Tris(benzimidazolyl)amine-Cu(II) coordination units bridged by carboxylates: structures and DNA-condensing property

(Supporting Information: 21 pages including this page)

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Comment S1: Details of the refinements of complexes **1**–**9**.

For **1**, In the refinement, both the perchlorate anion (Cl1/O2-O5 and Cl2/O6-O9) were found to be disordered over two sites. The command DFIX were used in the refinement to restrain some distances (eg. Cl-O=1.42(1)Å and O-O=2.55(2)Å). The thermal factors of some disordered oxygen atoms were restrained using commands of EADP and ISOR. The final most satisfactory occupancies for the Cl1-, Cl2-involved perchlorate anions were 0.55(1):0.45(1) and 0.52(1):0.48(1), respectively. Some residual electron densities, which should be considered as peaks from disordered methanol or water molecules, did not give a chemical meaningful result after a careful refinement. Therefore, the contributions of the disordered solvent molecules (c.a. 107 e/unit cell) were removed from the diffraction data using the SQUEEZE routine of PLATON software and then final refinements were carried out. These electron densities account to ca. four methanol and four water molecules, i.e. the suitable formula should be **1**·$(CH_3OH)_2$·$(H_2O)_2$.

For **2**, In the refinement, two perchlorate anion (Cl2/O7-O10, Cl3/O11-O14) were found to be disordered at two sites. Then the command DFIX was used to restrain some distances (eg. Cl-O=1.38(1) Å and O-O=2.25(2) Å). For O12', EADP was used to restrain its thermal factor to be same as that of O12. Because the electron densities of solvent molecules are too diffused to allow the accurate refinement of one unit molecule, the occupancies for water O17-O20 molecules were refined freely and their final occupancies are ca. 0.67, 0.59, 0.34 and 0.40 respectively. All the C- and N-bounded hydrogen atoms were located geometrically. Hydrogen atoms attached to water oxygen atoms were positioned best matching their hydrogen-bond environment with O-H=0.82 Å and $U_{iso}(H)=1.2U_{eq}(O)$.

For **3**, In the refinement, all the four perchlorate anion (Cl1/O1-O4, Cl2/O5-O8, Cl3/O9-O12 and Cl4/O13-O16)) were found to be disordered over two sites. The commands DFIX, EADP and ISOR were used in the refinement to restrain some distances (eg. Cl-O=1.38(1) Å and O-O=2.25(2) Å) and thermal factors. The final most satisfactory occupancies for the Cl1-, Cl2-, Cl3- and Cl4-involved perchlorate anions were 0.63(1):0.37(1), 0.56(1):0.44(1), 0.56(1):0.44(1) and 0.59(1):0.41(1), respectively. All the C- and N-bounded hydrogen atoms were positioned geometrically. For the residual electron densities, only water O17 molecule can be assigned unambiguously. For the other residual electron densities which should be considered as peaks from disordered water molecules, did not give a chemical meaningful result after a careful refinement. Therefore, the contributions of the disordered solvent molecules (c.a. 113 e/unit cell) were removed from the diffraction data using the SQUEEZE routine of PLATON software and then final refinements were carried out. These electron densities account to ca. eleven water molecules, i.e. the suitable moiety formula should be $(Cu_2C_{58}H_{50}N_{16})$·$(ClO_4)_4$·$(H_2O)_{6.5}$.

For structures of **4** and **5**, they are almost identical to each other except for the central C26-C26 (1-*x*, 1-*y*, 1-*z*) bond distances. In **4**, the occupancies of the disordered Cl1/O3-O6 perchlorate anion and O10 water molecule are both of 0.56(1):0.44(1) for the major and minor components, respectively. In **5**, the occupancies of the disordered Cl1/O3-O6 anion and the O10 water molecule are of 0.62(1):0.38(1) and 0.57(1):0.43(1), respectively. On the other hand, the C26 atom in the central alphatic linkage was also disordered over two sites with the occupancies of 0.65(1):0.35(1). 'DFIX' command was used in the refinement to restrain the Cl-O and O…O distances of 1.38(1) and 2.42(2) Å for the anion, respectively, and the O-H and H…H distances of 0.82(1) and 1.35(2) Å. 'SADI' command was used to restrain the C26-C26 (1-*x*, 1-*y*, 1-*z*) distance.

For **6**, no apparent disorder was present for the anions and water O7 molecule. Both the

perchlorate Cl1 and Cl2 atoms lie on two-fold axis with 0.5 occupancies. No restraint was used in the refinement.

For **7a**, In the refinement, the ClO_4^- anion was found to be disordered over two sites with the final occupancies of 0.57(1):0.43(1) for the major and minor components, respectively. Command 'DFIX' was used during the refinement to restrain the Cl-O bond lengths and O...O distances of 1.38(1) Å and 2.25(1) Å, respectively. Because the electron densities of solvent molecules are too diffused to allow the accurate refinement of one unit molecule, the occupancies of water O8-O10 atoms were refined freely and their final outcome are of ca. 0.70(1), 0.60(1) and 0.20(1), respectively. All the C- and N-bounded hydrogen atoms were positioned geometrically. Hydrogen atoms attached to water oxygen atoms were positioned best matching their hydrogen-bond environment with O-H=0.82 Å and $U_{iso}(H)=1.2U_{eq}(O)$.

For **7b**, In the refinement, the perchlorate O3, O4 and O6 atoms were found to be disordered over two sites with the final satisfactory occupancies of 0.53(1):0.47(1) for the major and minor components, respectively. Command 'DFIX' was used to restrain the Cl-O bond lengths and O...O distances of 1.38(1) Å and 2.25(2) Å, respectively. These sites of water O16 and O17 atoms are only partially occupied with the final occupancies of ca. 0.52(1) and 0.48(1), respectively. All the C- and N-bounded hydrogen atoms were positioned geometrically. Hydrogen atoms attached to water oxygen atoms were positioned best matching their hydrogen-bond environment with O-H=0.82 Å and $U_{iso}(H)=1.2U_{eq}(O)$.

For **8a**, In the refinement, the Cl1/O3-O6 perchlorate anion was symmetrically disordered about a two-fold axis and the Cl1'/O3'-O5' perchlorate anion was symmetrically disordered by an inversion center. Then, 'PART -1' instruction was used for these atoms and the occupancies of all atoms in this group were set to 0.5. Also in the refinement command 'DFIX' was used to restrain the Cl-O and O...O distances of 1.42(1) Å and 2.45(2) Å, respectively. 'ISOR' was used to restrain some abnormal thermal factors of these oxygen atoms.

For **8b**, In the refinement, all the three perchlorate anions were found to be disordered over two sites and command 'SADI' was used to restrain the Cl-O and O...O distances to be equal to each other. The final occupancies are of 0.73(1):0.27(1), 0.74(1):0.26(1) and 0.51(1):0.49(1) for the Cl1/O3-O6, Cl2/O7-O10 and Cl3/O11-O14 anions, respectively.

For 9, In the refinement, the three perchlorate anions were slightly disordered and command 'SADI' was used to restrain the Cl-O and O...O distances to be equal to each other. Both the Cl3/O13-O16 and Cl4/O17-O20 anions were disordered by inversion centers and the atomic occupancies of these atoms were assigned to be 0.5. Command 'ISOR' was also used to restrain some abnormal thermal factors. Due to the very large thermal factors, the occupancies of water O21 and O22 atoms were refined freely and their final outcome are of ca. 0.60(1) and 0.40(1), respectively.

