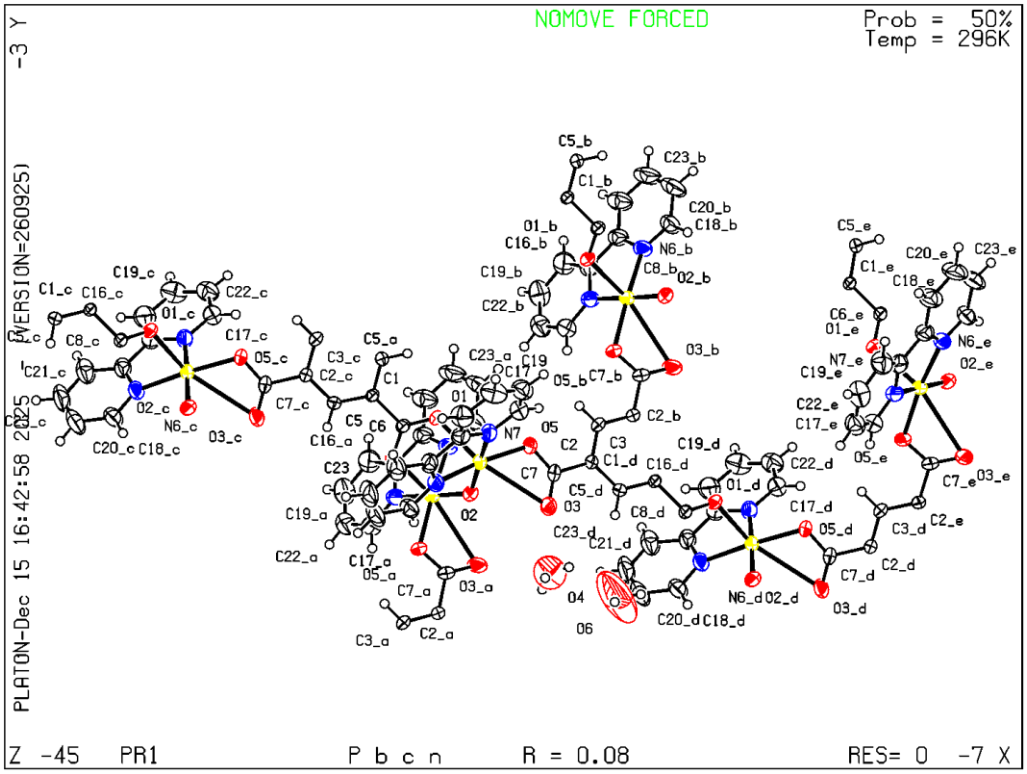

Figure S2. ORTEP diagram of system **2**.

Table S4. Bond distances (Å) for system **2.**

Bond	Value (Å)	Bond	Value (Å)	Bond	Value (Å)
Cu1-O2	2.265(3)	C7-C13	1.507(9)	C6-H6	0.93
Cu1-O3	1.957(3)	C8-C14	1.386(6)	C4-H4	0.93
Cu1-O4	1.898(2)	C8-H8	0.93	C5-C2	1.405(11)
Cu1-N6	2.031(4)	N9-C10	1.347(8)	C5-H5	0.93
Cu1-N9	2.003(5)	N9-C3	1.338(7)	C2-C9	1.359(10)
C12-C14	1.386(6)	C10-C16	1.487(9)	C2-H2	0.93
C12-C14	1.386(6)	C10-C5	1.359(10)	C1-H1	0.93
C12-H12	0.93	C11-C14	1.504(7)	C9-H9	0.93
O2-C13	1.252(4)	C16-C1	1.378(9)	O6-H6a	0.85
O3-C11	1.277(6)	C15-C6	1.363(12)	O6-H6b	0.85
O5-C11	1.228(7)	C15-C4	1.389(9)	O1-H1a	0.85
N6-C16	1.324(8)	C15-H15	0.93	O1-H1a	0.85
N6-C4	1.335(8)	C3-C9	1.384(10)	O1-H1b	0.85
C7-C8	1.398(5)	C3-H3	0.93	O1-H1b	0.85
C7-C8	1.398(5)	C6-C1	1.392(11)	H1a-H1b	1.1(2)

