Supplementary Material (ESI) for CrystEngComm

A novel green phosphorescent silver(I) coordiantion polymer with three-fold interpenetrated $CdSO_4$-type net generated *via in-situ* reaction

Yun Ling,[a, b] Zhen-Xia Chen,[a, b] Ya-Ming Zhou,*[a] Lin-Hong Weng,[a] Dong-Yuan Zhao*[a,b]

[a] Department of Chemistry, Fudan University, Shanghai (200433), China; Tel.: +86 21 65642261; Fax: +86 21 65643925; E-mail: ymzhou@fudan.edu.cn

[b] Laboratory of Advanced Materials, Fudan University, Shanghai (200433), China; Tel.:+86 21 51630205; Fax: +86 21 51630307; E-mail: dyzhao@fudan.edu.cn

Fig. S1. The PXRD data of the solvothermal product obtained from AgCl and dmtrz in the mixed solution of acetonitrile and water. (Peaks at 2θ = 27.9, 32.3, 46.3 march well with the peaks of AgCl crystallized in Fm-3m space group with cell dimensions a = b = c = 5.54500)

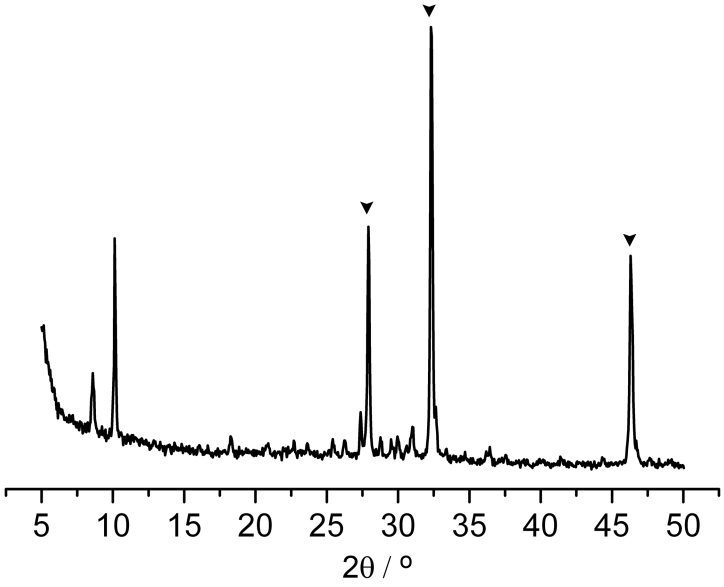


Fig.S2. IR data for $[Ag_3(dmtrz)_2(CN)]_n$ (**1**), $\{[Ag_7(dmtrz)_6](ClO_4)\cdot 6H_2O\}_n$ (**2**), $\{[Ag_6(dmtrz)_4Cl](OH)\cdot 9H_2O\}_n$ (**3**), γ-$[Ag(dmtrz)]_n$, and β-$[Ag(dmtrz)]_n$