Table S1 Single crystal data collection, cell parameters and basic information of complexes **1**–**9**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$(CuC_{24}H_{23}N_7O)\cdot(ClO_4)_2$	$(Cu_2C_{54}H_{46}N_{15}O_2)\cdot(ClO_4)_3\cdot 4(H_2O)$	$(Cu_2C_{58}H_{50}N_{16})\cdot(ClO_4)_4\cdot(H_2O)$	$(Cu_2C_{52}H_{44}N_{14}O_4)\cdot(ClO_4)_2\cdot 8(H_2O)$	$(Cu_2C_{52}H_{46}N_{14}O_4)\cdot(ClO_4)_2\cdot 8(H_2O)$	$(Cu_2C_{53}H_{48}N_{14}O_4)\cdot(ClO_4)_2\cdot 2(H_2O)$
Formula weight	687.94	1434.55	1514.04	1399.12	1401.14	1307.07
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*Pnna*
Unit cell dimensions						
a (Å)	11.693(3)	14.9417(6)	13.8253(10)	10.8077(6)	10.7934(11)	16.6780(9)
b (Å)	12.334(3)	15.2306(7)	16.9498(11)	11.9857(6)	11.9882(13)	17.1571(10)
c (Å)	15.004(4)	16.0023(7)	17.9303(13)	13.8019(7)	13.8076(14)	19.0110(11)
α (°)	80.155(5)	71.288(1)	68.450(2)	112.315(1)	112.292(2)	90
β (°)	67.328(4)	63.771 (1)	84.851(2)	98.880(1)	99.127(2)	90
γ (°)	81.907(5)	82.833 (1)	69.359(2)	100.592(1)	100.434(2)	90
Volume ($Å^3$)	1960.6(9)	3093.4(2)	3653.3(4)	1575.62(14)	1574.2(3)	5439.9(5)
Z	2	2	2	1	1	4
Calc. density (Mg/m^3)	1.165	1.540	1.376	1.475	1.478	1.596
F(000)	702	1472	1548	722	724	2688
Crystal size (mm)	0.12×0.12×0.10	0.20 ×0.04 × 0.02	0.23×0.13×0.10	0.15×0.10×0.06	0.13×0.10×0.10	0.10×0.06×0.04
θ range (°)	2.10-25.01	1.85-26.50	1.58-25.00	1.65-26.50	1.65-26.50	2.14-25.500

Reflections collected	11333	33501	35001	25694	17215	103378
Independent reflections	6830	12601	12662	6445	6448	5045
Number of parameters/R_{int}	394/0.0535	935/0.0368	1046/0.0687	483/0.0303	493/0.0481	385/0.1050
Goof %	0.870	1.038	0.976	1.052	1.011	1.062
Final *R* indices [$I > 2\sigma$(I)]	R_1=0.0835 wR_2= 0.1835	R_1=0.0599 wR_2=0.1717	R_1 = 0.0800 wR_2 = 0.2135	R_1 = 0.0559 wR_2 = 0.1353	R_1 = 0.0440 wR_2 = 0.1126	R_1=0.0675 wR_2= 0.1738
R indices (all data)	R_1=0.1393 wR_2= 0.2068	R_1=0.0844 wR_2=0.1856	R_1 = 0.1235 wR_2 = 0.2335	R_1 = 0.0690 wR_2 = 0.1441	R_1 = 0.0555 wR_2 = 0.1225	R_1=0.1051 wR_2= 0.1957
Max. diff. peak and hole ($eÅ^{-3}$)	0.550, -0.317	0.814, -0.523	0.756, -0.465	0.485, -0.299	0.475, -0.375	0.961, -0.519

Table S1 continued

	7a	**7b**	**8a**	**8b**	**9**
Empirical formula	$(Cu_2C_{54}H_{50}N_{14}O_4)\cdot(ClO_4)_2\cdot 5(H_2O)$	$(C_{102}H_{90}Cu_4N_{28}O_4)\cdot(ClO_4)_6\cdot 4(H_2O)$	$(Cu_2C_{56}H_{46}N_{14}O_4)\cdot(ClO_4)_2$	$(Cu_4C_{104}H_{88}N_{28}O_4)\cdot(ClO_4)_6$	$(Cu_4C_{106}H_{88}N_{28}O_8)\cdot(ClO_4)_6\cdot 2(H_2O)$
Formula weight	1375.14	2697.00	1305.05	2644.88	2768.94
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*P2₁/c*	*P*-1	*C2/c*	*P*-1	*P*-1
Unit cell dimensions					
a (Å)	20.3801(12)	11.1837(13)	23.243(2)	10.543(8)	10.1980(9)
b (Å)	15.1830(9)	14.2473(16)	13.6868(15)	14.6474(10)	17.0069(18)
c (Å)	10.2220(6)	19.720(2)	20.161(2)	19.1303(12)	18.553(2)
α (°)	90	71.091(2)	90	72.599(1)	74.333(2)
β (°)	94.282(1)	84.728(2)	105.859(3)	85.227(1)	74.272(3)
γ (°)	90	71.533(2)	90	74.410(1)	77.117(2)
Volume ($Å^3$)	3154.2(3)	2819.3(5)	6169.8(11)	2715(2)	2943.0(5)
Z	2	1	4	1	1
Calc. density (Mg/m^3)	1.448	1.588	1.405	1.617	1.562
F(000)	1420	1382	2672	1350	1414
Crystal size (mm)	0.13×0.10×0.08	0.23×0.10×0.04	0.23×0.13 × 0.10	0.36×0.20×0.04	0.30×0.6×0.02
θ range (°)	1.67-25.01	1.59-26.50	2.10-25.00	1.60-25.00	1.52-25.00

Reflections collected	21408	30234	22203	26502	20739
Independent reflections	5476	11484	5362	9525	10085
Number of parameters/R_{int}	443/0.0452	812/0.0615	433/0.0476	892/0.0980	832/0.0998
Goof %	0.856	0.979	1.043	0.938	0.902
Final *R* indices [$I > 2\sigma(I)$]	R_1=0.0743 wR_2=0.1889	R_1 = 0.0642 wR_2 =0.1590	R_1=0.0684 wR_2=0.1942	R_1 =0.0622 wR_2 =0.1439	R_1 = 0.0915 wR_2 = 0.2148
R indices (all data)	R_1=0.1205 wR_2=0.2012	R_1 =0.1084 wR_2 =0.1761	R_1=0.0905 wR_2=0.2110	R_1 =0.1002 wR_2 =0.1584	R_1 = 0.1592 wR_2 = 0.2389
Max. diff. peak and hole ($eÅ^{-3}$)	0.726, -0.403	0.963, -0.491	1.227, -0.680	1.231, -0.487	1.085, -0.622

Table S2 Some selected bond lengths (Å) and angles (°) data for **1**–**9**. (Note: X_1 denotes atoms N15 in **3** and O1 in all the other compounds. X_2 denotes atoms N16 in **3**, O2 in **7b/8b** and O4 in **9,** respectively.)