Table S5. Angles (°) for system **2.**

Angle	Value (°)	Angle	Value (°)	Angle	Value (°)
O3-Cu1-O2	106.65(15)	H8-C8-C7	119.6(3)	C9-C3-N9	122.1(6)
O4-Cu1-O2	91.32(17)	H8-C8-C14	119.6(3)	H3-C3-N9	118.9(4)
O4-Cu1-O3	91.70(15)	C10-N9-Cu1	115.5(4)	H3-C3-C9	118.9(4)
N6-Cu1-O2	85.09(17)	C3-N9-Cu1	125.6(4)	C1-C6-C15	120.1(7)
N6-Cu1-O3	165.5(2)	C3-N9-C10	118.8(6)	H6-C6-C15	119.9(4)
N6-Cu1-O4	96.60(17)	C16-C10-N9	113.6(6)	H6-C6-C1	119.9(5)
N9-Cu1-O2	92.08(17)	C5-C10-N9	121.8(6)	C15-C4-N6	121.7(7)
N9-Cu1-O3	91.01(18)	C5-C10-C16	124.6(6)	H4-C4-N6	119.2(4)
N9-Cu1-O4	174.87(15)	O5-C11-O3	123.9(5)	H4-C4-C15	119.2(5)
N9-Cu1-N6	79.9(2)	C14-C11-O3	115.4(5)	C2-C5-C10	119.3(7)
C14-C12-C14	120.3(6)	C14-C11-O5	120.6(4)	H5-C5-C10	120.4(4)
H12-C12-C14	119.9(3)	O2-C13-O2	126.9(6)	H5-C5-C2	120.4(5)
H12-C12-C14	119.9(3)	C7-C13-O2	116.5(3)	C9-C2-C5	118.7(7)
C13-O2-Cu1	124.3(3)	C7-C13-O2	116.5(3)	H2-C2- C5	120.6(5)
C11-O3-Cu1	114.3(3)	C8-C1-C12	119.8(5)	H2-C2-C9	120.6(4)
Cu1-O4-Cu1	135.4(3)	C11-C14-C12	121.5(4)	C6-C1-C16	117.6(8)
C16-N6-Cu1	114.1(4)	C11-C14-C8	118.7(4)	H1-C1-C16	121.2(5)
C4-N6-Cu1	125.0(5)	C10-C16-N6	115.0(5)	H1-C1-C6	121.2(5)
C4-N6-C16	119.5(5)	C1-C16-N6	122.6(6)	C2-C9-C3	119.2(7)
C8-C7-C8	118.4(6)	C1-C16-C10	122.4(7)	H9-C9-C3	120.4(4)
C13-C7-C8	120.8(3)	C4-C15-C6	118.4(7)	H9-C9-C2	120.4(4)
C13-C7-C8	120.8(3)	H15-C15-C6	120.8(4)	H6b-O6-H6a	104.5
C14-C8-C7	120.9(4)	H15-C15-C4	120.8(5)	H1a-O1-H1a	171(28)

Table S6. Dihedral angles (°) for system **2**.

Angle	Value (°)	Angle	Value (°)	Angle	Value (°)
Cu1-O2-C13-O2	27.8(6)	C12-C14-C8-C7	-0.9(5)	N6-C16 C1 C6	1.9(7)
Cu1-O2-C13-C7	-152.17(19)	C12-C14-C11-O3	0.5(5)	N6-C4-C15-C6	-1.3(8)
Cu1-O3-C11-O5	6.0(5)	C12-C14-C11-O3	0.5(5)	C7-C8-C14-C11	-179.7(4)
Cu1-O3-C11-C14	-173.7(4)	C12-C14-C11-O5	-179.2(5)	C7-C8-C14-C11	179.7(4)
Cu1-N6-C16-C10	14.8(4)	C12-C14-C11-O5	-179.2(5)	N9-C10-C16-C1	174.6(6)
Cu1-N6-C16-C1	-167.3(5)	O2-C13-C7-C8	-5.4(3)	N9-C10-C5-C2	1.9(7)
Cu1-N6-C4-C15	165.4(6)	O2-C13-C7-C8	174.6(3)	N9-C3-C9-C2	0.1(8)
Cu1-N9-C10-C16	-3.8(4)	O3-C11-C14-C8	-178.2(5)	C10-C16-C1-C6	179.7(7)
Cu1-N9-C10-C5	176.2(5)	O5-C11-C14-C8	2.1(7)	C10-C5-C2-C9	-1.3(8)
Cu1-N9-C3-C9	-177.0(5)	N6-C16-C10-N9	-7.4(6)	C16-C1-C6-C15	-3.2(8)
C12-C14-C8-C7	0.9(5)	N6-C16-C10-C5	172.5(6)	C3-C9-C2-C5	0.4(8)

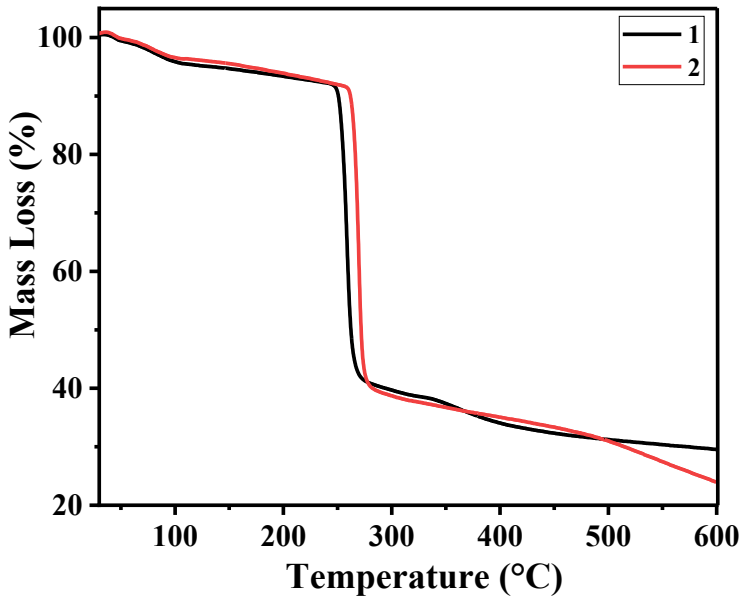

Figure S3. TGA curves for **1** and **2**.

