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Aliphatic Amine Mediated Assembly of $[M_6(mna)_6]$ (M = Cu/Ag) into Extended Two-dimensional Structures: Synthesis, Structure and Lewis Acid Catalytic Studies

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Table S1 Elemental analysis result of the compound **I** and **II** at the various stages

Elemental analysis result	**% of C**			**% of H**			**% of N**			**% of S**		
	I	**IIAg_6**	**IICu_6**	**I**	**IIAg_6**	**IICu_6**	**I**	**IIAg_6**	**IICu_6**	**I**	**IIAg_6**	**IICu_6**
Calculated	23.94	24.72	24.72	3.01	3.16	3.16	8.88	8.24	8.24	8.72	9.43	9.43
As synthesized	23.21	24.08	23.98	2.60	2.55	2.46	8.03	7.76	7.65	8.14	8.89	8.76

Table S2 Selected bond lengths (Å) and bond angles (deg) for **I**, **II M_6 (M = Ag/Cu)**

Bond length		Bond angle	
I M_6 (M=Ag)			
Cd(1)-N(4)	2.271(4)	N(4)#1-Cd(1)-N(4)	180
Cd(1)-O(3)	2.319(3)	N(4)#1-Cd(1)-O(3)#1	85.83(14)
Cd(1)-O(1)#2	2.381(3)	N(4)-Cd(1)-O(3)#1	94.17(14)
Cd(2)-N(7)	2.328(4)	N(4)-Cd(1)-O(3)	85.83(14)
Cd(2)-N(6)	2.330(5)	O(3)#1-Cd(1)-O(3)	180.00(16)
Cd(2)-O(7)	2.354(4)	N(4)#1-Cd(1)-O(1)#2	87.57(13)
Ag(1)-N(1)	2.296(4)	N(4)-Cd(1)-O(1)#2	92.43(13)
Ag(1)-S(2)	2.4809(12)	O(3)#1-Cd(1)-O(1)#2	99.68(13)
Ag(1)-S(3)#5	2.4973(12)	O(3)-Cd(1)-O(1)#2	80.32(13)
Ag(1)-Ag(3)#5	2.9378(5)	N(4)#1-Cd(1)-O(1)#3	92.43(13)
Ag(1)-Ag(2)	2.9920(6)	N(4)-Cd(1)-O(1)#3	87.57(13)
Ag(2)-N(2)	2.259(4)	O(3)#1-Cd(1)-O(1)#3	80.32(13)
Ag(2)-S(1)	2.4808(12)	O(3)-Cd(1)-O(1)#3	99.68(13)
Ag(2)-S(3)	2.4878(12)	O(1)#2-Cd(1)-O(1)#3	180.00(16)
Ag(2)-Ag(3)	2.9518(5)	N(7)#4-Cd(2)-N(7)	180
Ag(3)-N(3)	2.290(4)	N(7)#4-Cd(2)-N(6)	103.38(15)
Ag(3)-S(2)	2.4833(12)	N(7)-Cd(2)-N(6)	76.62(15)
Ag(3)-S(1)#5	2.4914(12)	N(7)-Cd(2)-N(6)#4	103.38(15)
		N(6)-Cd(2)-N(6)#4	180
		N(7)#4-Cd(2)-O(7)	95.43(14)
		N(7)-Cd(2)-O(7)	84.57(14)
		N(6)-Cd(2)-O(7)	86.18(16)
		N(6)#4-Cd(2)-O(7)	93.82(16)
		N(7)#4-Cd(2)-O(7)#4	84.57(14)
		N(7)-Cd(2)-O(7)#4	95.43(14)
		N(6)-Cd(2)-O(7)#4	93.82(16)
		N(6)#4-Cd(2)-O(7)#4	86.18(16)
		O(7)-Cd(2)-O(7)#4	180
		N(1)-Ag(1)-S(2)	119.08(10)
		N(1)-Ag(1)-S(3)#5	121.04(10)
		S(2)-Ag(1)-S(3)#5	112.53(4)
		N(1)-Ag(1)-Ag(3)#5	89.29(10)

		S(2)-Ag(1)-Ag(3)#5	135.64(3)
		S(3)#5-Ag(1)-Ag(3)#5	71.63(3)
		N(1)-Ag(1)-Ag(2)	85.30(10)
		S(2)-Ag(1)-Ag(2)	73.91(3)
		S(3)#5-Ag(1)-Ag(2)	136.79(3)
		Ag(3)#5-Ag(1)-Ag(2)	75.551(14)
		N(2)-Ag(2)-S(1)	127.16(10)
		N(2)-Ag(2)-S(3)	119.95(10)
		S(1)-Ag(2)-S(3)	110.38(4)
		N(2)-Ag(2)-Ag(3)	84.44(10)
		S(1)-Ag(2)-Ag(3)	128.18(3)
		S(3)-Ag(2)-Ag(3)	71.51(3)
		N(2)-Ag(2)-Ag(1)	88.58(10)
		S(1)-Ag(2)-Ag(1)	70.75(3)
		S(3)-Ag(2)-Ag(1)	129.01(3)
		Ag(3)-Ag(2)-Ag(1)	70.459(14)
		N(3)-Ag(3)-S(2)	121.39(10)
		N(3)-Ag(3)-S(1)#5	118.76(10)
		S(2)-Ag(3)-S(1)#5	111.89(4)
		N(3)-Ag(3)-Ag(1)#5	87.94(10)
		S(2)-Ag(3)-Ag(1)#5	136.51(3)
		S(1)#5-Ag(3)-Ag(1)#5	71.58(3)
		N(3)-Ag(3)-Ag(2)	87.01(10)
		S(2)-Ag(3)-Ag(2)	74.62(3)
		S(1)#5-Ag(3)-Ag(2)	136.88(3)
		Ag(1)#5-Ag(3)-Ag(2)	75.905(14)
		C(1)-S(1)-Ag(2)	106.86(15)
		C(1)-S(1)-Ag(3)#5	109.32(15)
		Ag(2)-S(1)-Ag(3)#5	93.87(4)
		C(7)-S(2)-Ag(1)	109.33(16)
		C(7)-S(2)-Ag(3)	105.34(15)
		Ag(1)-S(2)-Ag(3)	87.37(4)
		C(13)-S(3)-Ag(2)	107.06(16)
		C(13)-S(3)-Ag(1)#5	107.81(15)
		Ag(2)-S(3)-Ag(1)#5	93.20(4)
		C(6)-O(1)-Cd(1)#6	124.4(3)
		C(12)-O(3)-Cd(1)	146.8(4)
		C(5)-N(1)-Ag(1)	126.5(3)
		C(1)-N(1)-Ag(1)	115.4(3)
		C(11)-N(2)-Ag(2)	123.2(3)
		C(7)-N(2)-Ag(2)	118.5(3)
		C(17)-N(3)-Ag(3)	125.9(3)
		C(13)-N(3)-Ag(3)	115.4(3)
		C(19)-N(4)-Cd(1)	114.1(3)
		C(21)-N(6)-Cd(2)	108.9(3)