	1	**2**	**3**	**4**	**5**	**6**
Cu1-N1	2.098(5)	2.147(3)	2.110(4)	2.470(3)	2.476(2)	2.147(4)
Cu1-N2	2.048(5)	1.998(3)	1.970(5)	2.009(3)	2.009(2)	2.039(4)
Cu1-N4	2.071(6)	1.992(3)	2.225(5)	1.993(3)	1.979(2)	2.103(4)
Cu1-N6	2.063(5)	2.140(3)	2.006(5)	1.979(3)	1.996(2)	2.049(4)
Cu1-X1	1.947(4)	1.931(2)	1.985(4)	1.957(2)	1.956(2)	1.913(4)
Cu2-N8		2.114(3)	2.092(5)			
Cu2-N9		2.175(3)	2.014(5)			
Cu2-N11		2.013(3)	2.086(5)			
Cu2-N13		2.009(3)	2.090(5)			
Cu2-X2		1.981(3)	1.972(4)			
N1-Cu1-N2	81.9(2)	82.24(13)	81.05(18)	77.20(10)	77.02(7)	80.56(14)
N1-Cu1-N4	80.5(2)	80.52(12)	81.15(17)	76.01(10)	77.00(8)	78.57(15)
N1-Cu1-N6	81.0(2)	79.76(12)	82.96(18)	77.26(10)	76.14(8)	79.32(15)
N2-Cu1-N4	120.6(2)	142.88(12)	111.83(17)	97.36(11)	93.75(8)	111.88(15)
N2-Cu1-N6	118.3(2)	100.11(13)	144.14(19)	93.75(11)	97.25(8)	127.88(15)
N4-Cu1-N6	114.1(2)	108.76(12)	97.03(17)	147.89(12)	147.76(9)	110.38(15)
X1-Cu1-N1	176.6(2)	176.49(12)	169.97(19)	130.96(9)	130.83(7)	173.46(16)
X1-Cu1-N2	99.5(2)	99.41(11)	94.49(19)	151.84(11)	152.15(8)	98.92(15)
X1-Cu1-N4	96.2(2)	96.41(11)	108.87(19)	91.33(11)	92.96(8)	95.69(16)
X1-Cu1-N6	100.8(2)	102.92(11)	95.83(19)	92.90(11)	91.26(8)	105.82(17)

N8 Cu2 N9	77.50(11)	80.6(2)
N8 Cu2 N11	83.13(11)	81.53(19)
N8 Cu2 N13	80.42(11)	80.2(2)
N9 Cu2 N11	97.41(11)	125.4(2)
N9 Cu2 N13	119.59(11)	125.9(2)
N11 Cu2 N13	134.50(11)	100.86(18)
X2 Cu2 N8	174.10(12)	174.6(2)
X2 Cu2 N9	104.60(11)	94.1(2)
X2 Cu2 N11	101.94(11)	100.66(18)
X2 Cu2 N13	93.81(12)	104.02(19)

Table S2 continued

	7a	**7b**	**8a**	**8b**	**9**
Cu1-N1	2.129(5)	2.327(4)	2.147(4)	2.187(4)	2.201(6)
Cu1-N2	2.102(5)	1.963(3)	2.114(4)	2.160(4)	2.123(6)
Cu1-N4	2.059(5)	2.043(4)	2.025(4)	1.957(4)	1.939(6)
Cu1-N6	2.065(5)	1.953(3)	2.047(4)	1.945(4)	1.933(7)
Cu1-X1	1.907(4)	1.975(3)	1.918(3)	1.984(3)	2.021(5)
Cu2-N8		2.255(4)		2.238(4)	2.320(7)
Cu2-N9		1.957(3)		1.970(4)	1.959(7)
Cu2-N11		2.128(3)		2.136(3)	2.032(6)
Cu2-N13		1.950(3)		1.957(4)	1.945(7)
Cu2-X2		2.001(3)		1.987(3)	2.015(5)
N1-Cu1-N2	79.62(19)	79.83(14)	79.69(15)	81.34(14)	81.7(2)
N1-Cu1-N4	80.36(19)	79.80(14)	80.82(15)	82.29(15)	82.7(2)
N1-Cu1-N6	80.1(2)	78.96(13)	78.56(16)	79.19(19)	80.4(3)
N2-Cu1-N4	105.46(18)	93.56(13)	116.78(16)	92.56(15)	95.4(3)
N2-Cu1-N6	121.71(18)	155.11(15)	100.13(16)	99.71(16)	100.2(3)
N4-Cu1-N6	123.89(19)	95.36(14)	133.23(16)	155.9(2)	155.1(3)
X1-Cu1-N1	173.3(2)	139.96(12)	178.92(16)	161.23(14)	169.6(2)
X1-Cu1-N2	106.0(2)	92.55(13)	100.01(14)	117.37(14)	108.4(2)
X1-Cu1-N4	94.43(19)	140.17(14)	100.23(15)	94.72(14)	98.7(2)
X1-Cu1-N6	99.52(19)	95.34(12)	100.48(15)	97.86(17)	94.8(3)
N8 Cu2 N9		79.95(13)		80.32(15)	80.2(3)
N8 Cu2 N11		81.34(14)		81.60(14)	77.9(3)

N8 Cu2 N13	80.37(15)	81.40(15)	79.9(3)
N9 Cu2 N11	99.69(13)	104.25(15)	94.8(2)
N9 Cu2 N13	153.99(16)	155.77(17)	156.5(3)
N11Cu2 N13	93.96(14)	88.60(15)	93.2(2)
X2 Cu2 N8	143.95(13)	139.66(13)	141.1(2)
X2 Cu2 N9	92.95(12)	88.66(15)	94.4(2)
X2 Cu2 N11	134.66(13)	138.70(14)	141.0(2)
X2 Cu2 N13	93.03(14)	95.12(15)	93.2(2)

Table S3 τ values around these copper centers (τ_1 for Cu1 and τ_2 for Cu2, respectively.) in **1**–**9**. (Note: For perfect trigonal-bipyramidal geometry τ = 1. For perfect tetragonal geometry τ = 0).[2]

	1	**2**	**3**	**4**	**5**	**6**	**7a**	**7b**	**8a**	**8b**	**9**
τ1	0.93	0.56	0.43	0.07	0.07	0.76	0.86	0.25	0.76	0.09	0.24
τ2	-	0.66	0.81	-	-	-	-	0.17	-	0.27	0.26

Table S4 Face-to-face π…π interactions in complexes **1**–**9**.

