Electronic Supplementary Information

Assembly of a dinuclear silver complex containing an Ag_2S_2 motif from a phosphorus-supported trishydrazone ligand. P=S→Ag^I coordination

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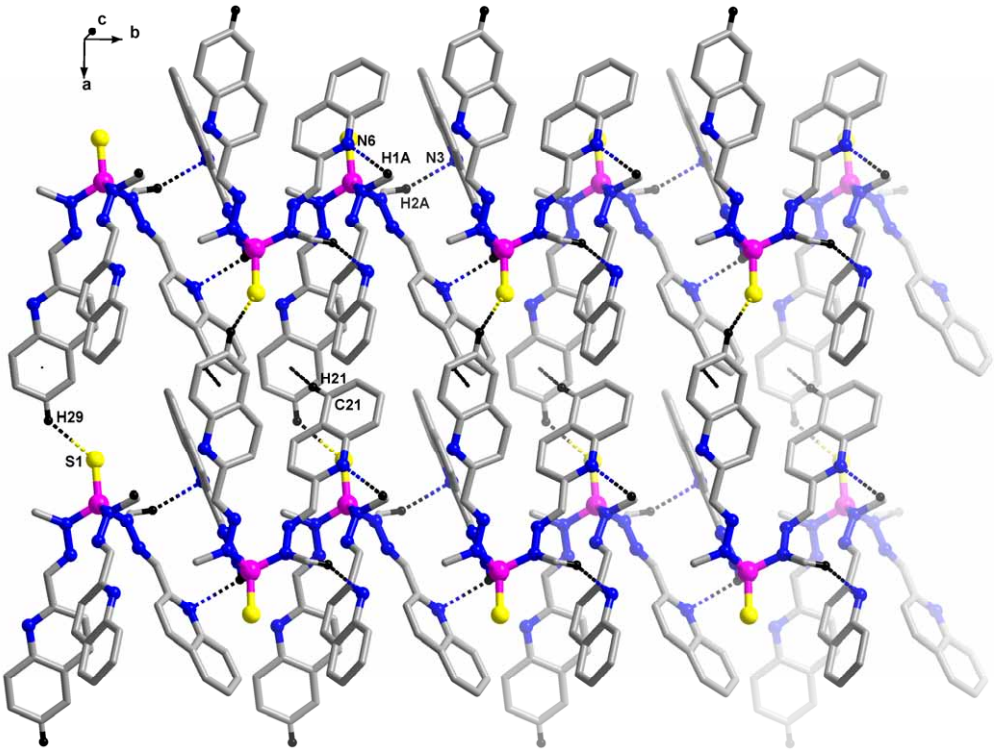
Table S1 Hydrogen-bonding parameters in the crystal structures **2**, **2**.3H_2O, **2**.2MeOH and **3**.4MeCN.