		C(22)-N(7)-Cd(2)	108.0(3)
II M_6(M = Ag)			
Cd(1)-N(4)	2.278(4)	N(4)-Cd(1)-N(4)#1	180
Cd(1)-N(4)#1	2.279(4)	N(4)-Cd(1)-O(1)	85.70(14)
Cd(1)-O(1)	2.281(3)	N(4)#1-Cd(1)-O(1)	94.30(14)
Cd(1)-O(1)#1	2.281(3)	N(4)-Cd(1)-O(1)#1	94.30(14)
Cd(1)-O(3)	2.383(4)	N(4)#1-Cd(1)-O(1)#1	85.70(14)
Cd(1)-O(3)#1	2.383(4)	O(1)-Cd(1)-O(1)#1	180
Ag(1)-N(1)	2.253(3)	N(4)-Cd(1)-O(3)	86.73(17)
Ag(1)-S(3)	2.4726(11)	N(4)#1-Cd(1)-O(3)	93.27(17)
Ag(1)-S(2)#2	2.4953(11)	O(1)-Cd(1)-O(3)	91.70(14)
Ag(1)-Ag(2)	2.8933(6)	O(1)#1-Cd(1)-O(3)	88.30(14)
Ag(1)-Ag(3)	2.9508(6)	N(4)-Cd(1)-O(3)#1	93.27(17)
Ag(3)-N(3)	2.271(4)	N(4)#1-Cd(1)-O(3)#1	86.73(17)
Ag(3)-S(1)	2.4798(11)	O(1)-Cd(1)-O(3)#1	88.30(14)
Ag(3)-S(2)#3	2.5047(12)	O(1)#1-Cd(1)-O(3)#1	91.70(14)
Ag(3)-Ag(2)#4	3.1283(6)	O(3)-Cd(1)-O(3)#1	180
Ag(2)-N(2)#2	2.295(4)	N(1)-Ag(1)-S(3)	124.39(9)
Ag(2)-S(1)	2.4654(11)	N(1)-Ag(1)-S(2)#2	125.32(9)
Ag(2)-S(3)#4	2.4934(12)	S(3)-Ag(1)-S(2)#2	104.49(4)
		N(1)-Ag(1)-Ag(2)	89.60(9)
		S(3)-Ag(1)-Ag(2)	131.46(3)
		S(2)#2-Ag(1)-Ag(2)	72.60(3)
		N(1)-Ag(1)-Ag(3)	87.06(9)
		S(3)-Ag(1)-Ag(3)	73.83(3)
		S(2)#2-Ag(1)-Ag(3)	132.86(3)
		Ag(2)-Ag(1)-Ag(3)	74.786(15)
		N(3)-Ag(3)-S(1)	132.15(11)
		N(3)-Ag(3)-S(2)#3	114.85(11)
		S(1)-Ag(3)-S(2)#3	111.13(4)
		N(3)-Ag(3)-Ag(1)	89.99(10)
		S(1)-Ag(3)-Ag(1)	70.66(3)
		S(2)#3-Ag(3)-Ag(1)	128.90(3)
		N(3)-Ag(3)-Ag(2)#4	80.12(10)
		S(1)-Ag(3)-Ag(2)#4	130.37(3)
		S(2)#3-Ag(3)-Ag(2)#4	68.35(3)
		Ag(1)-Ag(3)-Ag(2)#4	73.595(15)
		N(2)#2-Ag(2)-S(1)	126.92(10)
		N(2)#2-Ag(2)-S(3)#4	115.62(10)
		S(1)-Ag(2)-S(3)#4	112.20(4)
		N(2)#2-Ag(2)-Ag(1)	90.25(9)
		S(1)-Ag(2)-Ag(1)	71.87(3)
		S(3)#4-Ag(2)-Ag(1)	133.93(3)
		N(2)#2-Ag(2)-Ag(3)#4	81.38(9)
		S(1)-Ag(2)-Ag(3)#4	137.21(3)
		S(3)#4-Ag(2)-Ag(3)#4	70.35(3)

		Ag(1)-Ag(2)-Ag(3)#4	77.418(15)
		C(13)#5-S(3)-Ag(1)	111.93(14)
		C(13)#5-S(3)-Ag(2)#4	101.27(15)
		Ag(1)-S(3)-Ag(2)#4	94.41(4)
		C(7)-S(2)-Ag(1)#2	110.85(14)
		C(7)-S(2)-Ag(3)#7	101.81(15)
		Ag(1)#2-S(2)-Ag(3)#7	97.88(4)
		C(1)-S(1)-Ag(2)	111.22(13)
		C(1)-S(1)-Ag(3)	106.14(13)
		Ag(2)-S(1)-Ag(3)	91.74(4)
		C(6)-O(1)-Cd(1)	129.4(3)
		C(12)-O(3)-Cd(1)	159.6(4)
		C(19)-N(4)-Cd(1)	126.4(3)
		C(7)-N(2)-Ag(2)#2	115.8(3)
		C(11)-N(2)-Ag(2)#2	125.9(3)
		C(5)-N(1)-Ag(1)	124.9(3)
		C(1)-N(1)-Ag(1)	116.2(3)
II M_6 (M = Cu)			
Cu(2)-N(2)	2.019(3)	N(2)-Cu(2)-S(1)	131.25(9)
Cu(2)-S(1)	2.2539(9)	N(2)-Cu(2)-S(3)#1	115.53(9)
Cu(2)-S(3)#1	2.2786(9)	S(1)-Cu(2)-S(3)#1	110.73(3)
Cu(2)-Cu(1)	2.7865(6)	N(2)-Cu(2)-Cu(1)	91.70(9)
Cu(2)-Cu(3)#1	2.9793(6)	S(1)-Cu(2)-Cu(1)	70.82(3)
Cu(1)-N(1)	2.003(3)	S(3)#1-Cu(2)-Cu(1)	127.94(3)
Cu(1)-S(2)	2.2488(9)	N(2)-Cu(2)-Cu(3)#1	83.48(9)
Cu(1)-S(3)	2.2674(10)	S(1)-Cu(2)-Cu(3)#1	130.50(3)
Cu(1)-Cu(3)	2.6841(6)	S(3)#1-Cu(2)-Cu(3)#1	66.07(3)
S(2)-Cu(3)#1	2.2793(9)	Cu(1)-Cu(2)-Cu(3)#1	74.864(17)
S(1)-Cu(3)	2.2504(10)	N(1)-Cu(1)-S(2)	126.95(8)
Cd(1)-N(4)#2	2.276(3)	N(1)-Cu(1)-S(3)	127.24(9)
Cd(1)-N(4)	2.276(3)	S(2)-Cu(1)-S(3)	100.48(3)
Cd(1)-O(2)	2.326(3)	N(1)-Cu(1)-Cu(3)	92.28(8)
Cd(1)-O(2)#2	2.326(3)	S(2)-Cu(1)-Cu(3)	127.31(3)
Cd(1)-N(4)#2	2.276(3)	S(3)-Cu(1)-Cu(3)	71.89(3)
		N(1)-Cu(1)-Cu(2)	90.29(9)
		S(2)-Cu(1)-Cu(2)	72.68(3)
		S(3)-Cu(1)-Cu(2)	129.01(3)
		Cu(3)-Cu(1)-Cu(2)	73.738(18)
		C(13)-S(3)-Cu(1)	108.57(12)
		C(13)-S(3)-Cu(2)#1	102.81(11)
		Cu(1)-S(3)-Cu(2)#1	102.73(4)
		C(7)-S(2)-Cu(1)	108.72(12)
		C(7)-S(2)-Cu(3)#1	101.60(12)
		Cu(1)-S(2)-Cu(3)#1	101.55(4)
		C(1)-S(1)-Cu(3)	107.91(12)
		C(1)-S(1)-Cu(2)	106.70(11)

		Cu(3)-S(1)-Cu(2)	93.60(4)
		C(11)-N(2)-Cu(2)	126.0(3)
		C(7)-N(2)-Cu(2)	115.1(2)
		N(4)#2-Cd(1)-N(4)	180
		N(4)#2-Cd(1)-O(2)	87.12(10)
		N(4)-Cd(1)-O(2)	92.88(10)
		N(4)#2-Cd(1)-O(2)#2	92.88(10)
		N(4)-Cd(1)-O(2)#2	87.12(10)
		O(2)-Cd(1)-O(2)#2	180.00(14)
		N(4)#2-Cd(1)-O(6)#3	91.50(10)
		N(4)-Cd(1)-O(6)#3	88.50(10)
		O(2)-Cd(1)-O(6)#3	89.91(10)
		O(2)#2-Cd(1)-O(6)#3	90.09(10)
		N(4)#2-Cd(1)-O(6)#4	88.50(10)
		N(4)-Cd(1)-O(6)#4	91.50(10)
		O(2)-Cd(1)-O(6)#4	90.09(10)
		O(2)#2-Cd(1)-O(6)#4	89.91(10)
		O(6)#3-Cd(1)-O(6)#4	180
		N(3)-Cu(3)-S(1)	127.67(9)
		N(3)-Cu(3)-S(2)#1	117.21(9)
		S(1)-Cu(3)-S(2)#1	108.81(4)
		N(3)-Cu(3)-Cu(1)	93.33(8)
		S(1)-Cu(3)-Cu(1)	72.91(3)
		S(2)#1-Cu(3)-Cu(1)	131.06(3)
		N(3)-Cu(3)-Cu(2)#1	85.78(9)
		S(1)-Cu(3)-Cu(2)#1	135.64(3)
		S(2)#1-Cu(3)-Cu(2)#1	68.48(3)
		Cu(1)-Cu(3)-Cu(2)#1	77.467(17)

Symmetry transformation used to generate equivalent atoms **I:** #1 -x+2,-y,-z #2 x+1,y,z #3 -x+1,-y,-z #4 -x,-y+1,-z #5 -x+1,-y+1,-z #6 x-1,y,z

II M_6 (M = Ag) : #1 -x,-y,-z #2 -x+1,-y,-z #3 x,y+1,z #4 -x+1,-y+1,-z #5 x+1,y+1,z-1 #6 -x+2,-y+1,-z+2 #7 x,y-1,z #8 x-1,y-1,z+1

II M_6 (M = Cu) : #1 -x+2,-y+2,-z+2 #2 -x+1,-y+1,-z+2 #3 x-1,y,z #4 -x+2,-y+1,-z+2 #5 -x+1,-y+2,-z+2 #6 x+1,y,z