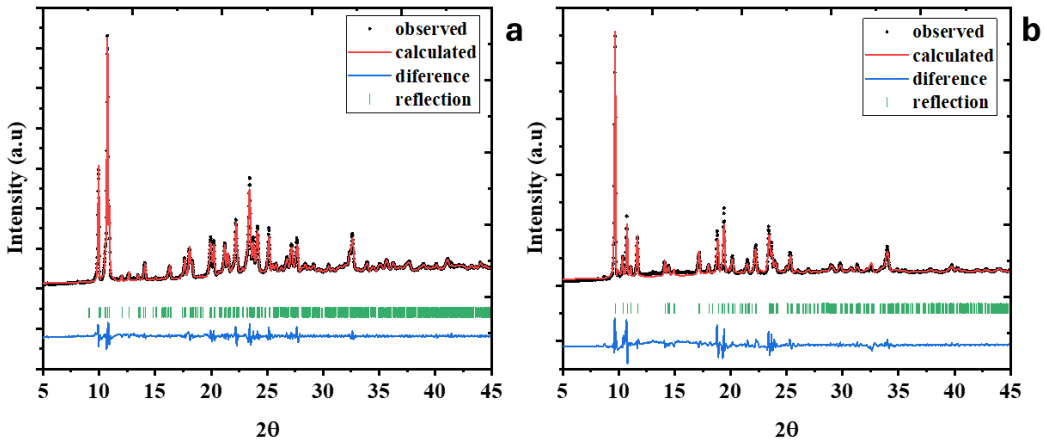

Figure S4. Diffraction patterns of a) **1** and b) **2**

Figure S5. Cluster model extracted from the optimized crystal structure of each phase.

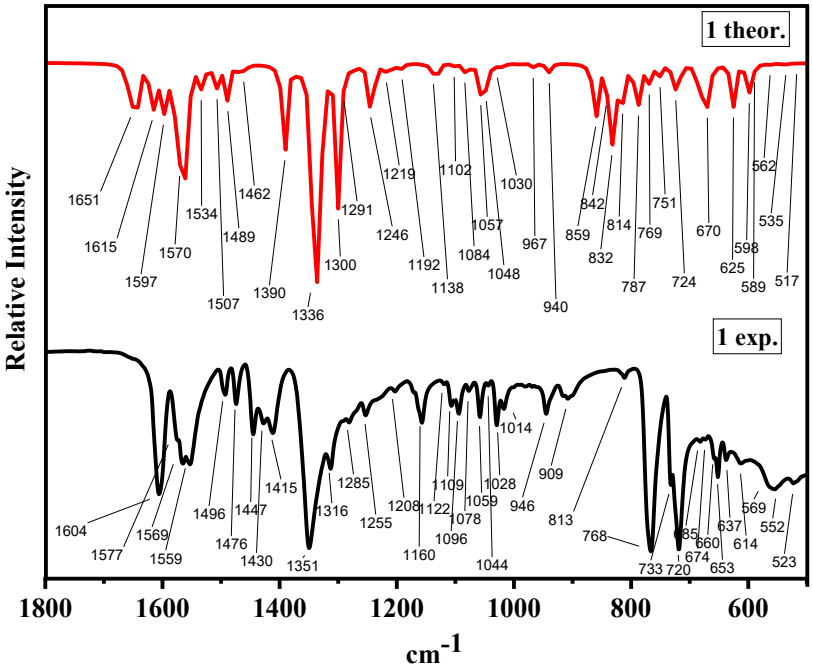

Figure S6. Theoretical (red line) and experimental (black line) IR spectra of the system **1.**

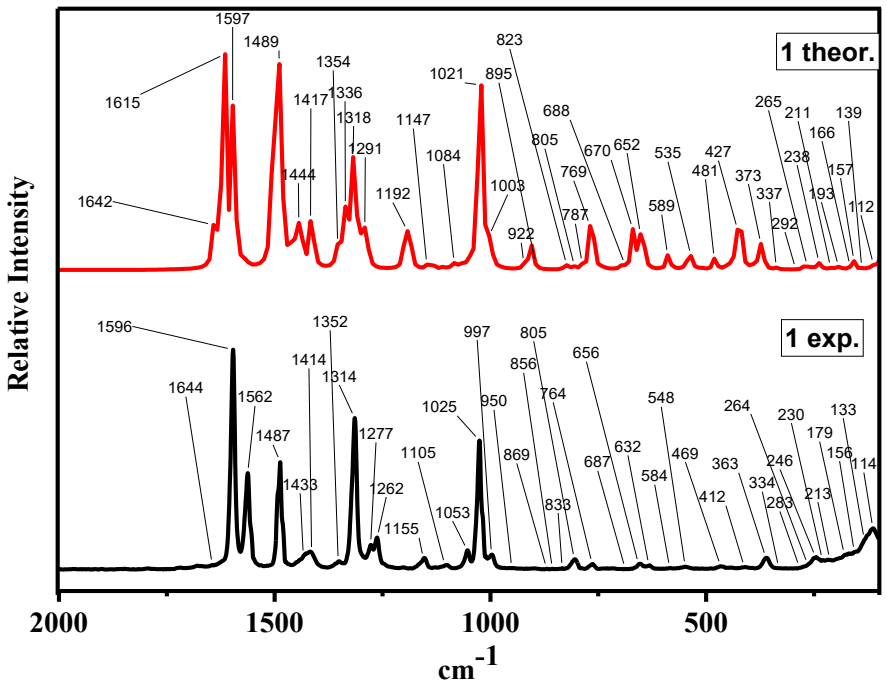

Figure S7. Theoretical (red line) and experimental (black line) Raman spectra of system **1.**