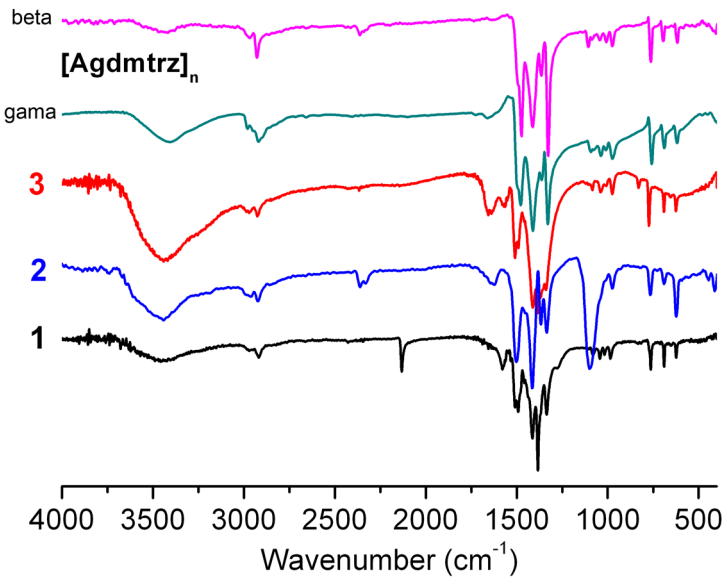
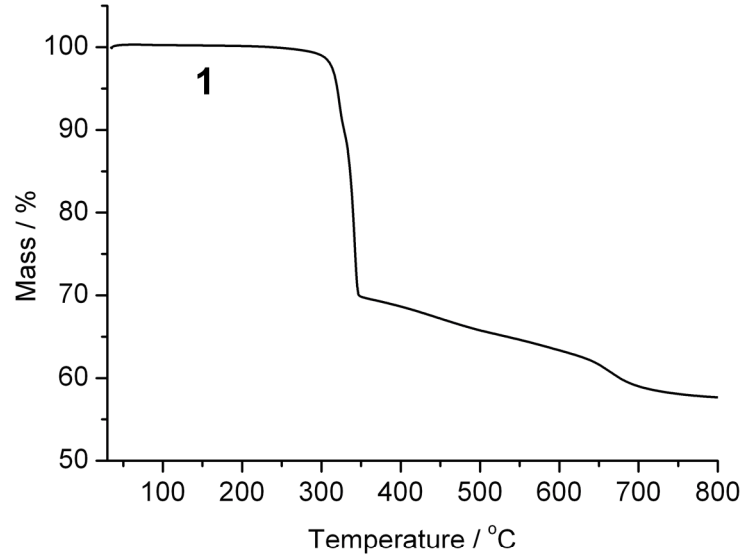
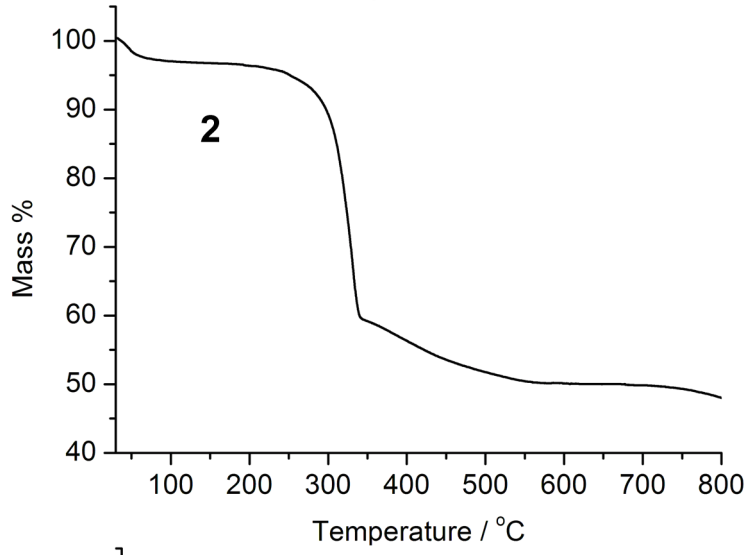


Fig.S3. TG curve of $[Ag_3(dmtrz)_2(CN)]_n$ (**1**), $\{[Ag_7(dmtrz)_6](ClO_4)\cdot 2H_2O\}_n$ (**2**), $\{[Ag_6(dmtrz)_4Cl]\cdot(OH)\cdot H_2O\}_n$ (**3**)





