Supporting Information

Structural tuning of meso-hexamer, chiral-trimer and chiral-chain by anion directed supramolecular interactions

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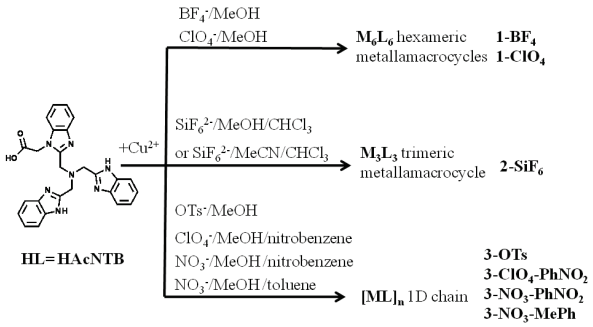
Preparation and characterization

All complexes were readily obtained by slow evaporation of the mixture containing corresponding hydrated copper salts and HAcNTB ligand in different solvent system as depicted in Scheme 2. Due to presence of large voids in the crystal lattice of all complexes, a great number of solvent molecules participate in crystallization. The sort and amount of the solvated molecules involved in crystallization seems randomly dependent on the solvent system used, which makes discrepancy of the molecular formula between the single crystal data and bulk sample elemental analyses results for some complexes. Nevertheless, the phase purity of the complexes (except **3-NO_3-MePh** which has been characterized by elemental analysis) has been satisfactorily confirmed by the comparison of the powder x-ray diffraction patterns with the simulated ones on the basis of the single crystal data (Fig. S1). Taking advantage of the solvent crystallization preference, we have tried different solvent systems to check the possibility of structural modulation by adding aromatic molecules. The results indicate that addition of aromatic molecules in solvent system can remarkably change the assembly process.



Scheme S1 Preparation conditions of complexes.