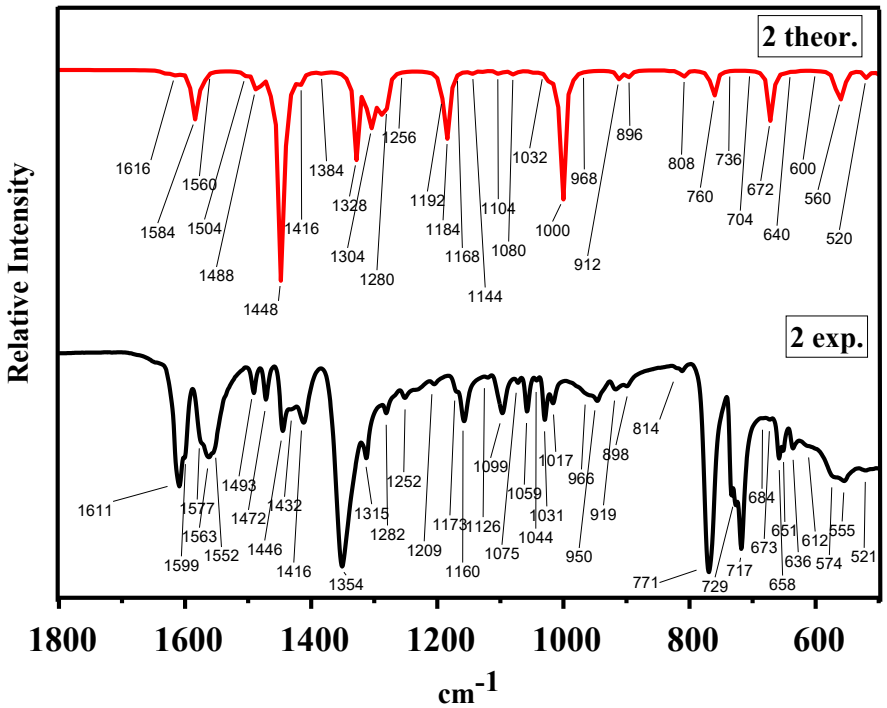

Figure S8. Theoretical (red line) and experimental (black line) IR spectra of the system **2.**

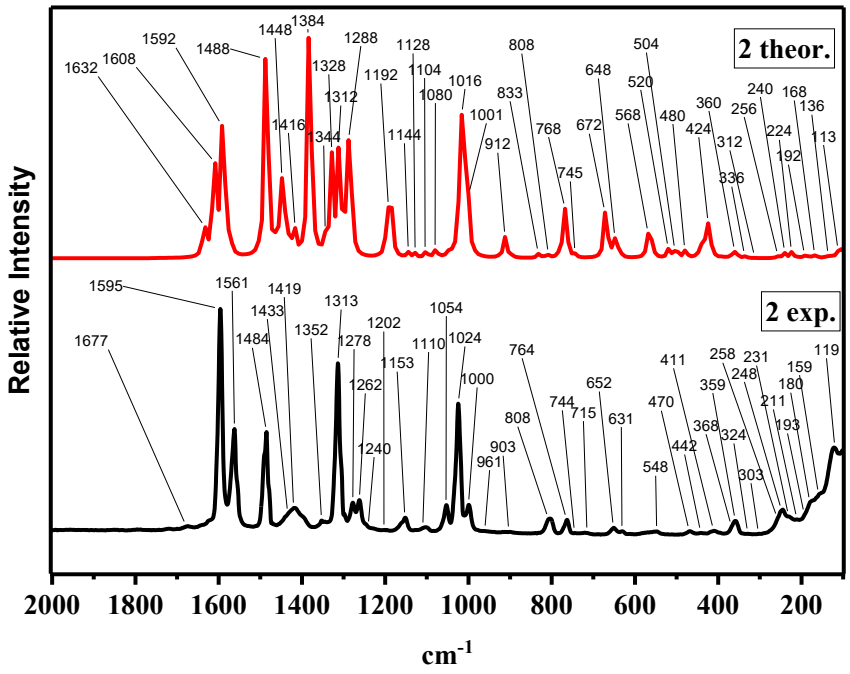

Figure S9. Theoretical (red line) and experimental (black line) Raman spectra of system **2.**

Table S7 presents a comparison of the experimental frequency values obtained by infrared (IR) and Raman spectroscopy with the theoretical values calculated by DFT for **1.** The assignments corresponding to the characteristic vibrational modes of the functional groups present in the structure are included.