Table S3 Hydrogen bond interaction table of compound **I** and compound **II**

Structure	Interaction	H . . . A	D . . . A	D - H . . . A	Symmetry
I M_6 (M=Ag)	N5 – H5A . . . O5	1.86	2.735(6)	166.7	x+1, y-1, z
	N5 – H5B . . . O9	1.85	2.725(8)	168.9	-x+2, -y, -z+1
	N5 – H5C . . . O6	2.05	2.940(6)	174.8	-x+1, -y, -z+1
	N5 – H5A . . . O5	1.861	2.735	166.67	
	N5 – H5B . . . O9	1.846	2.724	168.89	
	N5 – H5C . . . O6	2.052	2.940	174.77	
II M_6 (M=Ag)	N6 – H6A . . . O4	2.131	2.894	143.20	x+1, y, z
	N6 – H6B . . . O9	1.888	2.710	152.69	-x+2, -y-1, -z-1
	N5 – H5A . . . O5	1.805	2.780	169.50	x-1, y, z+1
	N5 – H5B . . . O6	1.988	2.790	176.42	-x+1, -y-1, -z
	O10 – H10A . . . O1	1.829	2.855	170.10	x, y, z-1

Table S4 Bond Valence sum of compound **I** and **II** M_6 **(M = Ag/Cu)**

Bond	Bond length (Å)	Bond valence
I		
N4-Cd1	2.271	0.431
N4-C19	1.476	0.984
Bond valence sum of N4		**1.415**
N6-Cd2	2.330	0.399
N6-C21	1.481	0.970
Bond valence sum of N6		**1.369**
N7-Cd2	2.328	0.370
N7-C22	1.469	1.003
Bond valence sum of N7		**1.373**
II M_6 **(M = Ag)**		
N4-Cd1	2.278	0.423
N4-C19	1.463	1.019

Bond valence sum of N4		**1.442**
II M_6 (M = Cu)		
N4-Cd	2.276	0.426
N4-C1	1.48	0.95
Bond valence sum of N4		**1.381**

Bond valence = exp {(R_o - R)/B}, where R_o and B are constants; B = 0.37, R_o = 1.96 (for Cd-N bond) and R_o = 1.47 (for C-N bond) and R is the bond length between two atoms.

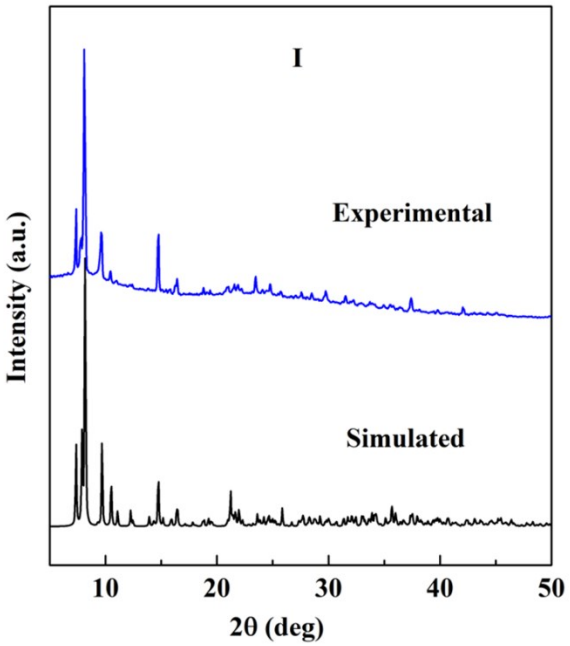
Table S5 The details of the TGA analysis of the synthesized compounds as follows

Compound	**% of Weight Loss (calculated)**	**Decomposed moieties and Temprature range**
[{Ag_6(2-*mna*)$_6$Cd(H*en*)$_2$}{Cd(*en*)$_2$2H_2O}·(H_2O)$_8$] (I)	5.7 (6.6)	8H_2O (40-85^{o}C)
	49.2 (54.5)	2 water, 4 ethylenediamine, 6 mercaptonicotinic acid (160-920^{o}C)
[{Ag_6(2-*mna*)$_6$Cd(H*en*)$_2$}·(H_2*en*)·(H_2O)$_{10}$] {II M_6 (M= Ag)}	6 (8.9)	10 H_2O (45-90^{o}C)
	58.9 (57.6)	4 ethylene diamine and 6 mercaptonicotinic acid (100-860^{o}C)
[{Cu_6(2-*mna*)$_6$Cd(H*en*)$_2$}·(H_2*en*)·(H_2O)$_{10}$] {II M_6 (M = Cu)}	7 (10)	8 H_2O (45-115^{o}C)
	14.4 (13.8)	4 ethylenediamine (190-275^{o}C)
	43 (52)	6 mercaptonicotinic acid (275-900^{o}C)

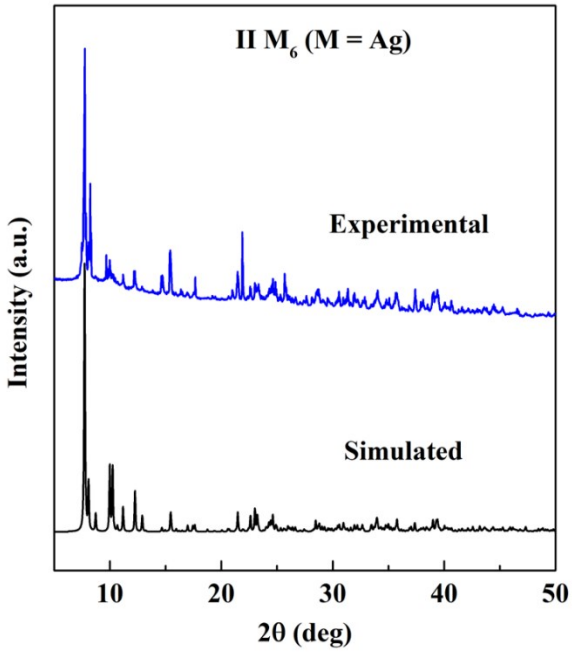
Table S6 Optimized condition for cyanation of imine

Entry	Catalyst	Solvent	Time (h)	Temperature (^{o}C)	Yield (%)
1	Compound **II** Ag_6	CH_2Cl_2	10	0	46
2	Compound **II** Ag_6	CH_2Cl_2	10	RT	48
3	Compound **II** Ag_6	CH_2Cl_2	16	0	90
4	Compound **II** Cu_6	CH_2Cl_2	4	0	60
5	Compound **II** Cu_6	CH_2Cl_2	8	0	95
6[(a)]	Compound **II** Cu_6	CH_2Cl_2	8	0	95
7	$Cd(NO_3)_2{\cdot}4H_2O$	CH_2Cl_2	16	0	26
8	$CdSO_4{\cdot}8H_2O$	CH_2Cl_2	16	0	28
9	No catalyst	CH_2Cl_2	16	0	trace

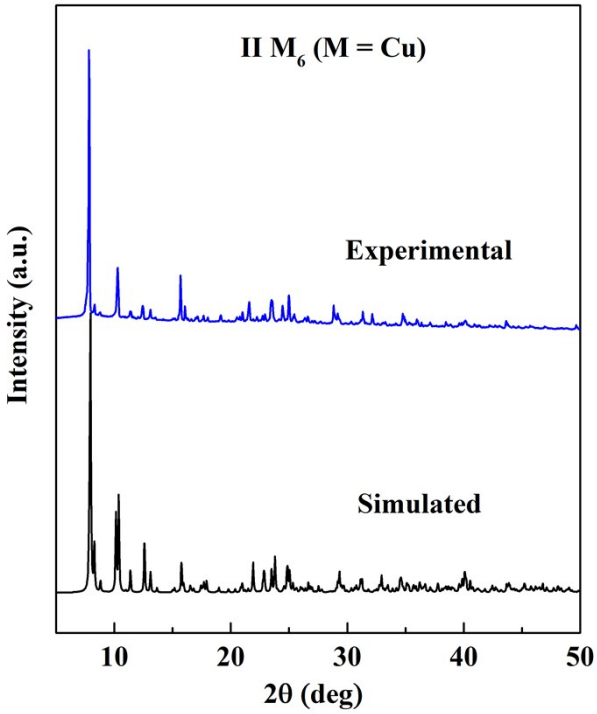
Reaction conditions: 0.5 mmol of N-benzylideneaniline, 0.75 mmol of TMS-CN and 5 ml of solvent was taken along with 0.05 mmol of catalyst. Isolated yields after thin layer chromatography. [(a)] 0.1 mmol of catalyst.



(a)



(b)



(c)

Fig. S1 Simulated and experimental PXRD patterns of **I** (a), **II M_6 (M = Ag)** (b) and **II M6 (M = Cu)** (c).