Structure	D-H---A	H---A (Å)	D---A (Å)	D-H---A (°)	Symmetry
2	C8-H8---C6(π)[a]	2.940(2)	3.889(3)	178.11(2)	x, y, z
	C24-H24---C4(π)[a]	2.916(2)	3.845(3)	166.05(2)	x, y, z
	C33-H33---C5(π)[a]	2.886(2)	3.823(3)	169.14(2)	x, y, z
	C1-H1A---N6	2.512(2)	3.247(4)	131.67(2)	1.5-x, -0.5+y, 0.5-z
	C2-H2A---N3	2.529(3)	3.396(4)	147.44(2)	1.5-x, -0.5+y, 0.5-z
	C21-H21--- π	2.921(8)	3.763(2)	148.41(2)	1+x, 1+y, z
	C29-H29---S1	2.833(7)	3.468(7)	125.11(2)	1+x, y, z
	π---π[b]		3.629(7)		0.5-x, 1.5+y, 1.5-z
2.3H_2O	S1---π[a]		3.619(2)		1-x+y, 1-x, -1+z
	N1---π[a]		3.659(3)		1-x+y, 1-x, z
	O1-H1W---N3[a]	1.958(3)	2.877(3)	172.48(4)	x, y, z
	O1-H2W---O1	2.035(5)	2.890(3)	174.51(5)	0.67-y, -0.67+x+y, 0.33+z
	π---π[c]		3.759(3)		1.33-y, 0.67+x-y, 1.67+z
2.2MeOH	C6-H6---N4[a]	2.833(2)	3.648(3)	146.93(16)	x, y, z
	π---π[a,c]		3.627(3)		x, y, z
	O2-H2---N7[a]	2.048(6)	2.855(8)	167.79(15)	x, y, z
	O1-H1---N9	2.108(3)	2.870(4)	154.44(15)	-1+x, y, z
	C3-H3A---O2	2.534(11)	3.474(16)	166.37(17)	1+x, y, z
	C9-H9---O1	2.612(8)	3.411(10)	144.34(18)	1-x, -y, 2-z
	C7-H7---π	2.812(8)	3.504(9)	132.05(16)	2-x, -y, 2-z
	C19-H19---π	2.673(8)	3.500(10)	148.44(17)	x, y, z
	π---π (N7)[b]		3.383(11)		1-x, -y, 2-z
	C29-H29---S1	3.006(10)	3.814(12)	146.19(21)	2-x, -y, 1-z
	C1-H1B---S1	3.012(9)	3.696(11)	129.38(17)	1-x, 1-y, 1-z
	C35-H35A---S1	3.003(11)	3.658(13)	126.64(21)	1-x, 1-y, 1-z
	π---π (N9)[b]		3.660(15)		-1+x, 1+y, z
3.4MeCN	C28-H28---π	2.632(8)	3.535(11)	164.08(4)	2-x, -y, 1-z
	π---π[b]		3.495(3)		2-x, -y, 1-z
	π---π (N8)[b]		3.569(9)		2-x, -y, 2-z
	C7-H7---S1	2.986(8)	3.762(8)	141.88(4)	-1+x, y, z
	π---π[b]		3.556(9)		1-x, 1-y, 1-z
	C36-H36C---N8	2.570(8)	3.510(12)	166.65(5)	2-x, -y, 2-z
	C2-H2C---N11	2.588(17)	3.520(11)	164.10(5)	1+x, -1+y, z
	C9-H9---O1	2.423(8)	3.338(13)	168.20(5)	x, y, z
	C18-H18---O2	2.684(8)	3.522(11)	150.41(5)	1-x, -y, 1-z
	C24-H24---O2	2.440(9)	3.219(12)	141.39(4)	1+x, y, z
	C26-H26---O2	2.696(9)	3.489(11)	143.69(4)	1+x, y, z
	C36-H36A---O2	2.453(9)	3.380(12)	162.43(6)	1-x, -y, 1-z
	C3-H3A---O3	2.695(8)	3.357(13)	126.63(4)	1+x, y, z
	C3-H3B---O3	2.417(9)	3.217(14)	140.63(4)	1-x, 1-y, -z
	C19-H19---O3	2.651(6)	3.553(9)	163.78(5)	1+x, -1+y, 1+z
	C2-H2A---O3	2.653(8)	3.465(10)	142.62(5)	1+x, y, 1+z
	C18-H18---O3	2.468(7)	3.337(11)	155.80(4)	1-x, -y, 1-z
	C2-H2A---O4	2.517(8)	3.446(11)	162.66(4)	1+x, y, 1+z
	C21-H21---O4	2.444(6)	3.370(9)	172.84(5)	2-x, -y, 1-z
	C36-H36B---O4	2.550(9)	3.107(14)	127.11(14)	x, y, 1+z

[a] Intramolecular interactions. [b] Parallel displaced π-stacking. [c] T-shaped π-stacking.

Supramolecular Architecture of 2: The unsolvated **2** forms a three-dimensional supramolecular architecture which can be explained as follows. Each trishydrozone molecule interacts with two other neighboring molecules by means of four proton donor-acceptor type of C-H---N interactions (H1A---N6 and H2A---N3) resulting in a one-dimensional tape (Fig. S1(a); Table S1). These one-dimensional tapes are connected by C-H---S (H29---S1) and C-H---π (H21---π) interactions to form a two-dimensional supramolecular assembly (Fig. S1(a); Table S1). Finally, one of the quinoline arms of each molecule present in the two-dimensional assembly (which involved in C-H---S interaction) is further π-stacked to form a three-dimensional supramolecular architecture (Fig. S1(b); Table S1). The interplanar distance in these interacting quinoline units is 3.629(7) Å (shortest contact of C31---C31: 3.423(11) Å) and their orientation is parallel displaced with a tilt angle of 22.6°.