Table S7. Vibrational modes assigned by IR and Raman spectroscopy, and their corresponding theoretical values calculated for system **1**.

IR exp. (cm^{-1})	IR theor. (cm^{-1})	Raman expe. (cm^{-1})	Raman theor. (cm^{-1})	Assignamen
3453	-	-	-	ν (O-H), H_2O
3370	3325	-	3533	ν (O-H) bridge
3085	3163	3068	3152	ν (C-H)
		1644	1642	ν (C=C) + ν (C=N) es 2,2-bipy
1604	1651			ν (C=C) + ν (C=N) es 2,2-bipy
1577	1615	1596	1615	ν_{as} (C=O) + ν (C=C) + ν (C=N) R 2,2′-bipy
1569	1597	1562	1597	ν_{as} (C=O) + ν (C=C) R BTC
1559	1570	1487	1489	ν_{as} (C=O) + δ (C-H) R BTC
1496	1534	1433	1444	δ (C-H)R 2,2′-bipy + δ (C-H) R BTC
1476	1507	1414	1417	ν_{as} (C=O) + δ (C=C) R BTC + δ (C-H)R 2,2′-bipy

1447	1489			ν_{as} (C=O) + δ (C=C) R BTC + δ (C-H)R 2,2′-bipy
1430	1462			δ (C-H)R 2,2′-bipy
1415	1390			δ (C-H) R 2,2′-bipy, R BTC + ν (C-C) R 2,2′-bipy + ν (C-C) R BTC + ν_s (C=O)
		1352	1354	δ (C-H) R 2,2′-bipy, R BTC + ν (C-C) R 2,2′-bipy + ν (C-C) R BTC + ν_s (C=O)
1351	1336	1314	1336	ν_s (C=O) + δ (C-H)R 2,2′-bipy + + δ (C=C), (C=N) R 2,2′-bipy
		1277	1318	ν_s (C=O) + δ R BTC + δ (C-H) R 2,2′-bipy + δ (C=C), (C=N)R 2,2′-bipy + ν (C-C) R 2,2′-bipy (C-C) R 2,2′-bipy
1316	1300			δ (C-H)R 2,2′-bipy, BTC + ν (C-C) R 2,2′-bipy
1285	1291	1262	1291	δ R 2,2′-bipy
1255	1246			δ (C-H) R BTC
1208	1219			τ R BTC + ν (C-C) R BTC + ν_s (C=O)
1160	1192	1155	1192	ν (C-C) R 2,2′-bipy
		1105	1147	δ (C-H)R 2,2′-bipy
1122	1138			δ (C-H)R 2,2′-bipy
1109	1102			δ (C-H)R 2,2′-bipy
1096	1084	1053	1084	δ (O-H) bridge
1078	1057			δ R BTC
1059	1048			δ (C-H) R 2,2′-bipy
1044	1030			δ (C=C), δ (C=N) R 2,2′-bipy + δ (C=C) R BTC
		1025	1021	δ (C=C), δ (C=N) R 2,2′-bipy
		997	1003	γ (C-H) R BTC + γ (C=C), + γ (C-H), γ (C=C), (C=N) R 2,2′-bipy
1028	967			γ (C-H)R BTC
1014	940			γ (C-H) R 2,2′-bipy
		950	922	τ (C=C) R BTC + ν (C-C) R BTC
		869	895	τ R BTC + ν (C-C) R BTC
946	859			γ (C-H) R 2,2′-bipy
909	842			γ (C-H) R 2,2′-bipy
813	832			γ (C-H) R 2,2′-bipy
		856	823	γ (C=C), (C=O)) R BTC
768	814			γ (C=C), (C=O) R BTC
		833	805	γ (C-H) R 2,2′-bipy
733	787	805	787	γ R BTC + τ R 2,2′-bipy
720	769	764	769	γ (C-H) R 2,2′-bipy
685	751			γ (C=C), (C=N) R 2,2′-bipy
674	724			γ (C=C), (C=N) R 2,2′-bipy
		687	688	γ (C=C), R BTC
660	670	656	670	ν (N-Cu) + τ R 2,2′-bipy
653	625			ν (Cu-OCO-Cu′) + τ R BTC
637	598			ν_{as} (Cu-OH-Cu′)
614	589			γ (C=C), (C=N) R 2,2′-bipy + ν_{as} (Cu-OH-Cu′)
		584	589	ν_{as} (Cu-OH-Cu′)
569	562			ν (Cu-OCO-Cu′) + τ R BTC
552	535	548	535	ν (Cu-OCO-Cu′) + τ R BTC + ν_{as} (Cu-OH-Cu′)