complex	ring(*i*)/ring(*j*)[*,#]	dihedral angle (*i*, *j*), °	distance between centroids, Å
1	N(2)/N(2)[b]	0.0	4.006(2)
	N(2)/C(4)[b]	1.3	3.716(2)
	N(6)/N(6)[u]	0.0	3.933(2)
	N(6)/C(20)[u]	1.8	3.724(2)
2	N(4)/C(12)[g]	0.42	3.606(3)
	N(6)/C(20)[b]	1.1	3.685(3)
	N(9)/N(9)[c]	0.00	3.686(2)
	N(9)/C(28)[c]	4.0	3.655(2)
3	N(4)/N(11)[h]	6.4	3.950(4)
	N(4)/C(46)[h]	4.4	3.745(4)
	N(6)/C(20)[b]	2.8	3.655(5)
	C(20)/C(20)[b]	0.00	3.921(5)
	C(54)/C(54)[k]	0	3.735(6)
4	N(2)/C(4)[d]	0.51	3.567(2)
	N(6)/C(20)[c]	0.77	3.843(3)
	C(4)/C(4)[d]	0.02	3.816(2)
	C(20)/C(20)[c]	0.00	3.885(3)
5	N(2)/C(4)[d]	0.41	3.564(2)
	N(4)/N(6)[g]	19.38	4.064(2)
	N(4)/C(12)[c]	0.82	3.844(2)
	C(4)/C(4)[d]	0.00	3.809(2)
	C(20)/C(20)[g]	0.00	3.886(2)
6	N(2)/C(4)[l]	1.96	3.772(3)
	N(4)/C(12)[m]	2.91	3.718(3)
	N(6)/C(20)[n]	0.18	3.532(3)
	C(4)/C(4)[l]	0.00	3.650(3)
	C(12)/C(12)[m]	2.62	3.791(3)
7a	N(6)/C(20)[o]	12.5	3.997(3)
7b	N(2)/C(28)	10.3	3.691(3)
	N(6)/N(13)	8.9	4.053(3)
	N(6)/C(28)[j]	8.9	3.796(3)
	N(6)/C(44)	8.8	4.049(3)
	C(4)/C(28)	10.0	4.069(3)
	C(12)/C(36)[p]	3.8	3.698(3)
	C(20)/C(28)[j]	9.9	3.950(3)
	C(20)/C(44)	9.7	3.930(3)
8a	N(4)/N(4)[q]	0.00	3.961(3)
	N(4)/C(12)[q]	3.2	3.795(3)
	N(6)/N(6)[b]	0.00	3.831(3)

8b	N(4)/C(28)	12.9	3.621(4)
	N(6)/N(13)	9.2	3.933(4)
	N(6)/C(28)^{j}	9.4	3.829(4)
	N(13)/C(20)	9.1	3.816(4)
	C(4)/C(36)^{p}	3.9	3.816(4)
	C(20)/C(28)^{j}	9.4	3.822(4)
	C(20)/C(44)	8.9	3.721(4)
9	N(2)/C(36)^{s}	3.2	3.721(6)
	N(13)/C(12)^{j}	2.1	3.803(5)
	C(4)/C(36)^{s}	5.9	3.836(5)
	C(12)/C(20)^{i}	9.3	3.773(6)
	C(12)/C(44)^{i}	2.7	3.949(6)
	C(28)/C(44)^{i}	2.8	3.691(6)

* N(i) indicates an imidazole ring and C(j) denotes a benzene ring. # Symmetry codes: (a) 1 - *x*, 1 - *y*, 2 - *z*; (b) 1- *x*, 1- *y*, 1 - *z*; (c) 2 - *x*, 2 - *y*, 1 - *z*; (d) 2 - *x*, 2 -*y*, 2 - *z*; (e) 1 - *x*, -*y*, 1 - *z*; (f) 1/2 -*x*, 1/2 -*y*, 1 - *z*; (g) 2 - *x*, 1 - *y*, 1 - *z*; (h) 2 - *x*, - *y*, 1 - *z*; (i) *x* -*1*, *y*, *z*; (j) 1 + *x*, *y*, *z*; (k) 2 - *x*, 1 - *y*, - *z*; (l) 1 - *x*, - *y*, - *z*; (m) *x*, 1/2 - *y*, 1/2 - *z*; (n) 1 - *x*, - *y*, - *z*; (o) *x*, 3/2 - *y*, -1/2 + *z*; (p) *x*, 1 + *y*, *z*; (q) 3/2 - *x*, 3/2 - *y*, 1 - *z*; (r) *x* - 1, *y*, *z*; (s) *x*, -1 + *y*, *z*； (t) 2 - *x*, 2 -*y*, - *z*； (u) 1 - *x*, 1 -*y*, - *z*.

Table S5 Hydrogen bonds in complexes **1**–**9**. (Note: Due to disorders of some solvents and anions, some hydrogen bonds have been omitted.)

	D-H…A	d(D-H), Å	d(H…A), Å	d(D…A), Å	∠(D-H…A), °
1	N(3)-H(3)...O(3)^{b}	0.86	2.13	2.97(2)	164.9
	N(3)-H(3)...O(3')^{b}	0.86	2.25	3.09(3)	165.1
	O(1)-H(1D)...O(5)	0.82	1.90	2.710(15)	168.7
	C(1)-H(1A)...O(8)	0.97	2.55	3.38(2)	143.3
	C12-H(12)...O7	0.93	2.59	3.38(2)	143.3
	C(17)-H(17A)...O(8)^{g}	0.97	2.52	3.42(4)	153.1
2	N(3)-H(3) ...O(16)^{u}	0.86	2.04	2.799(7)	147.3
	N(5)-H(5A)...O(15)	0.86	1.94	2.780(4)	166.3
	N(7)-H(7)...O(17)^{b}	0.86	2.01	2.836(8)	161.4
	N(10)-H(10)...O(2)^{c}	0.86	1.98	2.840(4)	174.6
	N(12)-H(12A)...O(9)^{v}	0.86	2.21	3.002(9)	153.3
	N(14)-H(14A)...O(20)^{t}	0.86	1.88	2.720(10)	163.8
	O(15)-H(15A)...O(8)	0.82	2.35	2.961(9)	132.3
	O(15)-H(15B)...O(3)^{g}	0.82	2.19	2.898(5)	143.9
	O(16)-H(16A)...O(9)^{g}	0.82	2.16	2.951(12)	162.3
	O(16)-H(16B)...O(12)^{b}	0.82	2.25	2.850(12)	130.7
	O(17)-H(17D)...O(4)	0.82	2.04	2.844(10)	167.4
	O(20)-H(20A)...O(6)^{b}	0.82	1.95	2.769(13)	175.4
	C(1)-H(1A)...O(12)^{u}	0.97	2.46	3.255(16)	138.9
	C(9)-H(9A)...O(8)	0.97	2.57	3.441(8)	149.6
	C(15)-H(15)...O(2)^{g}	0.93	2.54	3.454(5)	166.2
	C(33)-H(33B)...O(14)^{y}	0.97	2.58	3.538(16)	169.3
	C(53)-H(53)...O(5)^{z}	0.93	2.52	3.400(6)	157.2
3	N(3)-H(3A)...O(17)^{a}	0.86	2.07	2.898(8)	162.4
	N(5)-H(5A)...O(11)^{s}	0.86	2.08	2.936(13)	178.6
	N(10)-H(10A)...O(8)^{g}	0.86	2.15	2.95(3)	155.6
	N(12)-H(12A)...O(9)^{g}	0.86	2.23	2.944(17)	140.8
	N(14)-H(14)...O(17)^{i}	0.86	2.00	2.849(8)	168.1
	O(17)-H(17C)...O(14)^{u}	0.82	2.10	2.850(15)	152.1
	C(29)-H(29)...O(4)^{b}	0.93	2.58	3.33(2)	137.2
	C(32)-H(32)...O(3)^{j}	0.93	2.49	3.08(2)	121.5
4	N(3)-H(3A)...O(5)^{c}	0.836(19)	2.14(2)	2.957(11)	165(4)
	N(3)-H(3A)...O(6)^{c}	0.836(19)	2.59(3)	3.234(14)	135(3)
	N(5)-H(5A)...O(8)^{j}	0.853(19)	1.92(2)	2.769(6)	173(4)
	N(7)-H(7A)...O(9)^{j}	0.842(19)	1.99(2)	3.336(5)	177(4)
	O(7)-H(7C)...O(2)	0.97	2.40	2.759(4)	163.3
	C(9)-H(9B)...O(1)^{g}	0.97	2.30	3.244(4)	163.9
	C(17)-H(17A)...O(1)^{g}	0.840(19)	1.92(2)	2.833(7)	177(7)
5	N(3)-H(3)...O(3)^{d}	0.86	2.10	2.928(8)	162.2
	N(5)-H(5)...O(7)^{j}	0.86	1.97	2.826(5)	172.3