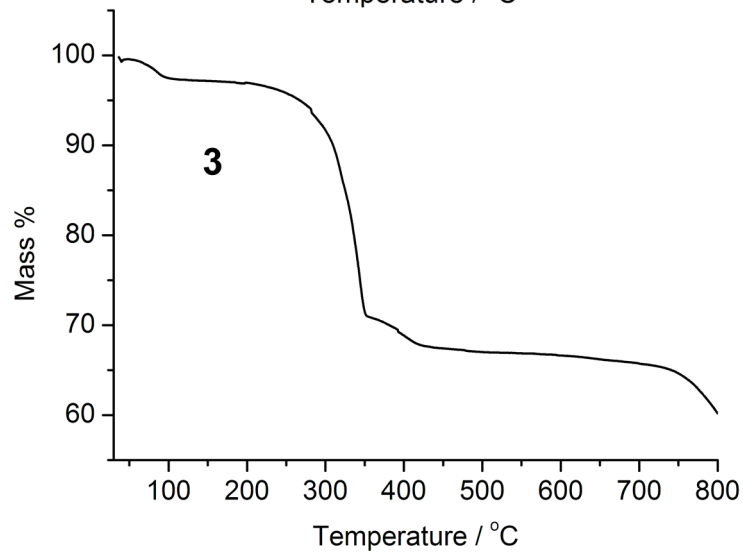


Fig.S4. (a) PXRD of $[Ag_3(dmtrz)_2(CN)]_n$ (**1**); (b) PXRD data of $\{[Ag_7(dmtrz)_6](ClO_4)\cdot 6H_2O\}_n$ (**2**), $\{[Ag_6(dmtrz)_4Cl](OH)\cdot 9H_2O\}_n$ (**3**), gama-$[Ag(dmtrz)]_n$, and beta-$[Ag(dmtrz)]_n$ (below: simulated data; up: experimental data)

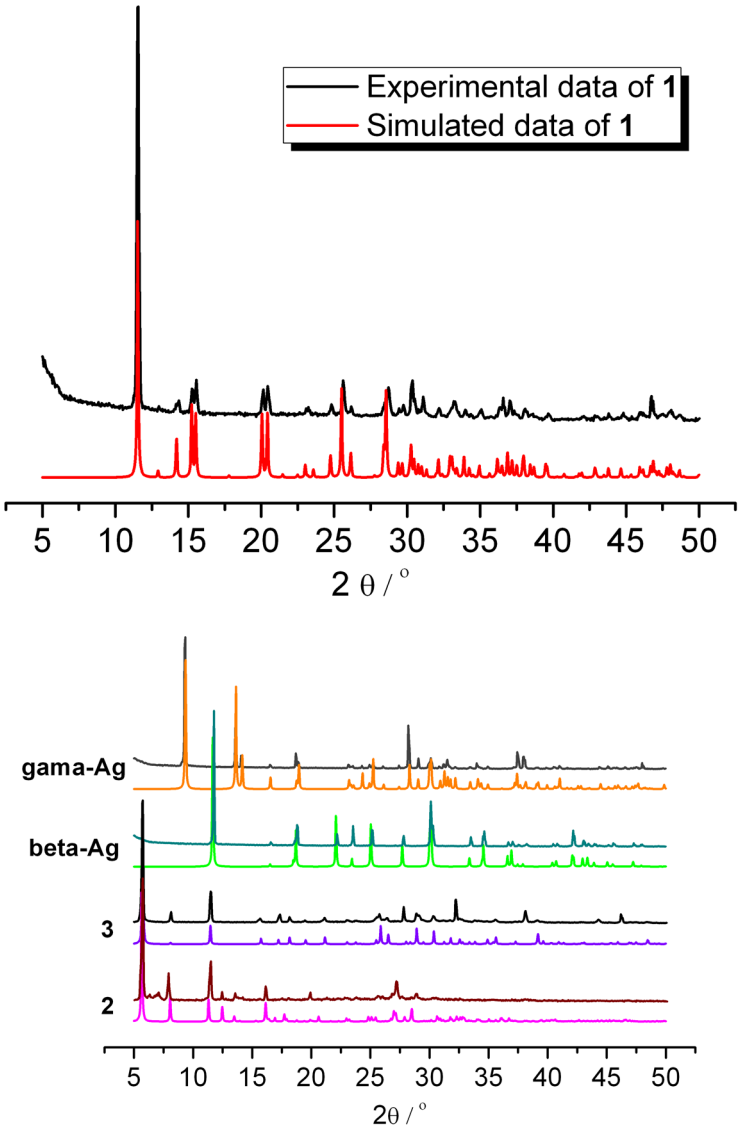


Fig.S5. (a) coordination motif of **1** (Symmetry code: A :3/2-x,3/2-y,1-z; B: 2-x,-y,1-z); (b) the weak Ag(1)···Ag(2)^{i} interaction generating the three-fold interpenetrated $CdSO_4$ net (i: x, 1+y, z)