(a)



(b)

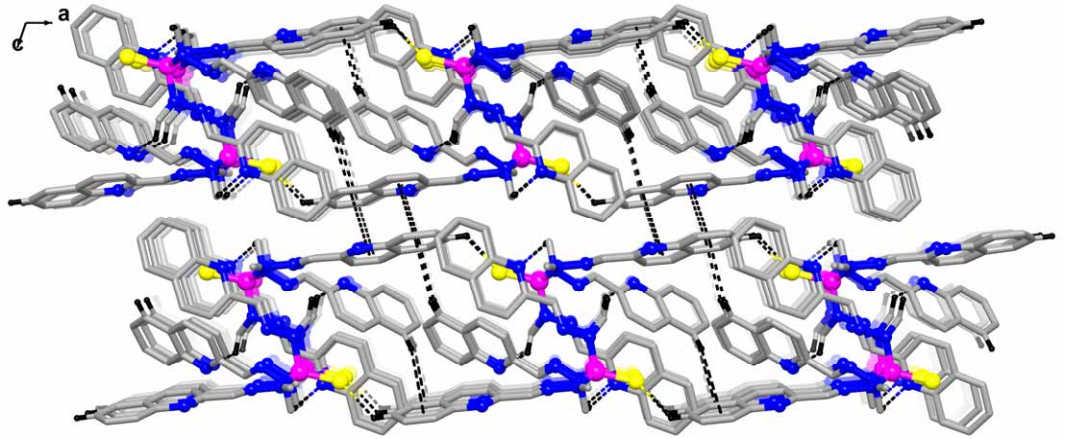


Fig. S1 View showing two (a) and three-dimensional (b) supramolecular assembly in the crystal structure of **2**.

Supramolecular Architecture of 2.2MeOH: The methanol solvated structure of **2** (**2**.2MeOH) shows rich supramolecular interactions in the solid state. Thus, the trishydrazone molecules are connected to each other by C-H---π (H19---π) and π-stacking interactions to form a one dimensional supramolecular tape (Fig. S2(a); Table S1). The interplanar distance (of interacting quinoline units) for the π-stacking interaction is 3.383(11) Å (shortest contact of C5---C11: 3.350(12) Å) and their orientation is parallel displaced with a tilt angle of 21.6°. In addition, the lattice methanol molecules are also found in contact with trishydrazone molecules through C-H---O (H9---O1 and H3A---O2) and O-H---N (H1---N9 and H2---N7) interactions to glue the supramolecular tape (Fig. S2(a); Table S1). These tapes are interconnected by three C-H---S interactions (H1B---S1, H29---S1 and H35A---S1) to form the three-dimensional supramolecular architecture (Fig. S2(a); Table S1).