	N(7)-H(7A)...O(9)^{j}	0.86	1.92	2.767(4)	169.7
	O(7)-H(7B)...O(10)^{p}	0.825(10	2.52(7)	2.890(12)	108(6)
	O(7)-H(7B)...O(10)^{d}	0.825(10)	2.24(5)	2.861(10)	132(6)
	O(8)-H(8A)...O(3)	0.851(10)	2.26(3)	3.054(10)	156(5)
	O(8)-H(8B)...O(2)	0.833(10)	1.935(14)	2.753(3)	167(5)
	O(9)-H(9D)...O(6)	0.825(11)	2.28(2)	3.095(11)	170(7)
	O(10)-H(10B)...O(8)^{b}	0.818(11)	2.30	2.826(8)	126(15)
	C(1)-H(1B)...O(5)^{j}	0.97	2.43	3.40(2)	172.2
	C(4)-H(4)...O(2)	0.93	2.49	3.331(3)	164.2
	C(9)-H(9A)...O(1)^{g}	0.97	2.40	3.244(3)	163.8
	C(17)-H(17B)...O(1)^{g}	0.97	2.27(15)	3.341(3)	149.7
6	N(3)-H(3)...O(3)	0.86	2.53	3.365(9)	165
	N(3)-H(3)...O(4)	0.86	2.49	3.067(8)	126
	N(7)-H(7A)...O(7)	0.86	2.796(5)	2.796(5)	164
	O(7)-H(7B)...O(3)	0.81	3.123(9)	3.123(9)	152
	O(7)-H(7C)...O(2)	0.81	3.309(8)	2.800(6)	160
	C(22)-H(22)...O(5)	0.97	2.800(6)	3.309(8)	150
	C(9)-H(9A)...O(2)	0.97	3.320(6)	3.320(6)	161
	C(17)-H(17A)...O(7)	0.93	3.355(8)	3.355(8)	173
7a	N(3)-H(3)...O(10)^{j}	0.86	2.18	2.918(12)	144.2
	N(5)-H(5A)...O(8)^{x}	0.86	2.05	2.805(10)	146.5
	N(7)-H(7A)...O(7)^{x}	0.86	1.89	2.742(8)	172.0
	O(7)-H(7C)...O(2)*	0.86	1.99	2.704(8)	141.4
	O(7)-H(7D)...O(8)*	0.85	1.95	2.791(13)	170.2
	O(8)-H(8A)...O(5)*	0.85	2.55	3.165(18)	129.8
	O(8)-H(8A)...O(10)^{b}	0.85	2.04	2.86(2)	161.6
	O(9)-H(9C)...O(9)$^{\sim}$	0.82	1.69	2.46(2)	154.7
	C(17)-H(17A)...O(5)^{o}	0.97	2.49	3.122(18)	123.0
7b	N(3)-H(3) ...O(15)^{r}	0.86	1.89	2.745(5)	171.6
	N(5)-H(5A)...O(3)	0.86	2.30	2.974(12)	135.8
	N(5)-H(5A)...O(6)	0.86	2.31	3.135(8)	160.0
	N(7)-H(7A)...O(11)^{s}	0.86	2.07	2.915(7)	167.3
	N(7)-H(7A)...O(13)^{s}	0.86	2.45	3.090(7)	131.3
	N(10)-H(10)...O(4)$^{\&}$	0.86	2.44	3.127(13)	137.2
	N(10)-H(10)...O(9)$^{\&}$	0.86	2.44	3.127	137.2
	N(12)-H(12A) ..O(9)^{s}	0.86	2.36	3.140(6)	151.9
	N(12)-H(12A)...O(10)^{s}	0.86	2.30	3.052(6)	146.8
	N(14)-H(14A)...O(16)^{s}	0.86	2.16	2.986(16)	161.9
	O(15)-H(15A)...O(3)	0.82	2.27	3.089(11)	179.3
	O(15)-H(15B)...O(7)^{ix}	0.82	2.05	2.874(8)	126.8
	O(16)-H(16A)...O(5)^{p}	0.82	2.13	2.95(2)	179.5
	O(16)-H(16B)...O(12)	0.82	2.03	2.719(12)	141.9
	O(16)-H(16B)...O(8)^{j}	0.82	2.59	3.148(11)	126.8
	O(17)-H(17C)...O(5')	0.82	2.09	2.91(3)	178.4

	O(17)-H(17D)...O(10)[j]	0.82	2.17	2.986(11)	178.7
	C(1)-H(1B)...O(7)	0.97	2.46	3.287(7)	143.4
	C(9)-H(9A)...O(7)	0.97	2.47	3.401(7)	161.7
	C(17)-H(17A) ..O(5)[ix]	0.97	2.54	3.487(13)	165.4
	C(20)-H(20)...O(13)[s]	0.93	2.55	3.217(7)	128.8
	C(25)-H(25A)...O(14)[ix]	0.97	2.56	3.199(7)	123.4
	C(25)-H(25B)...O(8)[&]	0.97	2.45	3.235(8)	137.7
	C(28)-H(28)...O(4)[&]	0.93	2.57	3.279(15)	133.3
8a	N(3)-H(3)...O(3) [xii]	0.86	2.37	3.103(7)	144.1
	N(5)-H(5A)...O(4')[xi]	0.86	1.96	2.812(9)	173.9
	N(7)-H(7A)...O(2)[b]	0.86	1.91	2.682(5)	148.2
	C(9)-H(9B)...O(5')[xi]	0.97	2.50	3.414(14)	157.0
8b	N(3)-H(3)...O(14)[t]	0.86	2.07	2.923(11)	171.5
	N(5)-H(5A)...O(5)[t]	0.86	2.55	3.183(8)	130.9
	N(7)-H(7A)...O(7)[g]	0.86	2.35	2.998(8)	132.6
	N(10)-H(10)...O(3)	0.86	2.40	2.986(7)	125.4
	N(12)-H(12A)...O(4)[b]	0.86	2.04	2.885(12)	162.3
	N(14)-H(14A)...O(12)[b]	0.86	2.45	3.046(13)	126.8
	N(14)-H(14A)...O(8)[g]	0.86	2.42	3.159(8)	144.0
	C(1)-H(1A)...O(6)[t]	0.97	2.40	3.344(13)	163.2
	C(25)-H(25B)...O(9)	0.97	2.45	3.312(8)	148.4
	C(33)-H(33A)...O(10)[b]	0.97	2.36	3.317(9)	168.1
	C(41)-H(41B)...O(9)	0.97	2.45	3.319(8)	148.4
9	N(3)-H(3)...O(14)[viii]	0.87	2.17	2.982(16)	154
	N(3)-H(3)...O(15)[viii]	0.87	2.28	3.030(15)	144
	N(5)-H(5A)...O(10)[#]	0.87	2.30	3.055(11)	145
	N(7)-H(7A)...O(12)[l]	0.87	2.48	3.334(16)	167
	N(10)-H(10)...O(17)[i]	0.87	2.34	3.14(2)	154
	N(12)-H(12A)...O(22)	0.87	2.28	3.068(18)	150
	N(14)-H(14A)...O(5)	0.87	2.09	2.955(13)	173
	O(2)-H(2)...O(3)	0.83	1.55	2.375(7)	171
	O(22)-H(22A)...O(18)[l]	0.82	2.18	2.90(3)	146
	O(22)-H(22B)...O(7)[l]	0.82	2.41	3.194(17)	160
	C(1)-H(1A)...O(22)[s]	0.98	2.49	3.407(18)	155
	C(9)-H(9B)...O(8)[i]	0.98	2.38	3.256(14)	148
	C(15)-H(15)...O(9)[i]	0.94	2.60	3.502(17)	161
	C(33)-H(33A)...O(13)[i]	0.98	2.43	3.41(2)	174
	C(33)-H(33A)...O(15)	0.98	2.47	3.147(18)	126
	C(33)-H(33B)...O(20)	0.98	2.45	3.31(2)	146
	C(41)-H(41B)...O(9)	0.98	2.47	3.405(14)	159
	C(47)-H(47)...O(6)	0.94	2.53	3.303(12)	141
	C(51)-H(51)...O(1)[l]	0.94	2.30	2.690(8)	104