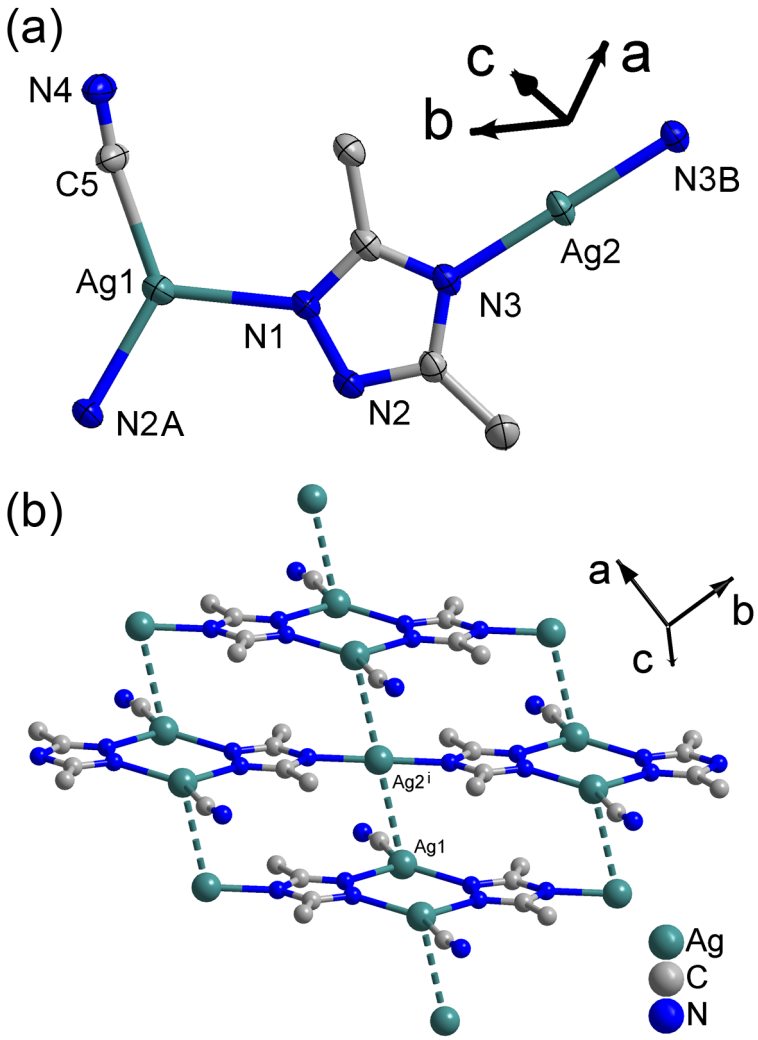
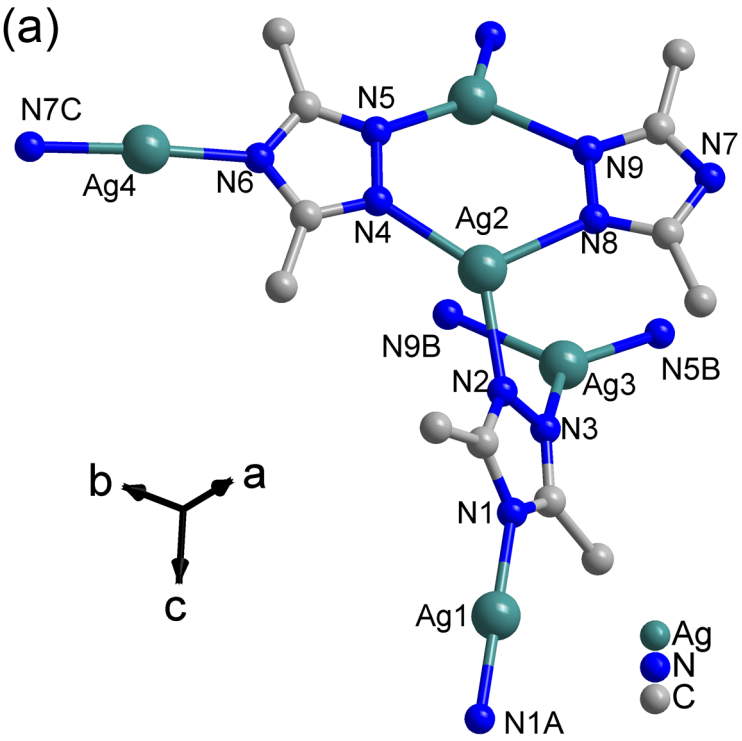