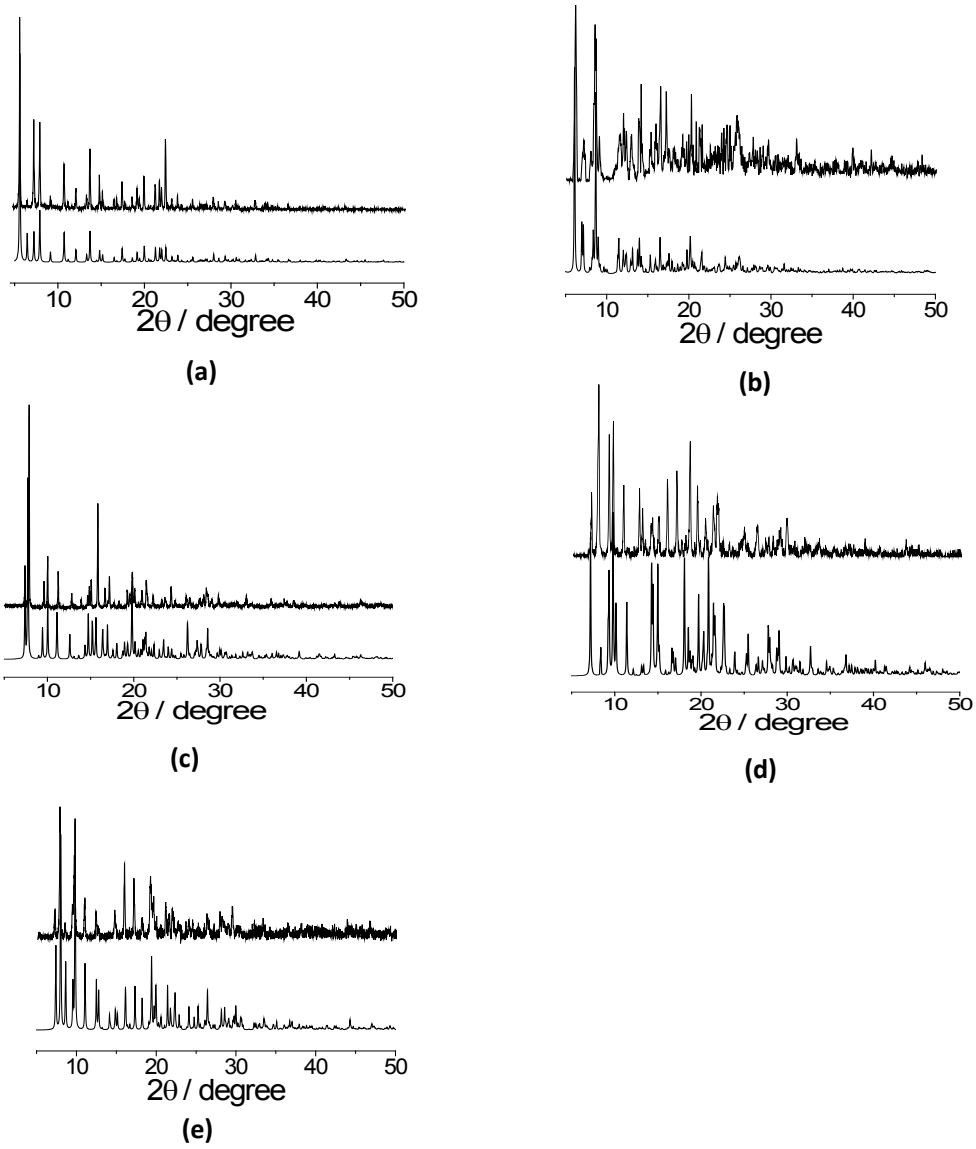


Fig. S1 X-ray powder diffraction patterns (upper) of complexes in comparison with the simulated ones on the basis of the single crystal data (lower): (a) **1-BF_4**, (b) **2-SiF_6**, (c) **3-ClO_4-PhNO_2**, (d) **3-OTs**, and (e) **3-NO_3-PhNO_2**.

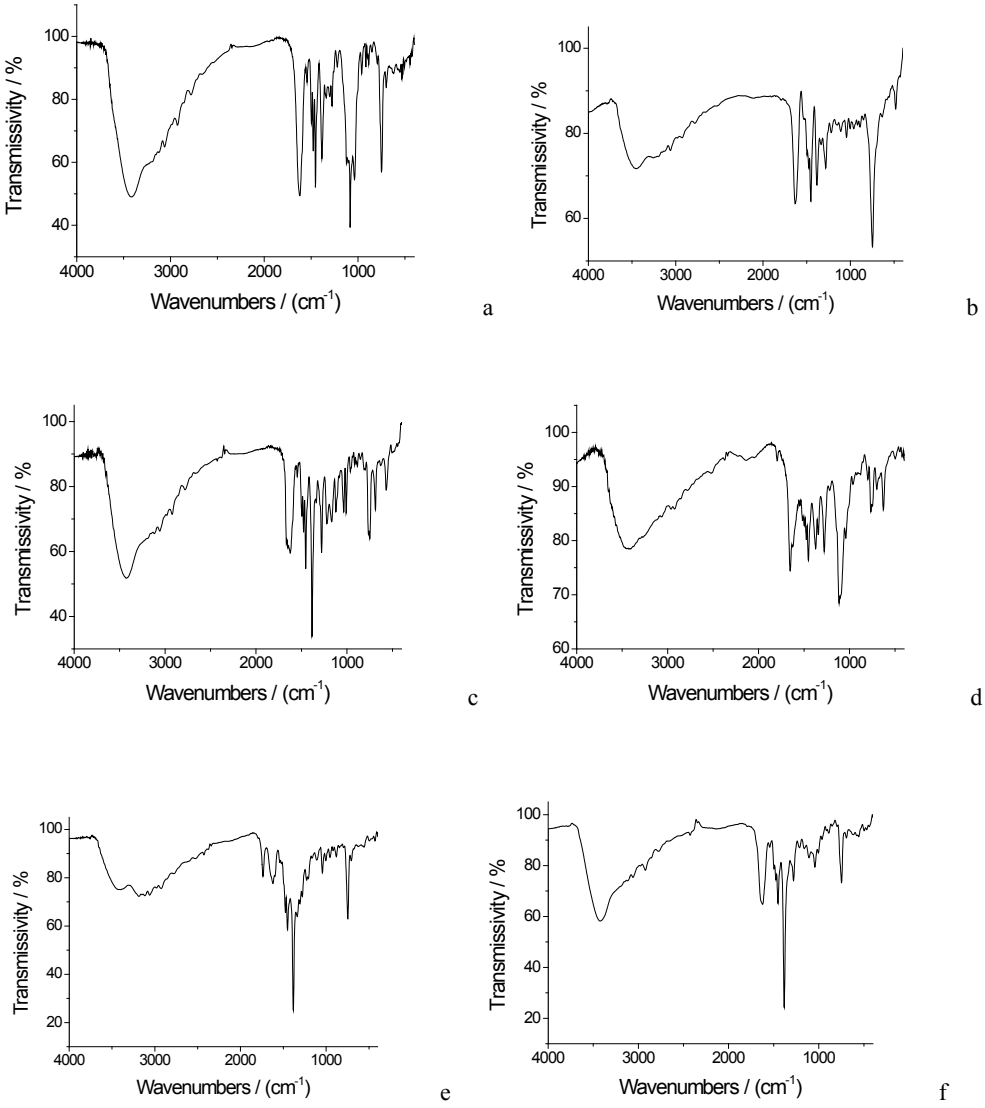
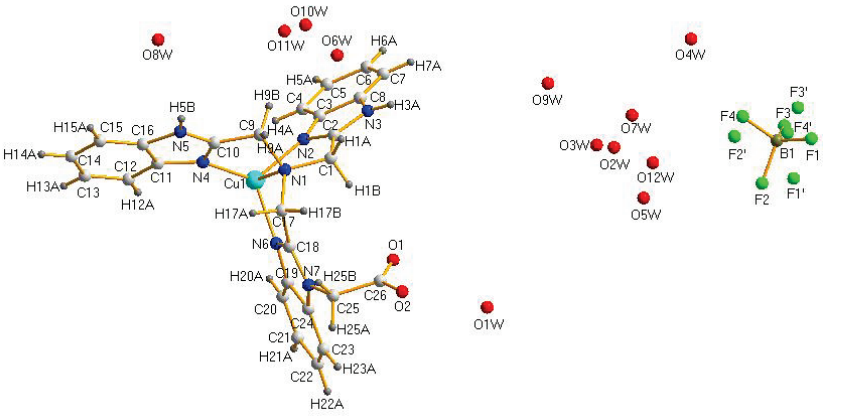
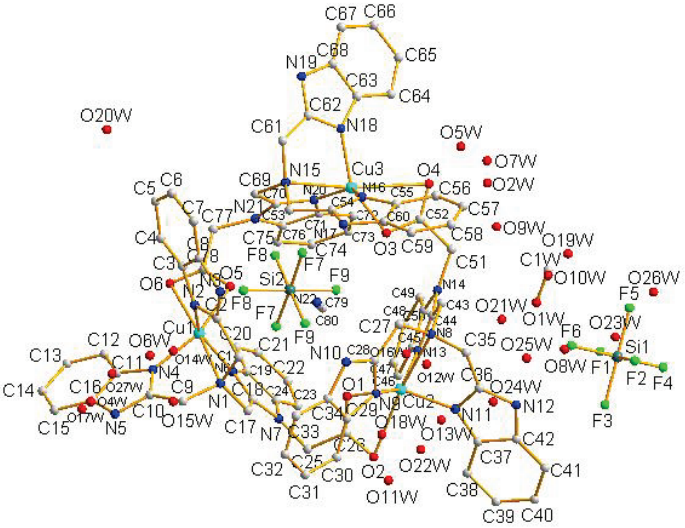