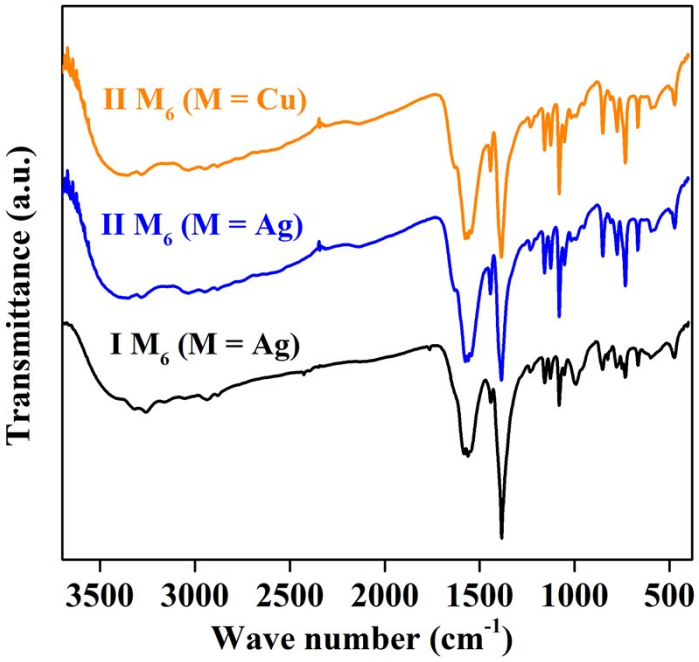


Fig. S2 IR spectra of **I**, **II** $\mathbf{M_6}$ **(M = Ag)** and **II** $\mathbf{M_6}$ **(M = Cu)**.

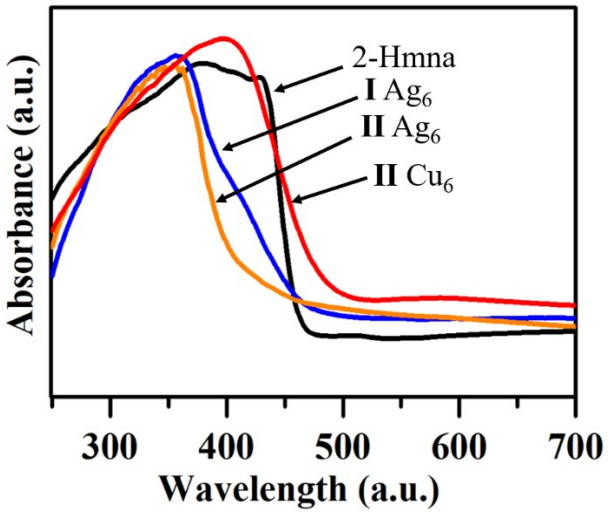
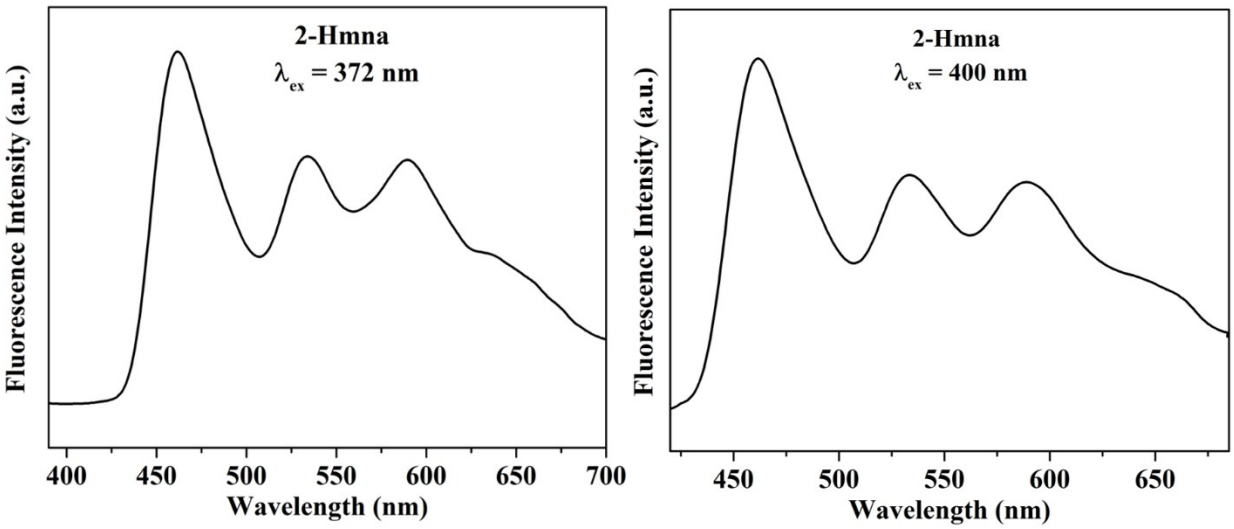
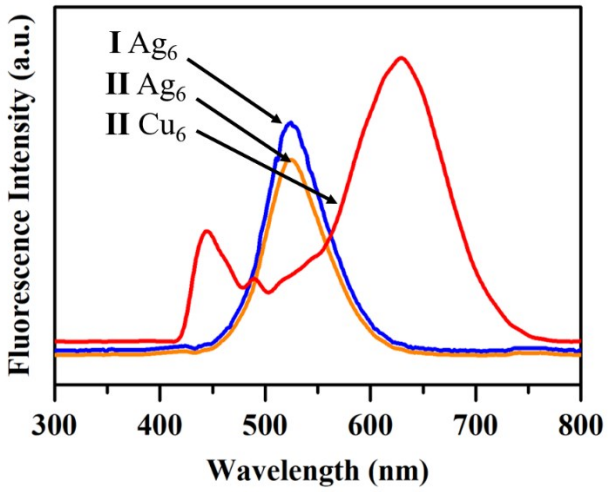


Fig. S3 UV spectra of Hmna, **I** M_6 (M = Ag), **II** M_6 (M = Ag) and **II** M_6 (M = Cu).



(a) (b)



(c)

Fig. S4 PL spectra of Hmna (a)/(b), **I** (λ_{ex} = 372 nm), **II M_6 (M = Ag)** (λ_{ex} = 372 nm) and **II M_6 (M = Cu)** (λ_{ex} = 400 nm) (c).

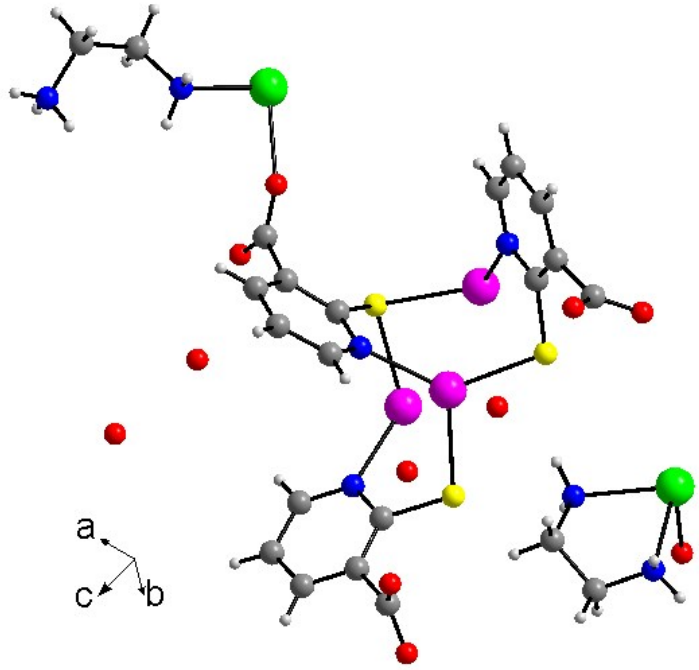


Fig. S5 Asymmetric unit of **I.**

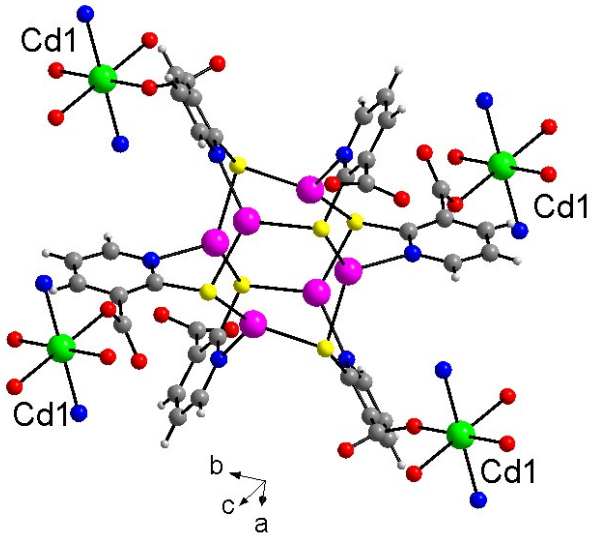


Fig. S6 $[Ag_6(2\text{-}mna)_6]^{6-}$ cluster and its connectivity with the Cd^{2+} ion of compound **I.**

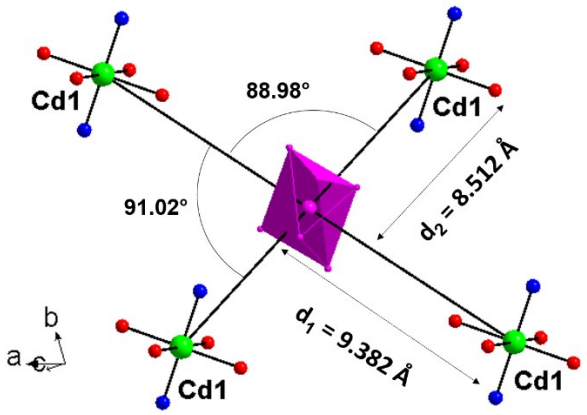


Fig. S7 Connectivity of Cd^{2+} with octahedral $[Ag_6(2\text{-}mna)_6]^{6-}$ cluster with distance measurements, where four Cd^{2+} ions are connected with the corresponding cluster in-plane.