Fig.S6. Coordination motif (a) and the $Ag_4(dmtrz)_6^{2-}$ SBU (b) of **2** (Symmetry code: A: 1-x, 1-y, 1-z; B: 1-x, 1-y, -z; C: -1+x, 1+y, z)



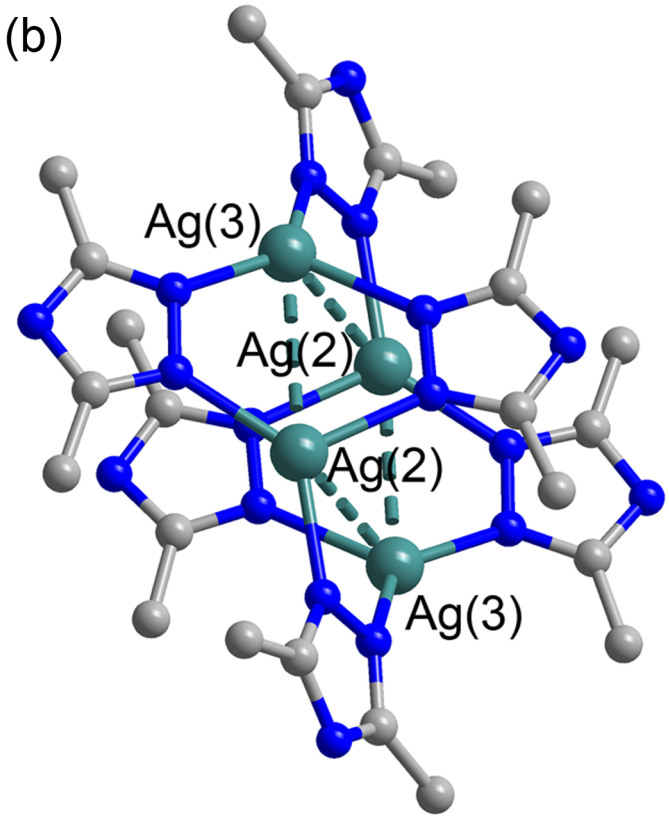


Fig. S7. Coordination motif in the $Ag_4(dmtrz)_4$ SBU of **3** (Symmetry code: A: -1+y, 1-x, z; B: -0.5+y, 0.5+x, 2-z)