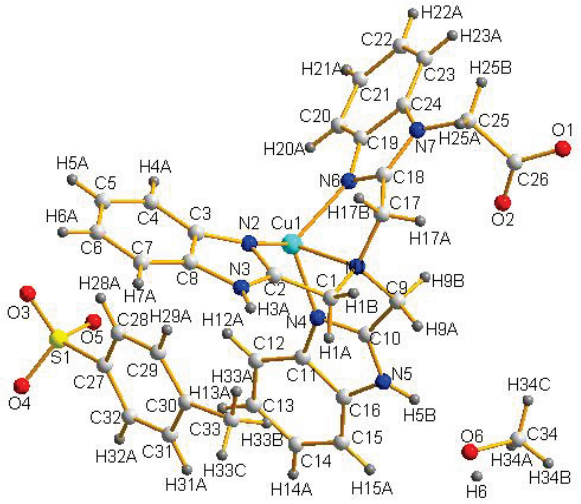
Fig. S2 FT-IR spectra of complexes: (a) **1-BF_4**, (b) **2-SiF_6**, (c) **3-OTs**, (d) **3-ClO_4-$PhNO_2$**, (e) **3-NO_3-$PhNO_2$**, and (f) **3-NO_3-MePh**.



a



b



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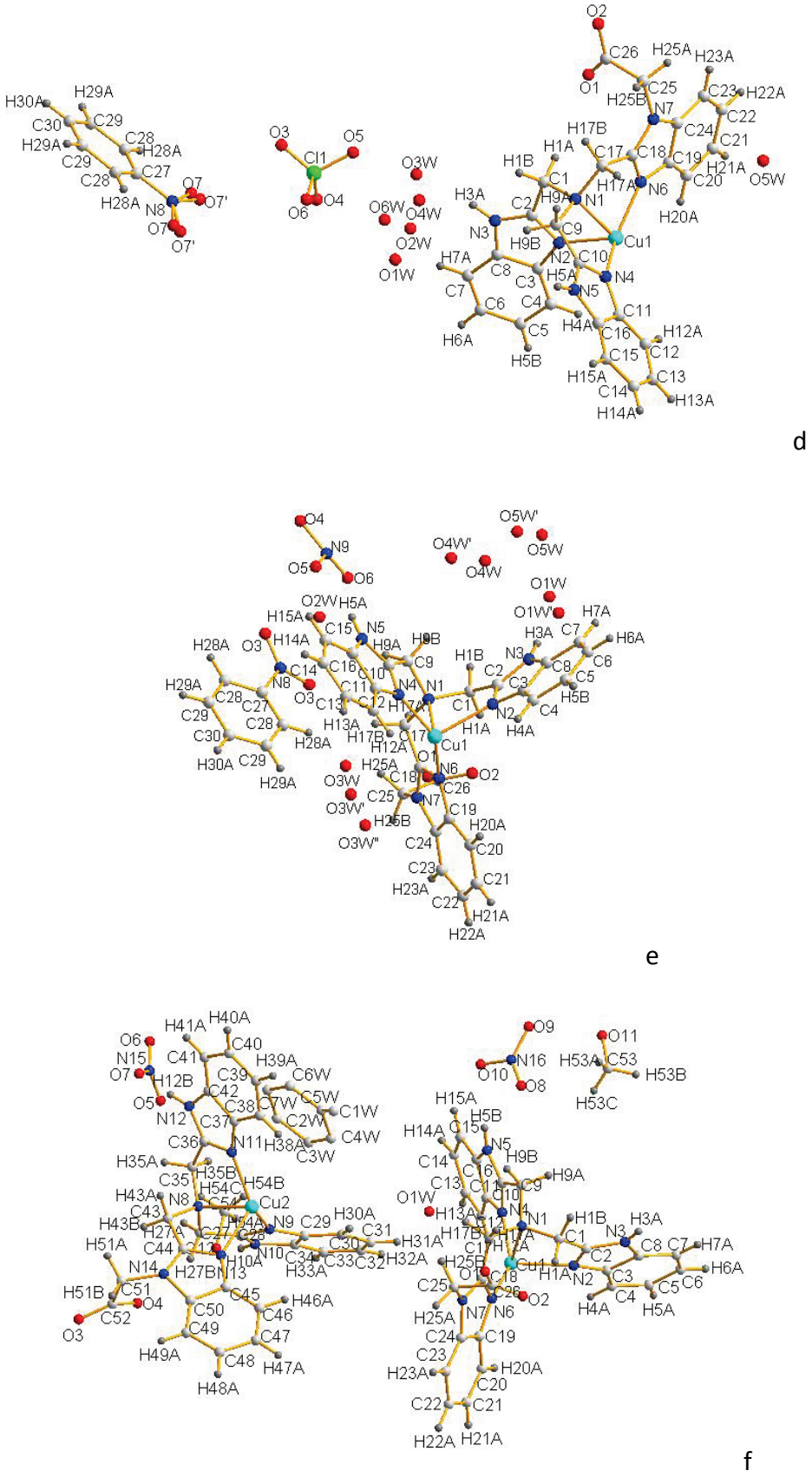

Fig. S3 The asymmetric unit in complexes: (a) **1-BF_4**, (b) **2-SiF_6** (H atoms are omitted for clarity, (c) **3-OTs**, (d) **3-ClO_4-PhNO_2**, (e) **3-NO_3-PhNO_2**, and (f) **3-NO_3-MePh**.