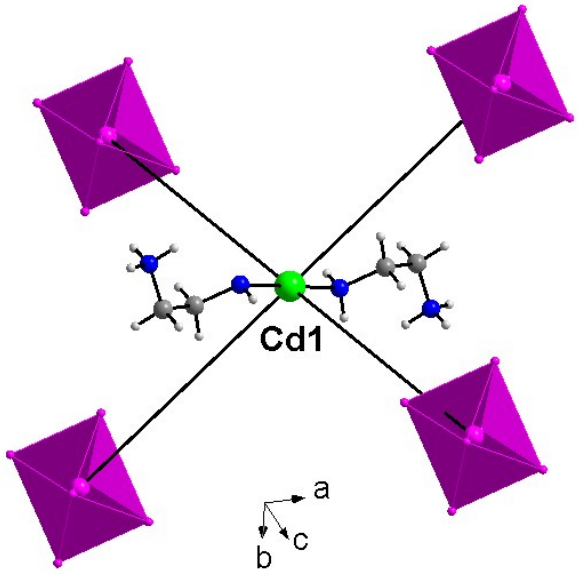


Fig. S8 Connectivity of cluster and ethylenediamine with Cd^{2+} ion.

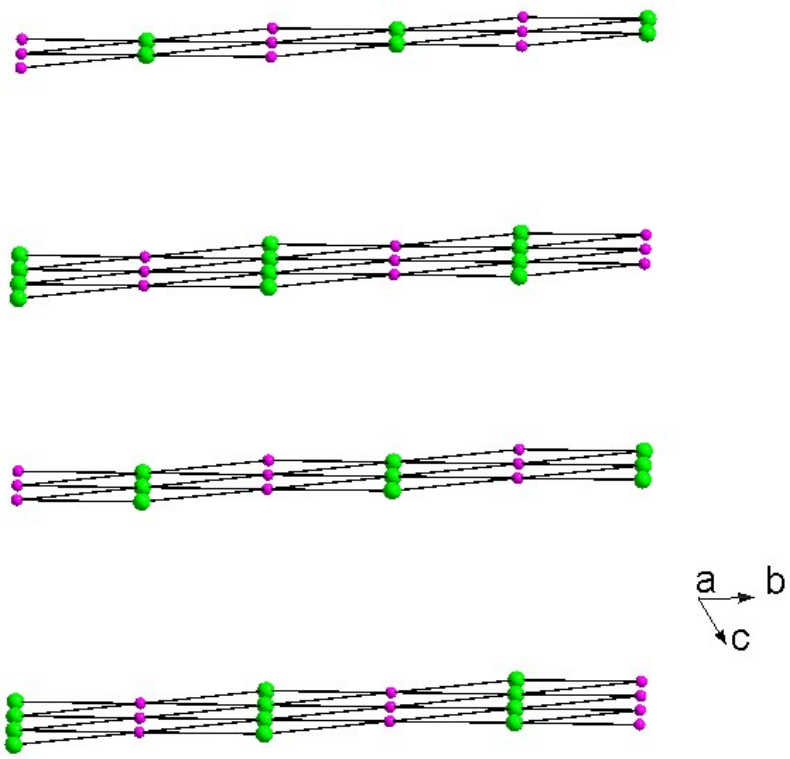


Fig. S9 Packing of (**I**) had been resolved which reveals A-B-A-B packing.

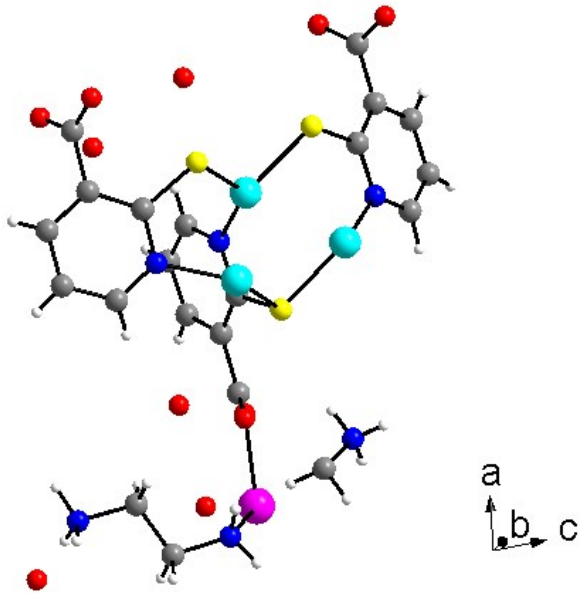


Fig. S10 Asymmetric unit of **II.**

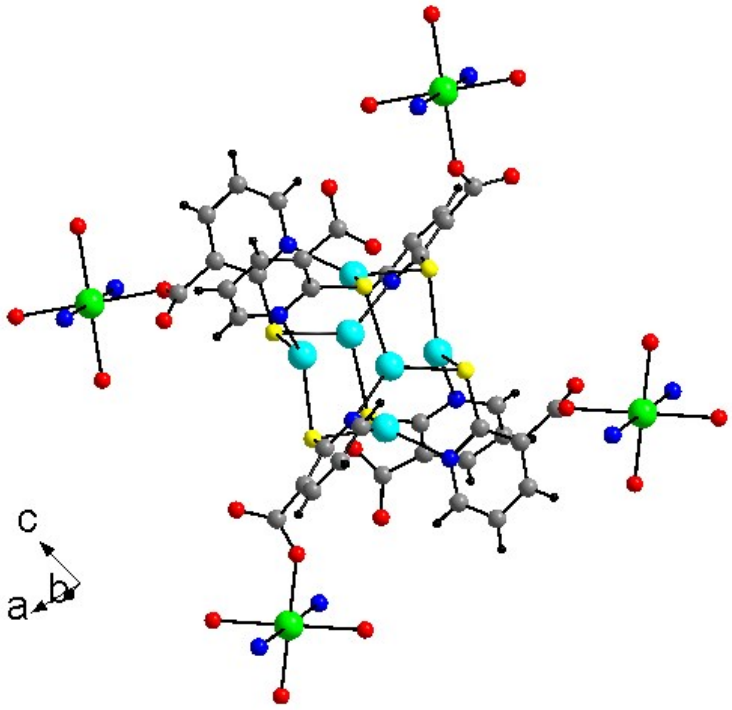


Fig. S11 $[Ag_6(2\text{-}mna)_6]^{6-}$ cluster and its connectivity with the Cd^{2+} ion of compound **II.**