[#] Symmetry codes: (a) 1 - *x*, 1 - *y*, 2 - *z*; (b) 1- *x*, 1- *y*, 1 - *z*; (c) 2 - *x*, 2 - *y*, 1 - *z*; (d) 2 - *x*, 2 -*y*, 2 - *z*; (e) 1 - *x*, -*y*, 1 - *z*; (f) 1/2 -*x*, 1/2 -*y*, 1 - *z*; (g) 2 - *x*, 1 - *y*, 1 - *z*; (h) 2 - *x*, - *y*, 1 - *z*; (i) *x* -*1*, *y*, *z*; (j) 1 +

x, *y*, *z*; (k) 2 - *x*, 1 - *y*, - *z*; (l) 1 - *x*, - *y*, - *z*; (m) *x*, 1/2 - *y*, 1/2 - *z*; (n) 1 - *x*, - *y*, - *z*; (o) *x*, 3/2 - *y*, -1/2 + *z*; (p) *x*, 1 + *y*, *z*; (q) 3/2 - *x*, 3/2 - *y*, 1 - *z*; (r) *x* - 1, *y*, *z*; (s) *x*, -1 + *y*, *z*; (t) 1 - *x*, 2 - *y*, 1 - *z*; (u) *x*, *y*, 1 + *z*; (v) 1 + *x*, 1 + *y*, z - *1*; (w) 1 - *x*, 2 - *y*, - *z*; (x) *x*, *y*, *z* - 1; (y) 1 + *x*, 1 + *y*, *z*; (z) 2 - *x*, 2 - *y*, - *z*; (i) 1 + *x*, *y*, *z* - 1; (ii) - x, 1 - y, 1 - z; (iii) 1 + *x*, *y* - 1, *z*; (iv) 1 + *x*, *y* - 1, *z* -1; (v) *x*, 1/2 - *y*, *z* - 1/2; (vi) 2 - *x*, 1 - *y*, 2 - *z*; (vii) 2 - *x*, 1/2 + *y*, 1/2 - *z*; (viii) *x* - 1, *y* - 1, *z*; (ix) 1 - *x*, 1 - *y*, - *z*; (x) - *x*, 1 - *y*, - *z*; (xi) *x*, 2 - *y*, *z* - 1/2; (xii) 1 - *x*, *y*, 3/2 - *z*; (!) - *x*, - *y*, 1 - *z*; (#) - *x*, - *y*, - *z*; ($) 1/2 - *x*, 1/2 - *y*, - *z*; (%)1/2 + *x*, 1/2 - *y*, 1/2 + *z* ; (^) *x*, 1 + *y*, *z* – 1; (&)- *x*, 1 - *y*, -*z*; (*) *x*, 3/2 - *y*, 1/2 + *z*; (~) - *x*, 2 - *y*, 1 – *z*; (/) *x* - 1, *y* + 1, *z*.

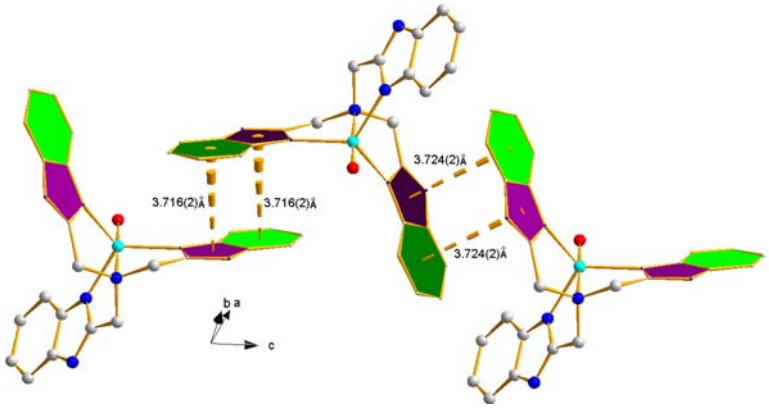
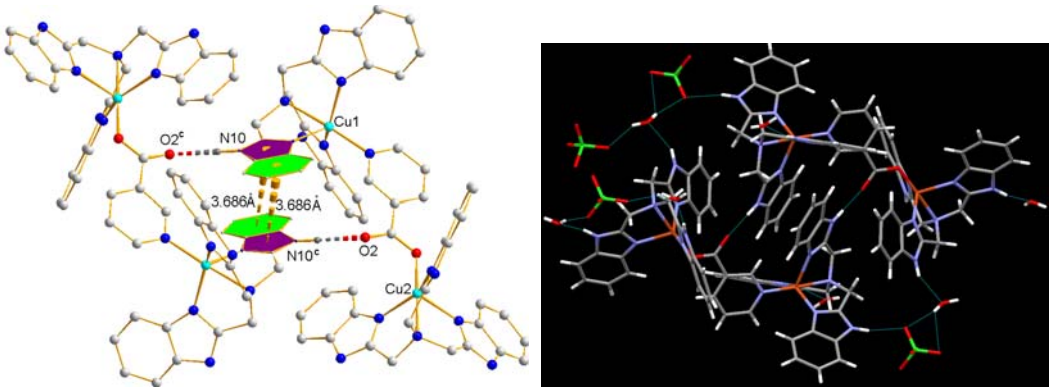


Figure S1 A one-dimensional chain parallel to the [001] axis sustained by π…π interactions in **1**.



(A) (B)

Figure S2 (A) Part of the crystal packing in **2**, showing the formation of a dimmer by N10…O2 hydrogen bond and one π…π interaction, symmetry code: (c) 2 - *x*, 2 - *y*, 1 - *z*; (B) Part of the crystal packing in 5, showing the formation of the three-dimensional hydrogen-bonded network.