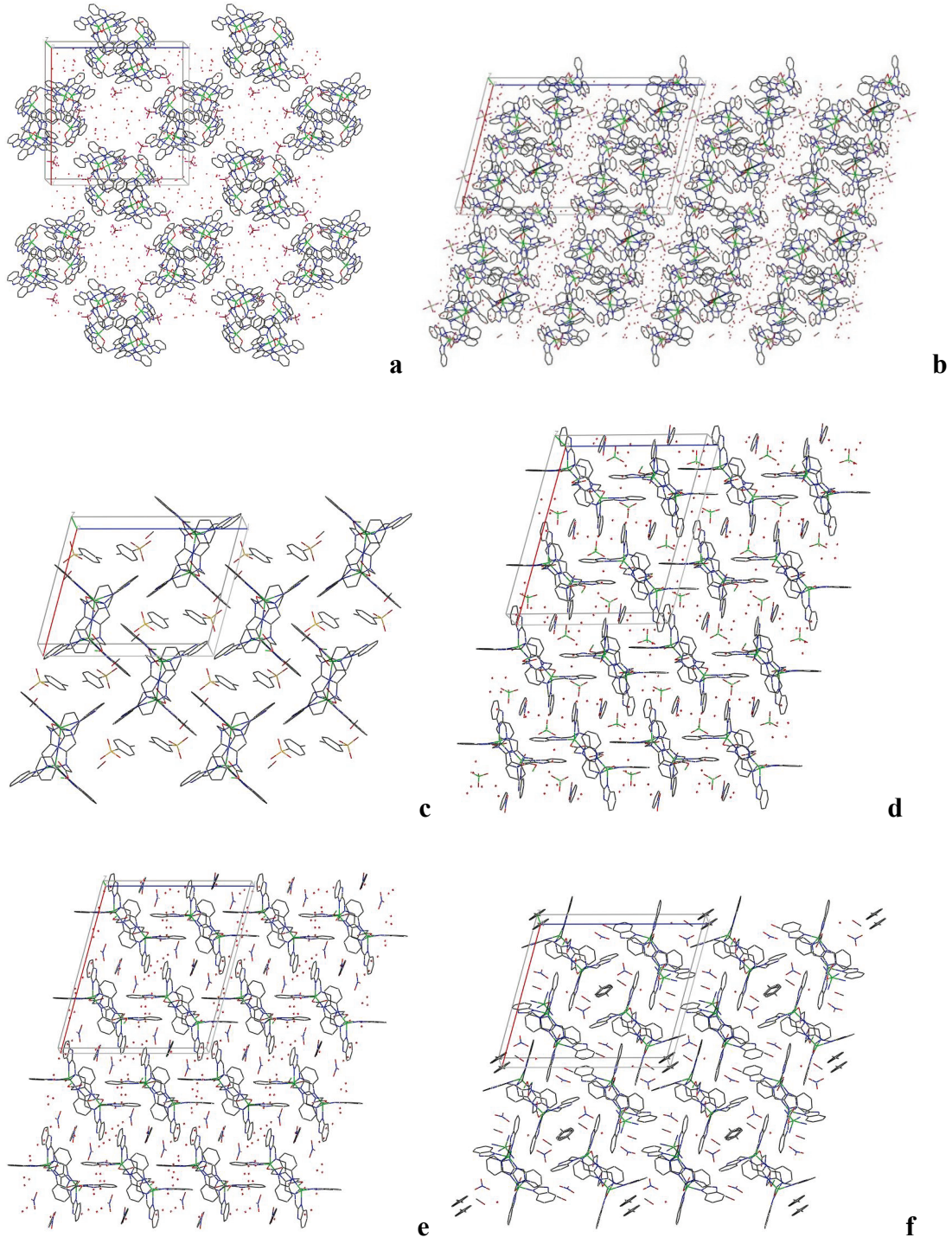

Fig. S4 Crystal packing showing solvent molecules and anions in the crystal lattice in complexes: (a) **1-BF_4**, (b) **2-SiF_6**, (c) **3-OTs**, (d) **3-ClO_4-$PhNO_2$**, (e) **3-NO_3-$PhNO_2$**, and (f) **3-NO_3-MePh**.

Table S1 Selected bond distances (Å) and angles (°) for complexes **1-BF_4**, **2-SiF_6**, **3-OTs**, **3-ClO_4-$PhNO_2$**, **3-NO_3-$PhNO_2$** and **3-NO_3-MePh**.