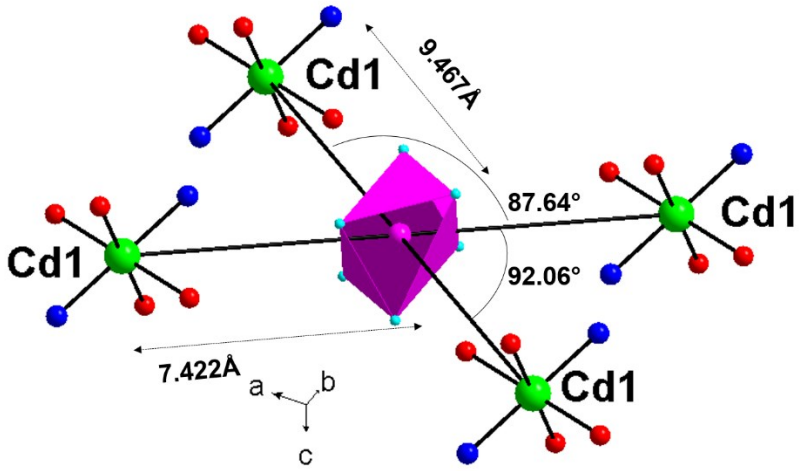


Fig. S12 Cadmium connectivity with Ag_6S_6-cluster of compound **II.**

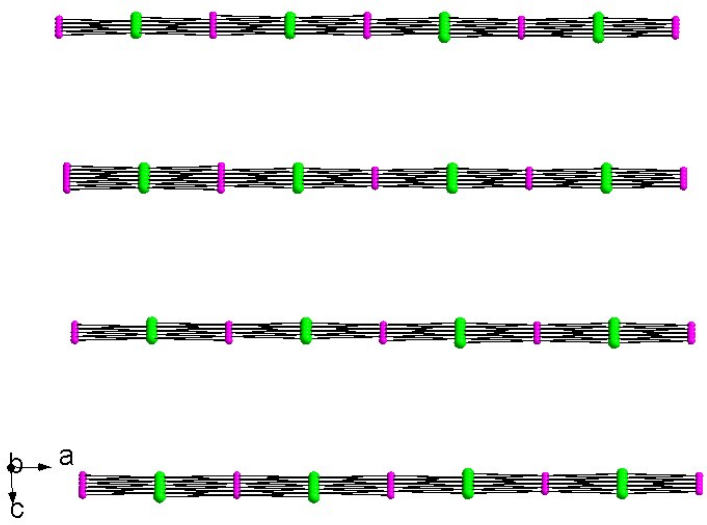


Fig. 13 The packing of the 2D frameworks of **II.**

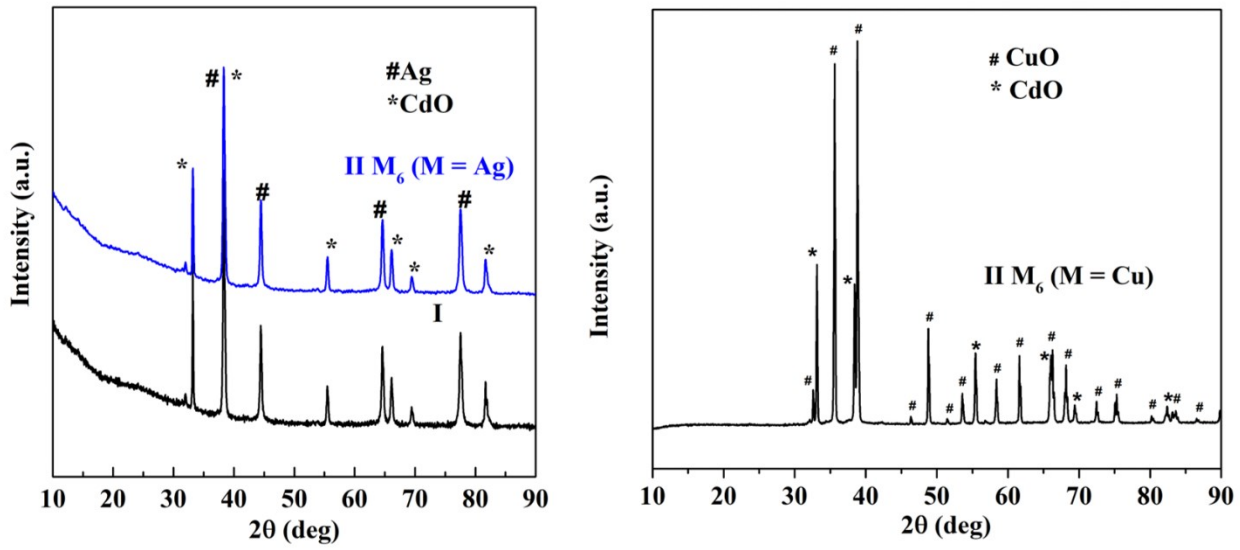


Fig. S14 PXRD of the calcined product of the compound **I**, **II M_6 (M = Ag)** and **II M_6 (M = Cu)**.

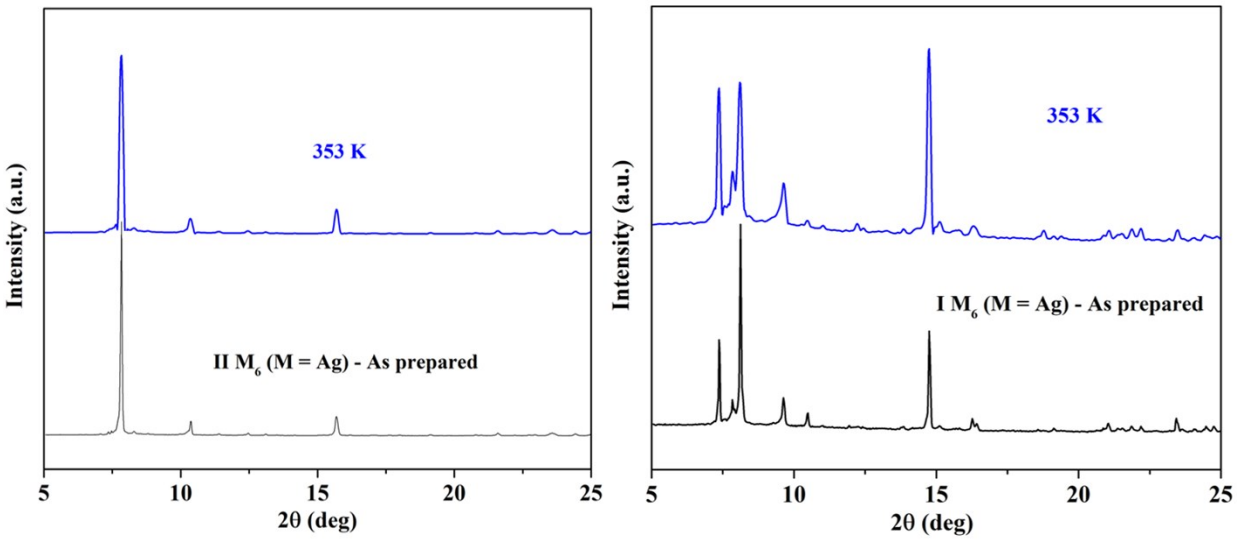
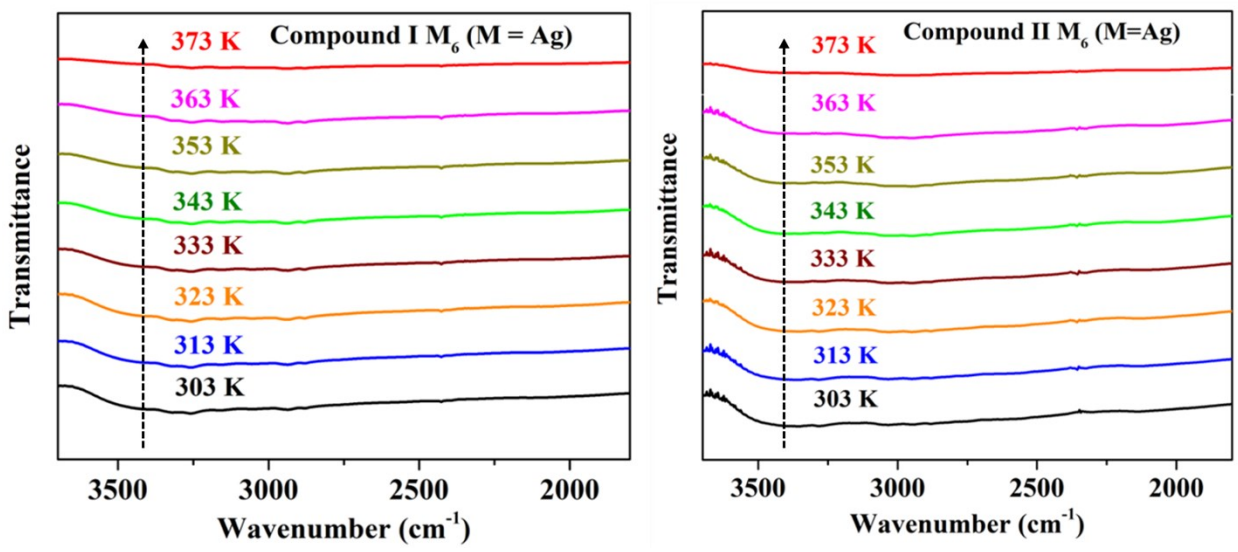


Fig. S15 PXRD of compound **I** (a) and **II** (b) after heating at 353 K.



(a) (b)

Fig. S16 (In-situ) Variable temperature IR of compound **I** (a) and compound **II** (b).