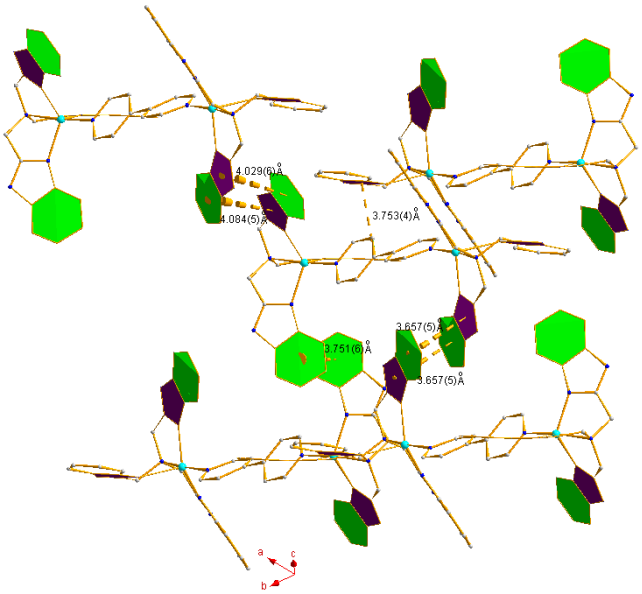


Figure S3 π…π interactions in the crystal packing of **3**.

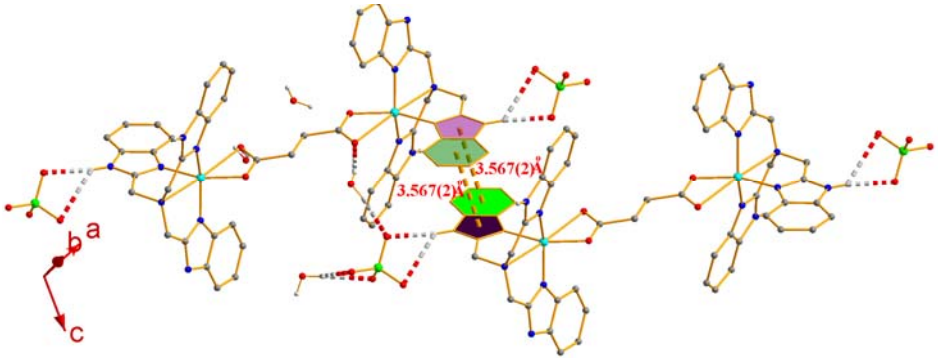


Figure S4 Part of the crystal packing, showing some hydrogen bonds and π…π interactions in **5**.

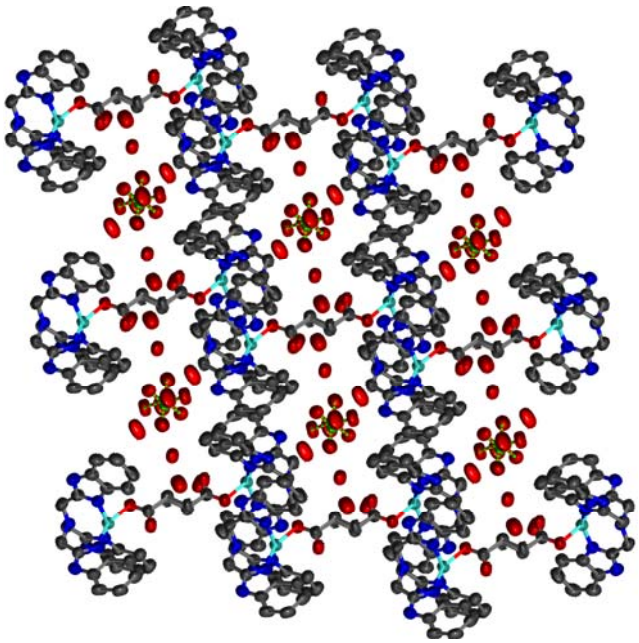


Figure S5 Part of the crystal packing in **5** view along the [010] direction, hydrogen atoms and disordered ClO_4^- and water oxygen atoms were omitted for clarity.

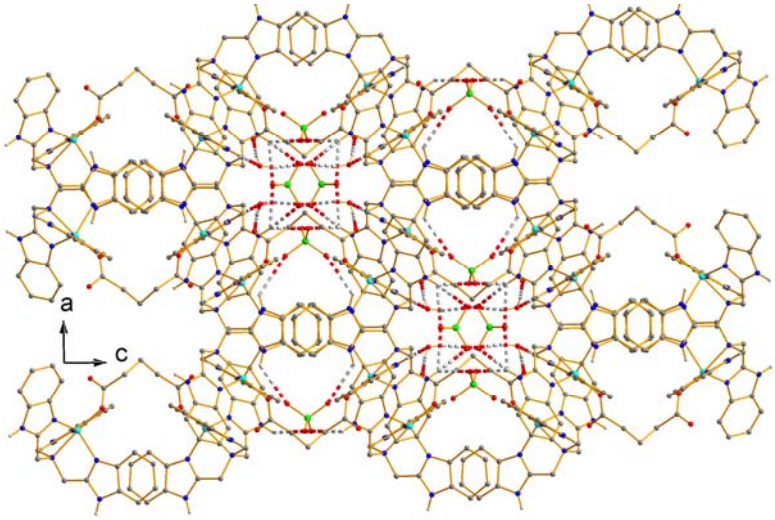


Figure S6 Three-dimensional network formed by hydrogen bonds and π…π interactions in 6, hydrogen atoms not involved in the motif have been omitted for clarity.

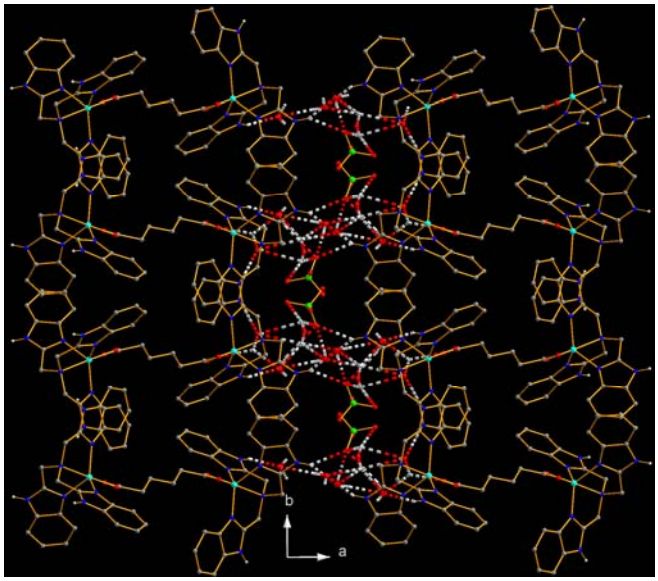


Figure S7 Three-dimensional network in **7a**, hydrogen bonds showing as dashed lines.