1-BF_4					
Cu(1)-O(1)#1	1.961(2)	Cu(1)-N(4)	2.041(3)	Cu(1)-N(2)	2.051(3)
Cu(1)-N(6)	2.112(3)	Cu(1)-N(1)	2.125(3)	O(1)#1-Cu(1)-N(4)	101.75(11)
O(1)#1-Cu(1)-N(2)	102.42(11)	N(4)-Cu(1)-N(2)	124.18(12)	O(1)#1-Cu(1)-N(6)	95.69(10)
N(4)-Cu(1)-N(6)	112.99(11)	N(2)-Cu(1)-N(6)	113.65(12)	O(1)#1-Cu(1)-N(1)	175.25(11)
N(4)-Cu(1)-N(1)	79.55(12)	N(2)-Cu(1)-N(1)	80.35(12)	N(6)-Cu(1)-N(1)	79.63(11)
2-SiF_6					
Cu(1)-N(6)	1.984(3)	Cu(1)-N(4)	1.987(3)	Cu(1)-O(5	2.003(2)
Cu(1)-N(2)	2.005(3)	Cu(1)-O(6)	2.519(2)	Cu(2)-N(13)	1.987(3)
Cu(2)-N(11)	1.996(3)	Cu(2)-N(9)	2.004(3)	Cu(2)-O(1)	2.007(2)
Cu(2)-O(2)	2.648(3)	Cu(3)-O(3)	1.977(3)	Cu(3)-N(20)	1.992(3)
Cu(3)-N(16)	2.007(3)	Cu(3)-N(18)	2.013(3)	Cu(3)-N(15)	2.459(3)
Cu(3)-O(4)	2.765(4)	N(6)-Cu(1)-N(4)	95.68(11)	N(6)-Cu(1)-O(5)	92.24(10)
N(4)-Cu(1)-O(5)	156.82(10)	N(6)-Cu(1)-N(2)	143.45(11)	N(4)-Cu(1)-N(2)	97.97(11)
O(5)-Cu(1)-N(2)	88.33(10)	N(6)-Cu(1)-O(6)	108.65(10)	N(4)-Cu(1)-O(6)	99.60(9)
O(5)-Cu(1)-O(6)	57.22(8)	N(2)-Cu(1)-O(6)	102.26(10)	N(13)-Cu(2)-N(11)	96.01(13)
N(13)-Cu(2)-N(9)	143.23(13)	N(11)-Cu(2)-N(9)	99.24(12)	N(13)-Cu(2)-O(1)	92.11(11)
N(11)-Cu(2)-O(1)	150.98(11)	N(9)-Cu(2)-O(1)	90.49(11)	N(13)-Cu(2)-O(2)	112.85(11)
N(11)-Cu(2)-O(2)	96.47(10)	N(9)-Cu(2)-O(2)	98.44(11)	O(1)-Cu(2)-O(2)	54.88(8)
O(3)-Cu(3)-N(20)	91.65(12)	O(3)-Cu(3)-N(16)	90.96(13)	N(20)-Cu(3)-N(16)	144.57(12)
O(3)-Cu(3)-N(18)	149.29(13)	N(20)-Cu(3)-N(18)	95.63(13)	N(16)-Cu(3)-N(18)	99.90(14)
O(3)-Cu(3)-N(15)	134.26(11)	N(20)-Cu(3)-N(15)	77.43(11)	N(16)-Cu(3)-N(15)	75.60(12)
N(18)-Cu(3)-N(15)	76.43(13)	O(3)-Cu(3)-O(4)	52.63(10)	N(20)-Cu(3)-O(4)	110.40(12)
N(16)-Cu(3)-O(4)	99.08(13)	N(18)-Cu(3)-O(4)	97.07(12)	N(15)-Cu(3)-O(4)	170.52(11)
3-OTs					
Cu(1)-O(1)#1	1.921(2)	Cu(1)-N(4)	2.051(3)	Cu(1)-N(6)	2.065(2)
Cu(1)-N(2)	2.076(3)	Cu(1)-N(1)	2.136(3)	O(1)#1-Cu(1)-N(4)	96.21(11)
O(1)#1-Cu(1)-N(6)	104.13(10)	N(4)-Cu(1)-N(6)	111.67(10)	O(1)#1-Cu(1)-N(2)	102.21(10)