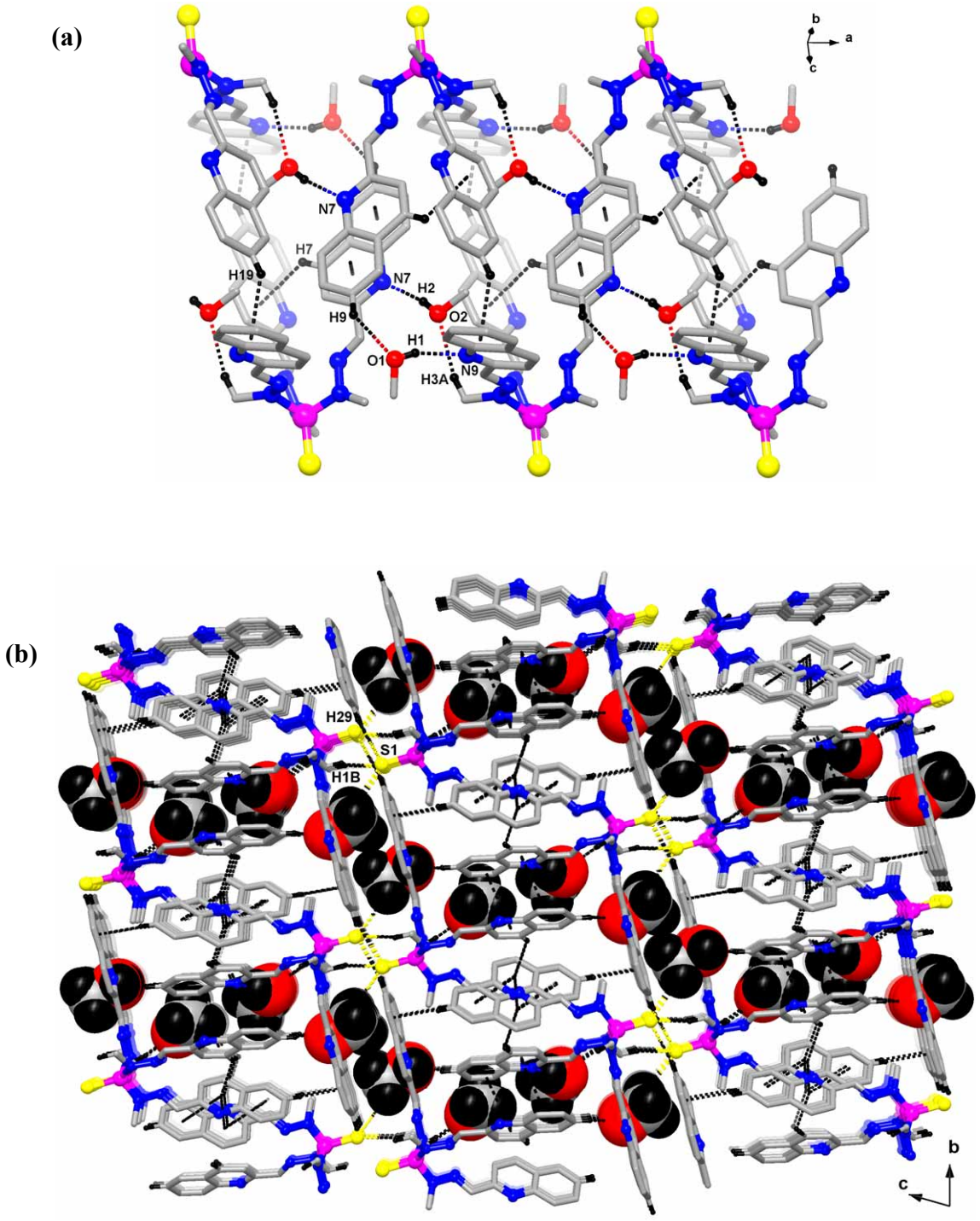
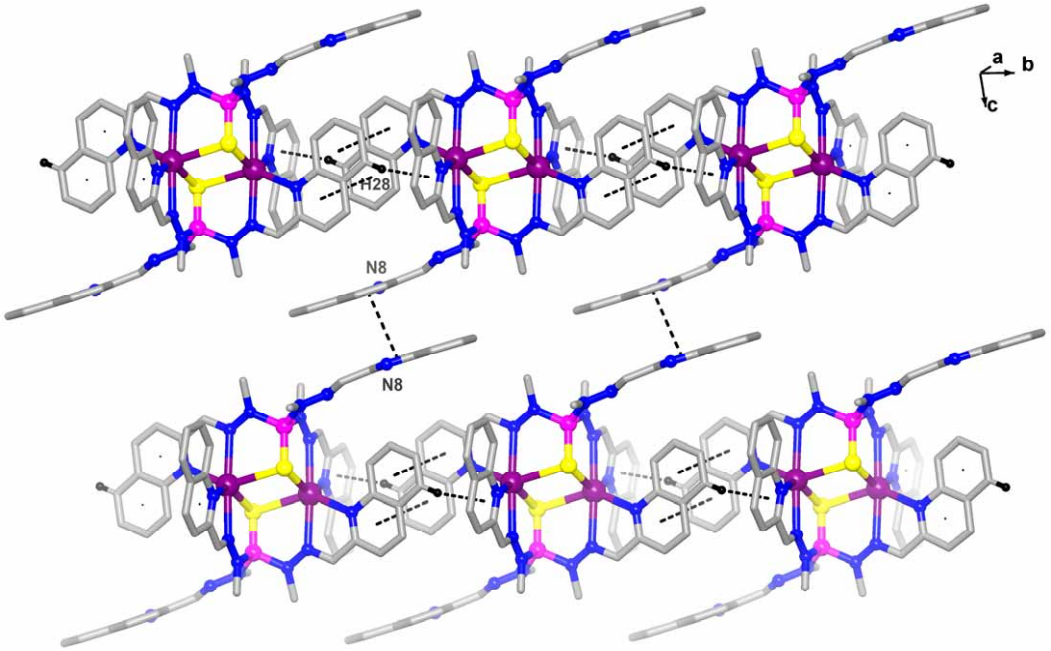