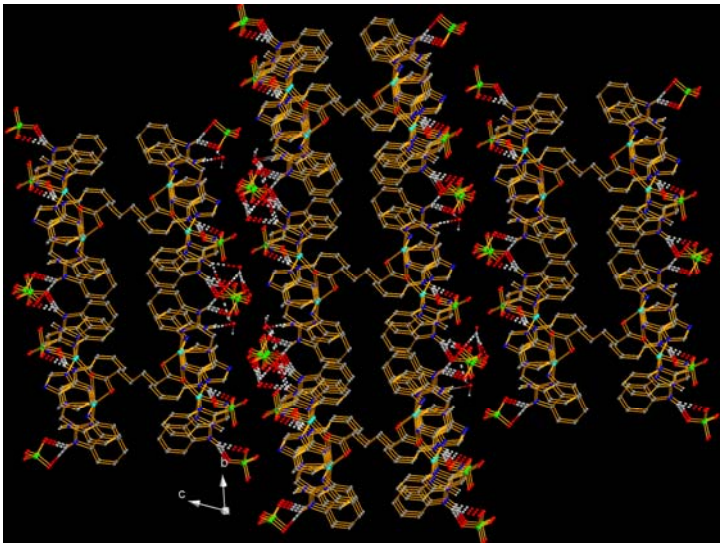


Figure S8 Three-dimensional network in **7b** formed by hydrogen bonds and π…π interactions,

hydrogen bonds showing as dashed lines.

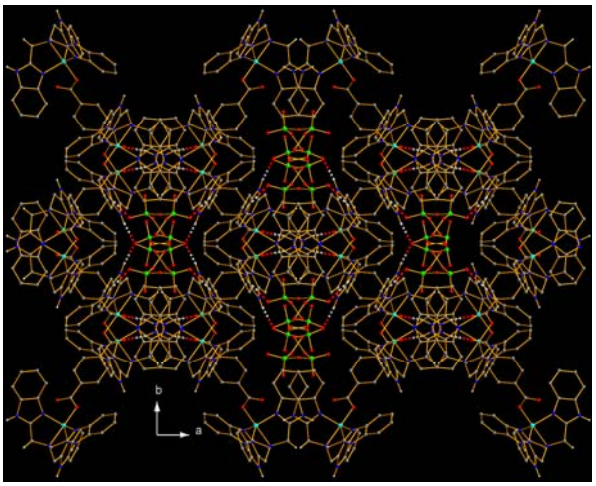


Figure S9 Three-dimensional network in **8a** formed by hydrogen bonds and π…π interactions, hydrogen bonds showing as dashed lines.

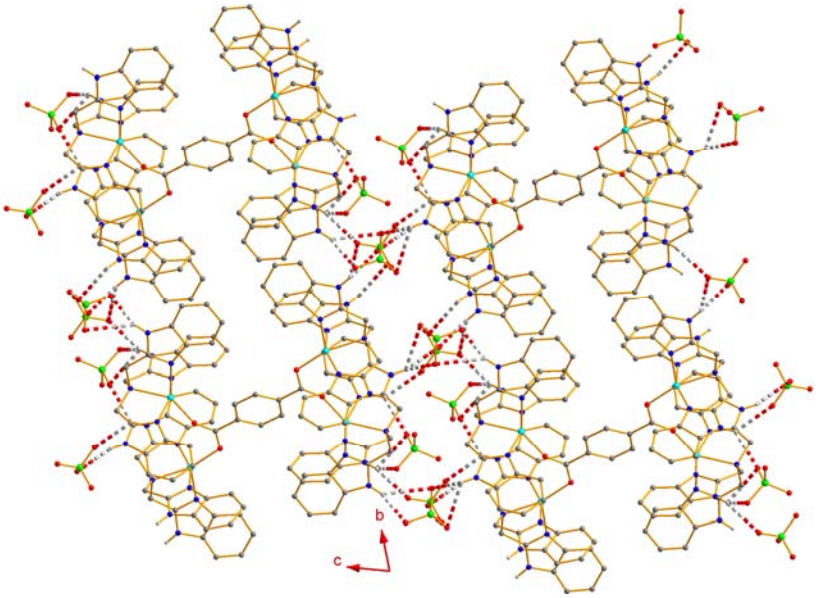


Figure S10 Three-dimensional network in **8b** formed by hydrogen bonds and π…π interactions, H-bonding shown as dashed lines.

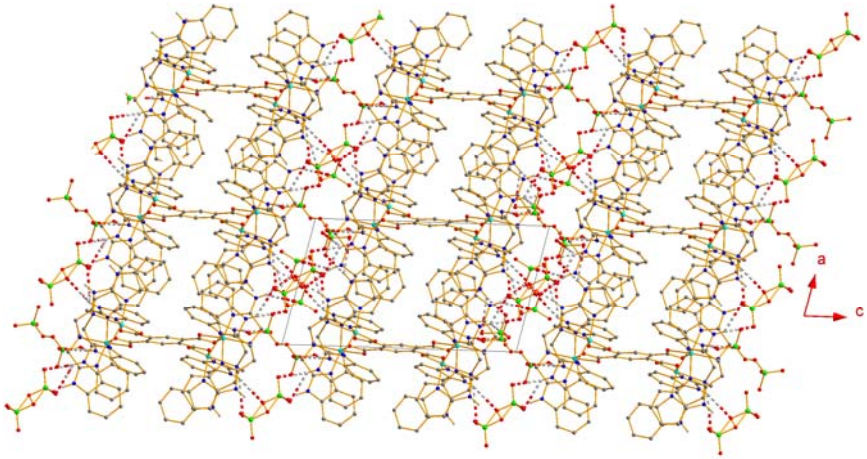


Figure S11 Three-dimensional network in **9** formed by H-bonds shown as dashed lines.

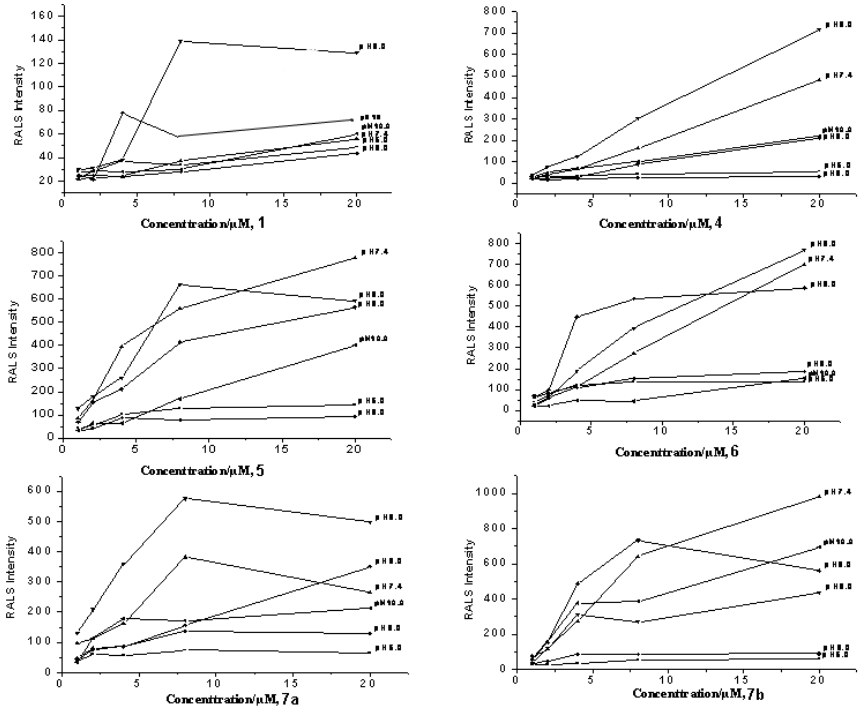


Figure S12 The pH dependences of the DNA condensation in the 1–20 μM ranges of complexes 1, **4**–**7** at room temperature.

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