N(4)-Cu(1)-N(2)	120.66(10)	N(6)-Cu(1)-N(2)	117.25(10)	O(1)#1-Cu(1)-N(1)	175.98(10)
N(4)-Cu(1)-N(1)	79.93(11)	N(6)-Cu(1)-N(1)	78.49(10)	N(2)-Cu(1)-N(1)	79.00(10)
3-ClO_4-$PhNO_2$					
Cu(1)-O(2)#1	1.960(3)	Cu(1)-N(4)	2.012(2)	Cu(1)-N(6)	2.017(3)
Cu(1)-N(2)	2.127(3)	Cu(1)-N(1)	2.173(3)	O(2)#1-Cu(1)-N(4)	101.48(11)
O(2)#1-Cu(1)-N(6)	100.28(11)	N(4)-Cu(1)-N(6)	137.92(12)	O(2)#1-Cu(1)-N(2)	99.96(12)
N(4)-Cu(1)-N(2)	101.29(11)	N(6)-Cu(1)-N(2)	109.82(11)	O(2)#1-Cu(1)-N(1)	177.21(11)
N(4)-Cu(1)-N(1)	81.18(11)	N(6)-Cu(1)-N(1)	78.09(11)	N(2)-Cu(1)-N(1)	78.59(11)
3-NO_3-$PhNO_2$					
Cu(1)-O(1)#1	1.964(4)	Cu(1)-N(4)	1.977(4)	Cu(1)-N(6)	1.998(5)
Cu(1)-N(1)	2.159(4)	Cu(1)-N(2)	2.180(5)	O(1)#1-Cu(1)-N(4)	98.75(17)
O(1)#1-Cu(1)-N(6)	96.05(17)	N(4)-Cu(1)-N(6)	143.10(19)	O(1)#1-Cu(1)-N(1)	171.80(16)
N(4)-Cu(1)-N(1)	81.91(17)	N(6)-Cu(1)-N(1)	78.97(18)	O(1)#1-Cu(1)-N(2)	108.69(17)
N(4)-Cu(1)-N(2)	100.73(17)	N(6)-Cu(1)-N(2)	106.18(18)	N(1)-Cu(1)-N(2)	79.10(17)
3-NO_3-MePh					
Cu(1)-N(4)#1	1.972(6)	Cu(1)-O(1)	1.973(4)	Cu(1)-N(6)#1	2.019(6)
Cu(1)-N(2)#1	2.157(6)	Cu(1)-N(1)#1	2.173(5)	Cu(2)-O(3)#2	1.920(5)
Cu(2)-N(9)	2.024(6)	Cu(2)-N(11)	2.064(6)	Cu(2)-N(8)	2.118(5)
Cu(2)-N(13)	2.158(6)	N(4)#1-Cu(1)-O(1)	95.9(2)	N(4)#1-Cu(1)-N(6)#1	143.2(2)
O(1)-Cu(1)-N(6)#1	96.9(2)	N(4)#1-Cu(1)-N(2)#1	102.0(2)	O(1)-Cu(1)-N(2)#1	110.3(2)
N(6)#1-Cu(1)-N(2)#1	105.5(2)	N(4)#1-Cu(1)-N(1)#1	81.3(2)	O(1)-Cu(1)-N(1)#1	170.3(2)
N(6)#1-Cu(1)-N(1)#1	80.3(2)	N(2)#1-Cu(1)-N(1)#1	79.3(2)	O(3)#2-Cu(2)-N(9)	95.7(2)
O(3)#2-Cu(2)-N(11)	101.7(2)	N(9)-Cu(2)-N(11)	131.2(2)	O(3)#2-Cu(2)-N(8)	176.1(2)
N(9)-Cu(2)-N(8)	80.7(2)	N(11)-Cu(2)-N(8)	79.6(2)	O(3)#2-Cu(2)-N(13)	105.6(2)
N(9)-Cu(2)-N(13)	101.4(2)	N(11)-Cu(2)-N(13)	116.6(2)	N(8)-Cu(2)-N(13)	76.8(2)

[a] Symmetry code for: **1-BF_4**: #1 y+1/2,z-1,-x+3/2; **3-OTs**: #1 -x+3/2,y+1/2,-z+1/2; **3-ClO_4-$PhNO_2$**: #1 -x+3/2,y-1/2,-z+3/2; **3-NO_3-$PhNO_2$**: #1 -x+3/2,y+1/2,-z+1/2; **3-NO_3-MePh**: #1 -x+1/2,y-1/2,-z+3/2; #2 -x+3/2,y-1/2,-z+3/2.

Table S2 Selected hydrogen bonds distances (Å) for complexes **1-BF_4**, **2-SiF_6**, **3-OTs**, **3-ClO_4-PhNO_2**, **3-NO_3-PhNO_2** and **3-NO_3-MePh**.