523	517			ν_{as} (Cu-OCO-Cu′) + τ R BTC + γ (O-H) bridge
		469	481	τ R 2,2′-bipy + τ R BTC
		412	427	γ R 2,2′-bipy + γ (OH,O′-Cu-N,N′) basal plane
		363	373	ν_{as} (Cu-OCO-Cu′) + τ R BTC + γ (O-H) bridge
		334	357	ν_{s} (Cu-OCO-Cu′) + ν_{s} (Cu-OH-Cu′) + τ R BTC
		283	292	+ τ (C=O) R BTC + τ R 2,2′-bipy + τ (Cu-N) basal plane
		264	265	γ (Cu-N) basal plane
		246	238	γ (Cu-N) basal plane
		230	211	τ DCu + τ (C=O) R BTC
		213	193	τ DCu
		179	166	τ (Cu-OH-Cu) + τ (Cu-N) basal plane
		156	157	τ (Cu-N) basal plane
		133	139	τ DCu + τ (C=O) R BTC
		114	112	τ DCu + τ R BTC + τ R 2,2′-bipy

Abbreviations used in the assignment of vibrational modes: ν, stretching mode; δ, in-plane bending; γ, out-of-plane bending; τ, torsion; as, antisymmetric vibration; s, symmetric vibration; sciss, twist; R-2,2′-bipy, 2,2′-bipyridine rings; R-BTC, BTC ring; DCu; dinuclear environment.

Table S8. Vibrational modes assigned by IR and Raman spectroscopy, and their corresponding theoretical values calculated for system **2**.

IR exp. (cm^{-1})	IR theor. (cm^{-1})	Raman expe. (cm^{-1})	Raman theor. (cm^{-1})	Assignamen
3453	-	-	-	ν (O-H), H_2O
3370	3325	-	3533	ν (O-H) bridge
3085	3163	3068	3152	ν (C-H)
		1677	1632	ν (C=C) + ν (C=N) es 2,2-bipy
1611	1616			ν (C=C) + ν (C=N) es 2,2-bipy
1599	1584	1595	1608	ν_{as} (C=O) + ν (C=C) + ν (C=N) R 2,2′-bipy
1577	-	1561	1592	ν_{as} (C=O) + ν (C=C) R BTC
1563	1560	1484	1488	ν_{as} (C=O) + δ (C-H) R BTC
1552	-	1433	1448	δ (C-H)R 2,2′-bipy + δ (C-H) R BTC
1493	1504			δ (C-H) R 2,2′-bipy
1472	1488			ν_{as} (C=O) + δ (C=C) R BTC + δ (C-H)R 2,2′-bipy

1446	1448			δ (C-H)R 2,2′-bipy
1432	-			δ (C-H) R 2,2′-bipy, R BTC + ν (C-C) R 2,2′-bipy + ν (C-C) R BTC + ν_s (C=O)
1416	1416	1419	1416	ν_{as} (C=O) + δ (C=C) R BTC + δ (C-H)R 2,2′-bipy
1354	1384	1352	1384	δ (C-H) R 2,2′-bipy, R BTC + ν (C-C) R 2,2′-bipy + ν (C-C) R BTC + ν_s (C=O)
		1313	1344	ν_s (C=O) + δ (C-H)R 2,2′-bipy + + ν (C-C) R 2,2′-bipy + δ (C=C), (C=N) R 2,2′-bipy
1315	1328	1278	1328	ν_s (C=O) + δ R BTC + δ (C-H) R 2,2′-bipy + δ (C=C), (C=N)R 2,2′-bipy + ν (C-C) R 2,2′-bipy
1282	1304			δ R 2,2′-bipy
		1262	1312	ν (C-C) R 2,2′-bipy
		1240	1288	ν (C-C) R 2,2′-bipy + δ R 2,2′-bipy + δ (C-H) R 2,2′-bipy
1252	1280			δ (C-H) R BTC
1209	1256			τ R BTC + ν (C-C) R BTC + ν_s (C=O)
1173	1192	1202	1192	δ (C-H)R 2,2′-bipy
1160	1184			δ (C-H)R 2,2′-bipy
1126	1168			δ (C-H)R 2,2′-bipy
1099	1144	1153	1144	δ (O-H) bridge
1075	1104			δ R BTC
1059	1080			δ (C-H) R 2,2′-bipy
		1110	1128	δ (C=C), δ (C=N) R 2,2′-bipy
		1054	1104	γ (C-H) R BTC + γ (C=C), + γ (C-H), γ (C=C), (C=N) R 2,2′-bipy
1047				δ (C=C), δ (C=N) R 2,2′-bipy + δ (C=C) R BTC
1031	1032			γ (C-H)R BTC
1017	1000			γ (C-H) R 2,2′-bipy
		1024	1080	τ (C=C) R BTC + ν (C-C) R BTC
		1000	1016	τ R BTC + ν (C-C) R BTC
		961	1001	γ (C-H) R BTC + δ (C=C), δ (C=N) R 2,2′-bipy
966	968			γ (C-H) R 2,2′-bipy
950	-			γ (C-H) R 2,2′-bipy
919	912			γ (C-H) R 2,2′-bipy
898	896	903	912	γ (C=C), (C=O)) R BTC