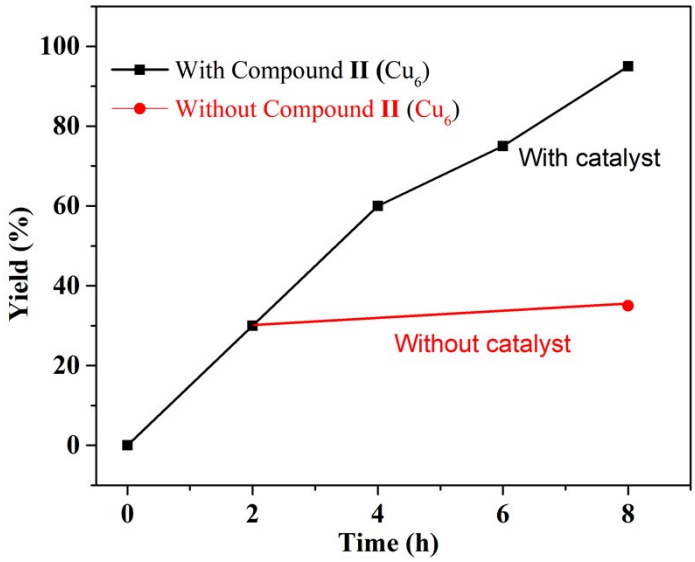


Fig. S17 Hot filtration study using compound **II** Cu_6. Reaction conditions: N-benzylideneaniline (0.5 mmol), TMS-CN (0.75 mmol) and catalyst (0.05 mmol) at 0°C.

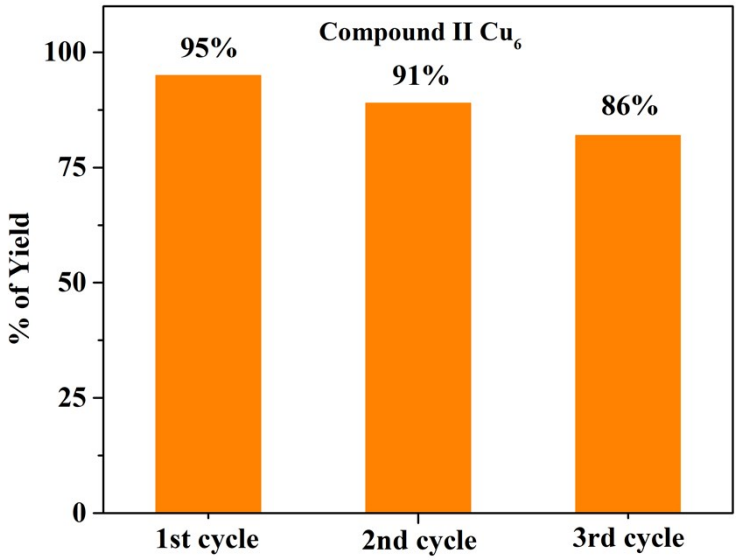


Fig. S18 The obtained yields in the recyclability test compound **II** Cu_6 (b). Reaction condition: N-benzylideneaniline (0.5 mmol), TMS-CN (0.75 mmol) and catalyst (0.05 mmol) at 0°C; Reaction time: 8 hours for **II** Cu_6.

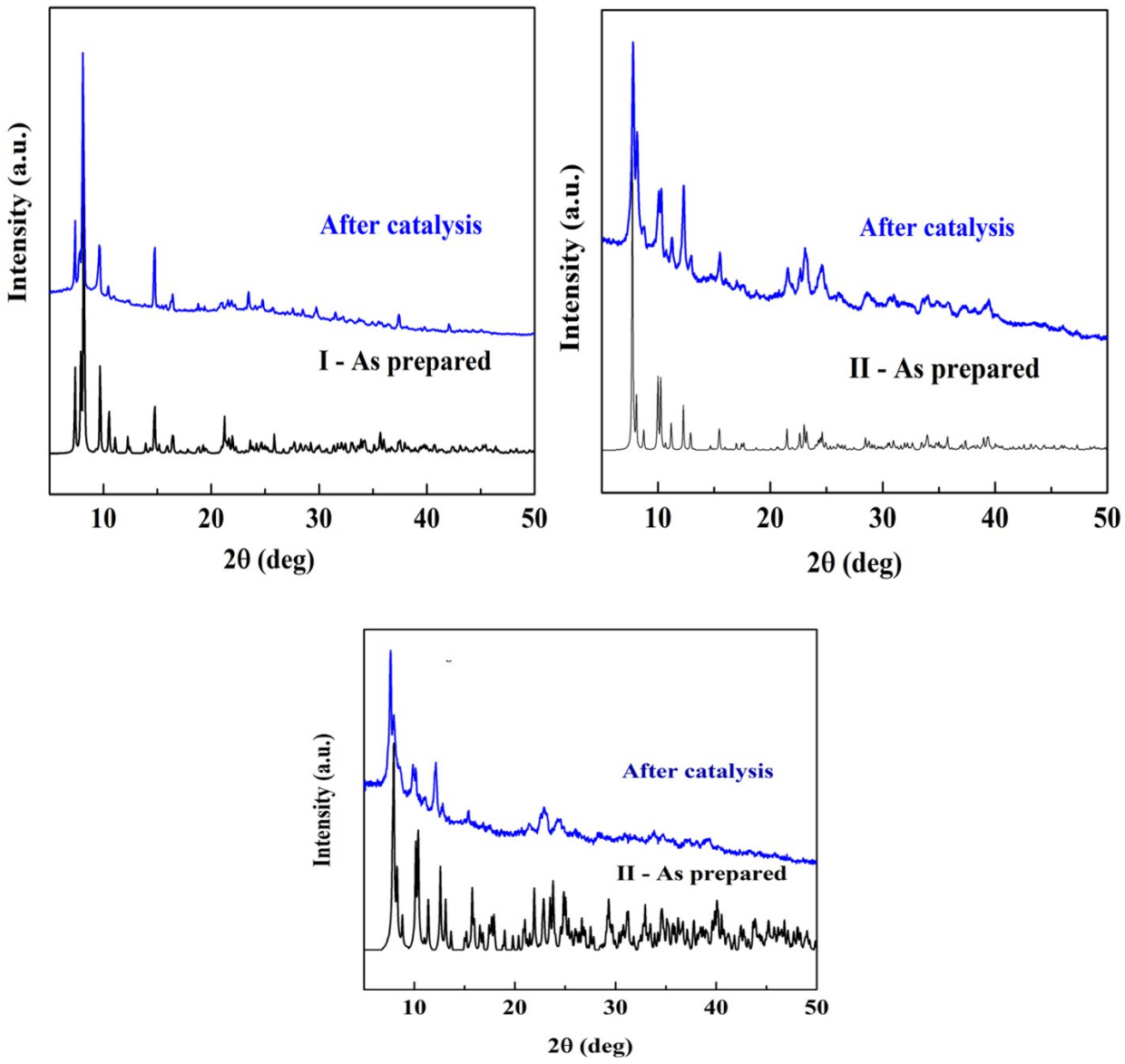
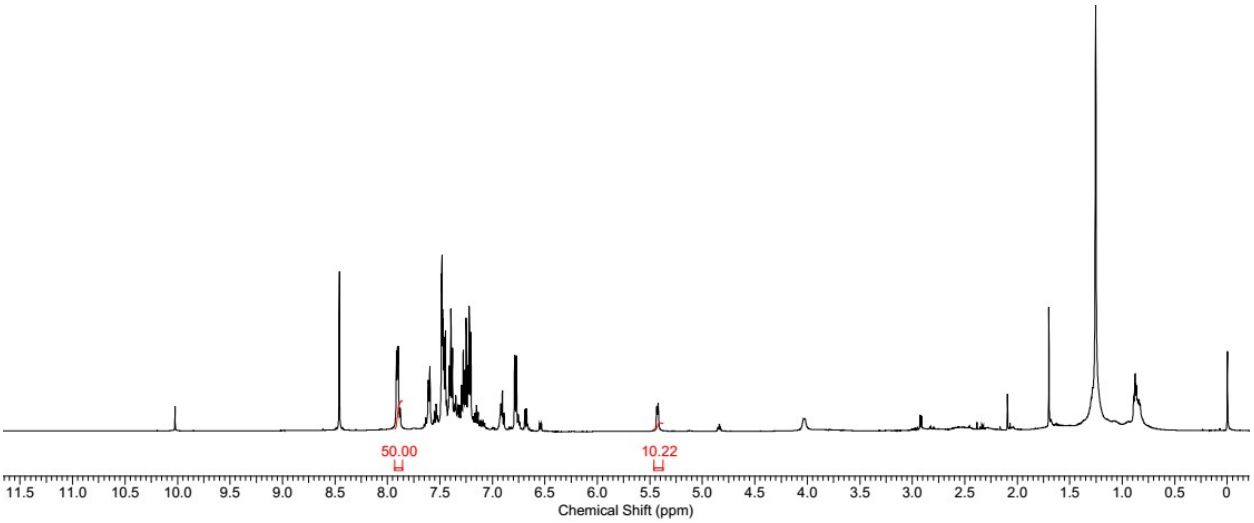
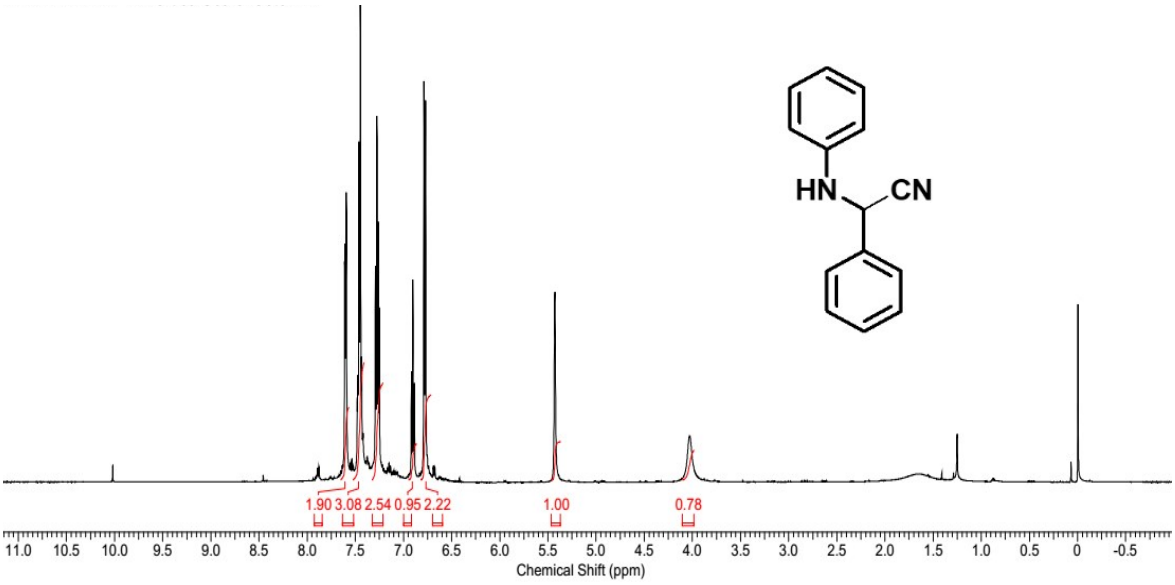