1-BF_4					
N(5)···O(2)	2.780(4)				
2-SiF_6					
N(3) ···F(7)	2.905(4)	N(3) ···F(8)	2.842(4)	N(10) ···F(7)	2.889(4)
N(10) ···F(9)	2.895(4)	N(17) ···F(8)	2.890(4)	N(17) ···F(8)	2.907(4)
N(5) ···F(4)	2.866(4)	N(5) ···F(5)	2.953(4)	N(12) ···F(6)	2.895(4)
N(12) ···F(3)	3.006(4)				
3-OTs					
N(3) ···O(4)	2.772(4)	N(5) ···O(6)	2.710(5)		
3-ClO_4-PhNO_2					
N(5) ···O(3)	3.254(6)	N(5) ···O(6)	2.951(6)		
3-NO_3-PhNO_2					
N(5) ···O(5)	2.84(2)	N(5) ···O(6)	2.924(11)		
3-NO_3-MePh					
N(5) ···O(8)	2.953(12)	N(5) ···O(10)	2.979(13)	N(12) ···O(7)	2.728(9)

Table S3 Selected π-π interacting distances (Å) and dihedral angles (°) for complexes **1-BF_4**, **2-SiF_6**, **3-OTs**, **3-ClO_4-PhNO_2**, **3-NO_3-PhNO_2** and **3-NO_3-MePh**.

1-BF_4		
Cg(1)	C(3)-C(4)-C(5)-C(6)-C(7)-C(8)	
Cg(2)	C(19)-C(20)-C(21)-C(22)-C(23)-C(24)	
Cg(1)-Cg(2)	3.759(2) Å	3.9(2)°
3-OTs		
Cg(1)	C(3)-C(4)-C(5)-C(6)-C(7)-C(8)	
Cg(2)	C(11)-C(12)-C(13)-C(14)-C(15)-C(16)	
Cg(3)	C(27)-C(28)-C(29)-C(30)-C(31)-C(32)	
Cg(4)	C(10)-N(4)-C(11)-C(12)-C(13)-C(14)-C(15)-C(16)-N(5)	
Cg(1)-Cg(2)	5.449(2) Å	77.03(18)°
Cg(1)-Cg(3)	5.137(2) Å	72.33(18)°
Cg(2)-Cg(3)	4.284(2) Å	16.81(19)°

Cg(4)-Cg(4)	3.850(2) Å	0°

3-ClO_4-PhNO_2

Cg(1)	C(2)-N(2)-C(3)-C(4)-C(5)-C(6)-C(7)-C(8)-N(3)
Cg(2)	C(10)-N(4)-C(11)-C(12)-C(13)-C(14)-C(15)-C(16)-N(5)
Cg(3)	C(27)-C(28)-C(29)-C(30)-C(31)-C(32)

Cg(1)-Cg(1)	3.627(3) Å	0°
Cg(2)-Cg(2)	3.644(3) Å	0°
Cg(1)-Cg(3)	4.961(2) Å	71.93(19) °
Cg(2)-Cg(3)	3.931(2) Å	20.19(18) °

3-NO_3-PhNO_2

Cg(1)	C(2)-N(2)-C(3)-C(4)-C(5)-C(6)-C(7)-C(8)-N(3)
Cg(2)	C(10)-N(4)-C(11)-C(12)-C(13)-C(14)-C(15)-C(16)-N(5)
Cg(3)	C(27)-C(28)-C(29)-C(30)-C(31)-C(32)

Cg(1)-Cg(1)	3.631(4) Å	0°
Cg(2)-Cg(2)	3.743(4) Å	0°
Cg(1)-Cg(3)	4.968(4) Å	69.0(3) °
Cg(2)-Cg(3)	4.103(4) Å	21.5(3) °

3-NO_3-MePh

Cg(1)	C(2)-N(2)-C(3)-C(4)-C(5)-C(6)-C(7)-C(8)-N(3)
Cg(2)	C(10)-N(4)-C(11)-C(12)-C(13)-C(14)-C(15)-C(16)-N(5)
Cg(3)	C(28)-N(9)-C(29)-C(30)-C(31)-C(32)-C(33)-C(34)-N(10)
Cg(4)	C(36)-N(11)-C(37)-C(38)-C(39)-C(40)-C(41)-C(42)-N(12)
Cg(5)	C(2W)-C(3W)-C(4W)-C(5W)-C(6W)-C(7W)

Cg(1)-Cg(3)	4.573(5) Å	5.1(3) °
Cg(2)-Cg(4)	4.655(5) Å	23.8(4) °
Cg(3)-Cg(5)	4.380(5) Å	16.0(4) °
Cg(4)-Cg(5)	4.564(5) Å	40.5(4) °

Cg(I): plane number I and atoms in ring; Cg(I)-Cg(J): distance between ring centroids (Å) and dihedral angle between planes I and J (°).