814	808			γ (C=C), (C=O) R BTC
		808	833	γ (C-H) R 2,2′-bipy
		764	808	γ R BTC + τ R 2,2′-bipy
771	760			γ (C-H) R 2,2′-bipy
729	736			γ (C-H) R 2,2′-bipy
				γ (C-H) R 2,2′-bipy
		744	768	+ γ (C=C), (C=N) R 2,2′-bipy
				γ (C-H) R 2,2′-bipy
		715	745	+ γ (C=C), (C=N) R 2,2′-bipy
717	704			γ (C=C), (C=N) R 2,2′-bipy
684	-			γ (C=C), (C=N) R 2,2′-bipy
673	672			γ (C=C), R BTC
658	-	652	672	ν (N-Cu) + τ R 2,2′-bipy
651	-			ν (N-Cu) + τ R 2,2′-bipy
				ν_{as} (Cu-OH-Cu′) + ν
		631	648	(Cu-OCO-Cu′) + τ R BTC
636	640			ν (N-Cu) + τ R 2,2′-bipy
612	600			ν_{as} (Cu-OH-Cu′) + τ R BTC
574	-			γ (C=C), (C=N) R 2,2′-bipy
				ν_{as} (Cu-OH-Cu′) + ν
555	560			(Cu-OCO-Cu′) + τ R BTC
		548	568	ν_{as} (Cu-OH-Cu′)
				ν (Cu-OCO-Cu′) + τ R BTC
521	520			ν_{as} (Cu-OCO-Cu′) + τ R BTC
				ν (Cu-OCO-Cu′) + τ R BTC + γ (O-H) bridge
		470	520	τ R 2,2′-bipy + τ R BTC
		442	504	γ R 2,2′-bipy + γ (OH,O′-Cu-N,N′) basal plane
		411	480	ν_{s} (Cu-OH-Cu′)
		368	424	ν_{s} (Cu-OCO-Cu′) + τ R BTC
		359	360	ν_{as} (Cu-OCO-Cu′) + τ (C=O) R BTC
		324	336	γ (Cu-N) basal plane
		303	312	γ (Cu-N) basal plane
		258	256	γ (Cu-OH-Cu)
		248	240	γ DCu
		231	224	τ (Cu-OH-Cu)
		193	192	τ (Cu-N) basal plane
		180	168	τ DCu + τ (C=O) R BTC

	159	136	τ DCu + τ R BTC + τ R 2,2´-bipy
	119	113	τ DCu basal plane+ τ R BTC

Abbreviations used in the assignment of vibrational modes: stretching mode; δ, in-plane bending; γ, out-of-plane bending; τ, torsion; as, antisymmetric vibration; s, symmetric vibration; sciss, twist; R-2,2´-bipy, 2,2´-bipyridine rings; R-BTC, BTC ring; DCu; dinuclear environment.

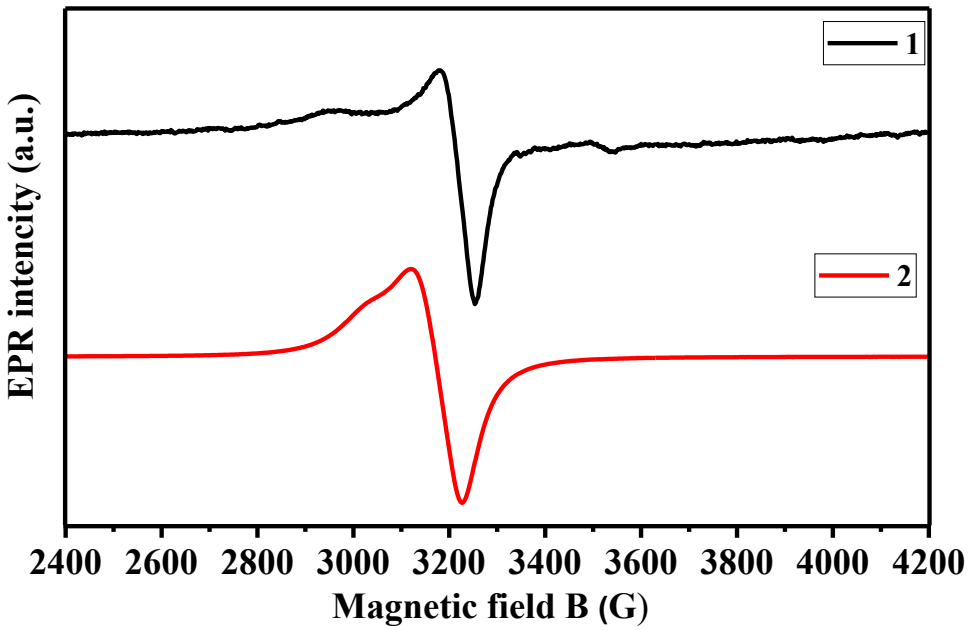

Figure S10. EPR spectrum of **1** and **2**.

Table S9. Magnetic moment per atom type in systems **1** and **2** expressed in Bohr magneton units (μ_B).