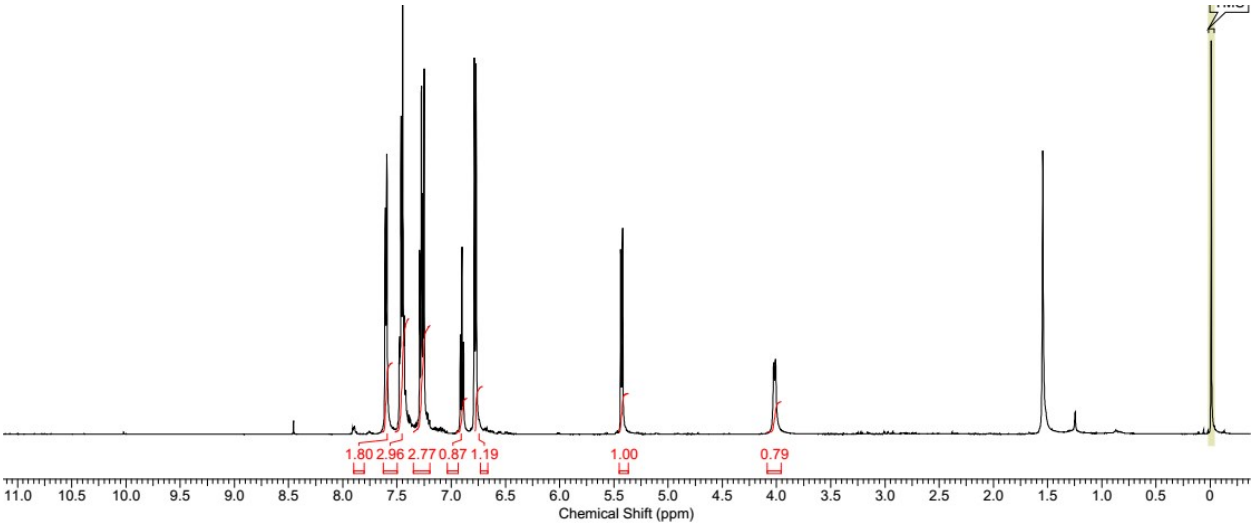
Fig. S19 PXRD of compound **I** (a), **II M_6 (M = Ag)** (b) and **II M_6 (M = Cu)** (c) after catalysis.


50.00
10.22
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

(a)

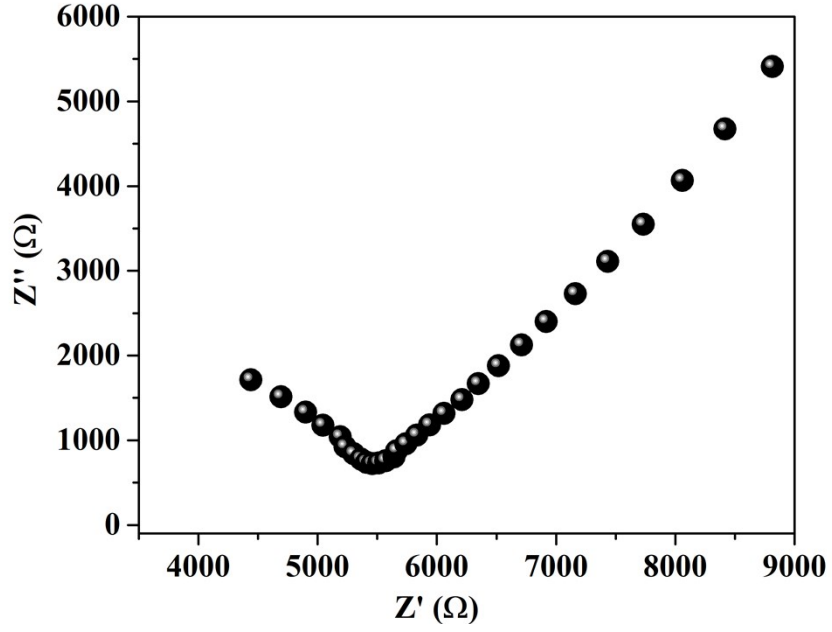

HN
CN
1.90 3.08 2.54 0.95 2.22
1.00
0.78
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)

(b)

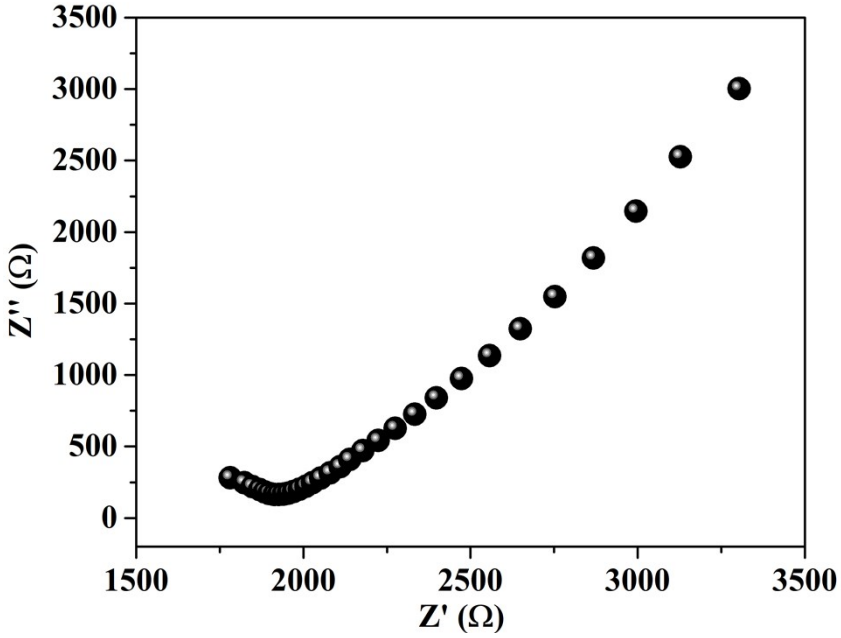


(c)

Fig. S20 1H NMR spectra of the product of cyanation of N-benzylideneaniline; (a) for Compound **I** Ag_6; (b) for Compound **II** Ag_6; (c) for Compound **II** Cu_6.



(a)



(b)

Fig. S21 Proton conductivity study for compound **I** (a) and compound **II** (b) under relative humidity of 98% (Nyquist plot).