Fig. S2 View showing two- (a) and three-dimensional (b) supramolecular assembly in the crystal structure of **2**.2MeOH.

Supramolecular Architecture of 3: A closer inspection of the crystal structure of **3** reveals that it also forms three-dimensional supramolecular architecture through extensive hydrogen-bonding interactions. Thus, the cationic molecules of **3** form a one-dimensional network mediated by C-H---π (H28---π) and π-stacking interactions (Fig. S3(a); Table S1). The π-stacking is parallel displaced interaction with the interplanar distance of 3.495(3) Å (shortest contact of C28---C33: 3.477(3) Å) and with a tilt angle of 22.1°. Such one-dimensional networks are connected each other by another π-stacking interaction to form the two-dimensional supramolecular network (Fig. S3(a); Table S1). This π-stacking also parallel displaced interaction with the interplanar distance of 3.569(3) Å (shortest contact of C15---C17: 3.533(3) Å) and a tilt angle of 21.3°. These two-dimensional networks are further connected through a C-H---S (H7---S1) and a π-stacking interaction to form the three-dimensional supramolecular architecture (Fig. S3(b); Table S1). This π-stacking also is parallel displaced with an interplanar distance of 3.556(9) Å (shortest contact of C6---C12: 3.546(9) Å) and with a tilt angle of 31.3°. In addition, numerous C-H---O and C-H---N interactions are seen in the crystal structure between lattice solvent molecules (MeCN), perchlorate anions and protons of the cationic molecules (Fig. S3(b); Table S1).

(a)



(b)

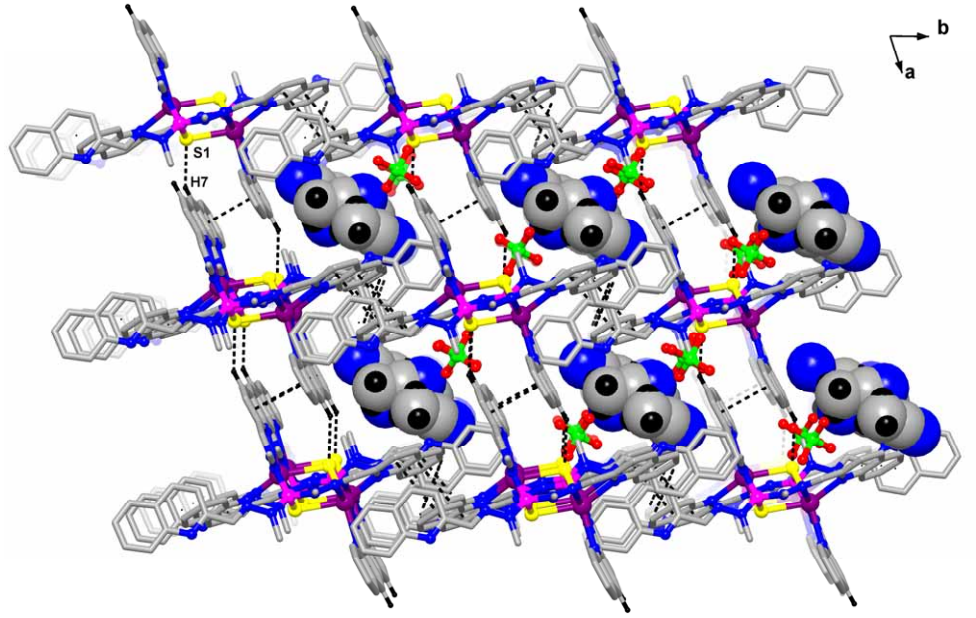


Fig. S3 View showing two- (a) and three-dimensional (b) supramolecular assembly in the crystal structure of **3**