1			**2**			
N°	Element	Spin Magnetic Moment (μ_B)	N°	Element	Spin Magnetic Moment (μ_B)	Type of bond with respect to Cu (II) atom
1	Cu	0.817	1	Cu	0.823	Cu atom
2	Cu	0.816	2	Cu	0.822	
3	Cu	0.817	3	Cu	0.822	
4	Cu	0.816	4	Cu	0.821	
5	Cu	0.816	5	Cu	0.822	
6	Cu	0.814	6	Cu	0.821	
7	Cu	0.814	7	Cu	0.822	
8	Cu	0.813	8	Cu	0.822	
12	O	0.105	40	O	0.108	O Bridges
13	O	0.108	41	O	0.109	
14	O	0.107	42	O	0.107	
15	O	0.108	43	O	0.109	
8	O	0.039	24	O	0.046	O Coordinated to the square base plane
9	O	0.043	25	O	0.047	
10	O	0.042	26	O	0.047	
11	O	0.042	27	O	0.046	
24	O	0.040	28	O	0.047	
25	O	0.041	29	O	0.047	
26	O	0.042	30	O	0.046	
27	O	0.041	31	O	0.046	
28	O	0.002	44	O	0.001	O Not Coordinated in a square-based plane
29	O	0.002	45	O	0.001	
30	O	0.002	46	O	0.001	
31	O	0.002	47	O	0.001	
32	O	0.002	48	O	0.001	
33	O	0.002	49	O	0.001	
34	O	0.002	50	O	0.001	
35	O	0.002	51	O	0.001	
40	N	0.044	32	N	0.038	N Coordinated in a square-based plane
41	N	0.043	33	N	0.038	
42	N	0.044	34	N	0.039	
43	N	0.044	35	N	0.039	
44	N	0.046	36	N	0.039	
45	N	0.044	37	N	0.039	
46	N	0.044	38	N	0.039	
47	N	0.045	39	N	0.039	
48	N	0.052	72	N	0.046	
49	N	0.051	73	N	0.046	
50	N	0.051	74	N	0.047	

51	N	0.052	75	N	0.047	
52	N	0.053	76	N	0.047	
53	N	0.052	77	N	0.046	
54	N	0.051	78	N	0.047	
55	N	0.052	79	N	0.046	
56	C	-0.005	88	C	-0.005	
57	C	-0.005	89	C	-0.005	
58	C	-0.005	90	C	-0.005	
59	C	-0.005	91	C	-0.005	C- carboxylate in the square base plane
80	C	-0.004	92	C	-0.005	
81	C	-0.004	93	C	-0.005	
82	C	-0.004	94	C	-0.005	
83	C	-0.004	95	C	-0.005	
20	O	0.002	16	O	0.001	
21	O	0.002	17	O	0.001	
22	O	0.002	18	O	0.001	
23	O	0.002	19	O	0.001	O equatorial
36	O	0.001	20	O	0.001	
37	O	0	21	O	0.001	
38	O	0	22	O	0.001	
39	O	0	23	O	0.001	

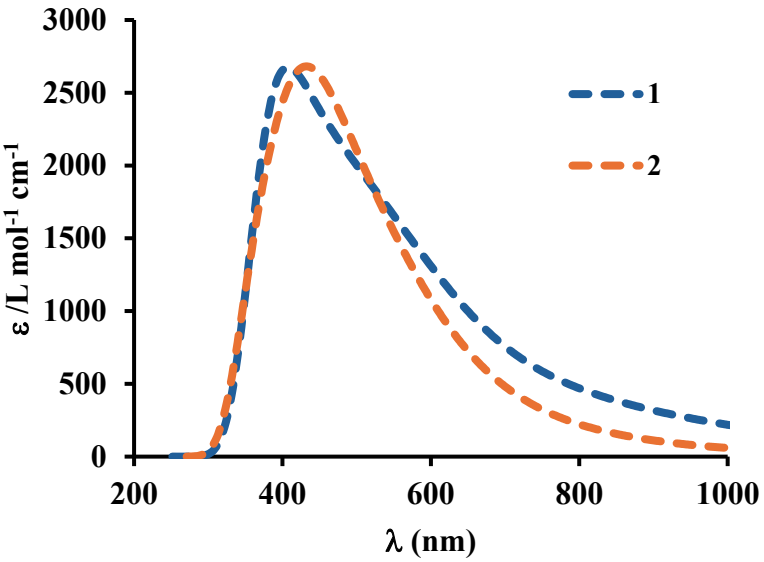

Figure S11. Theoretical electronic absorption spectra of **1** and **2.**

Table S10. Valence and conduction band edges and band-gap (Eg) values of MOFs **1** calculated using different exchange-correlation functionals. Band gap corrections (DFT1/2, Hubbard U) and spin magnetic moment (μ_B) are also included.

Functional	Valence Band (eV)	Conduction Band (eV)	Eg (eV)[a]	Spin Magnetic Moment (μ_B) per atom Cu
HSE06	-0.54	0.54	1.08	0.00
HLE16	-1.21	1.14	2.35	-0.74
PBE-DFT1/2	-0.25	0.25	0.50	0.00
PBE0	-0.75	0.74	1.49	0.00
PBE	-0.32	0.32	0.64	0.00
PBE, U=4	-0.81	0.78	1.59	0.64
PBE, U=7	-0.85	0.85	1.70	0.75
PBE,U=9	-0.94	0.86	1.80	0.81
PBE,U=11	-095	087	1.82	0.86
PBE,U=13	-0.95	0.87	1.82	0.90
PBE,U=15	-0.06	0.15	0.21	0.14

[a]Experimental band gap is 2.21 eV.