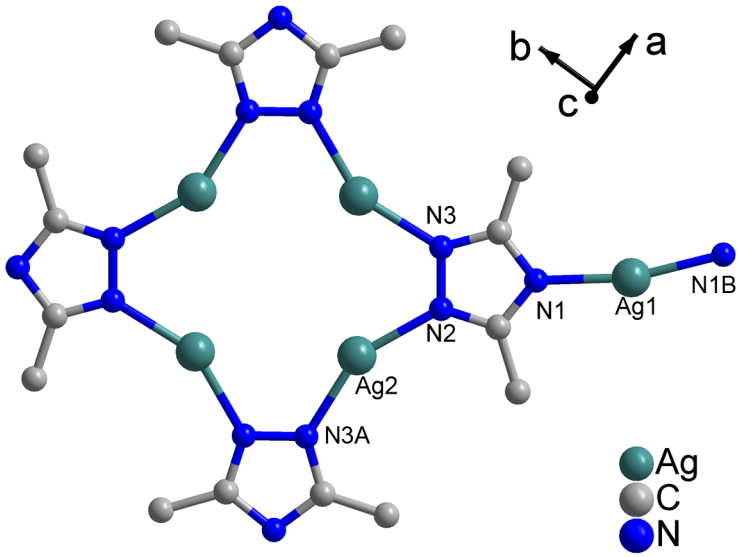


Fig. S8. (a) IR spectra of the products (red one (top) represents the product obtained with $AgNO_3$ as reactant; black one (below) represents the product obtained with $AgClO_4$ as reactan, no obvious CN^- groups were detected in the range of 2158~2135 cm^{-1} in the case of $AgClO_4$); (b) The PXRD data of the product obtained with $AgNO_3$ as reactant (the product obtained with $AgNO_3$ as reactant was confirmed to be AgCN crystallized in *R3m* space group based on IR data and PXRD data)

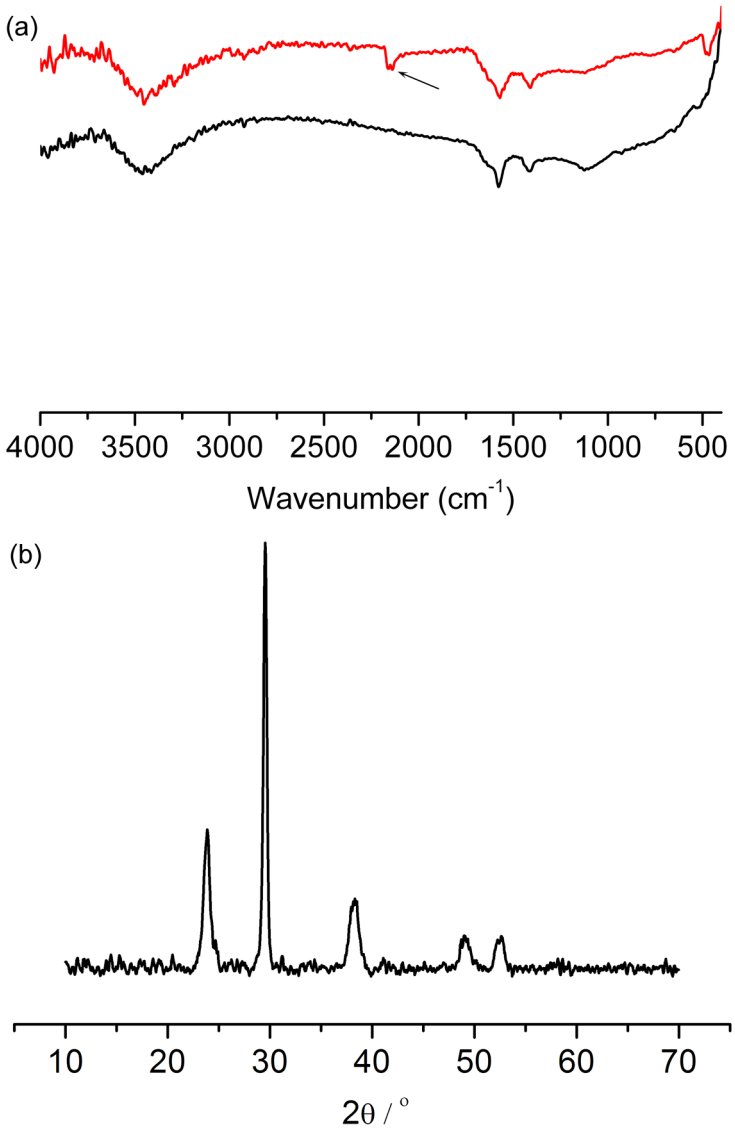


Fig. S9. (a) the phosphorescent emission of **1** (solid green curve) with maximum peak at 519 nm excitated by 322 nm (dot red curve); (b) room-temperature luminescence decay curve of **1**

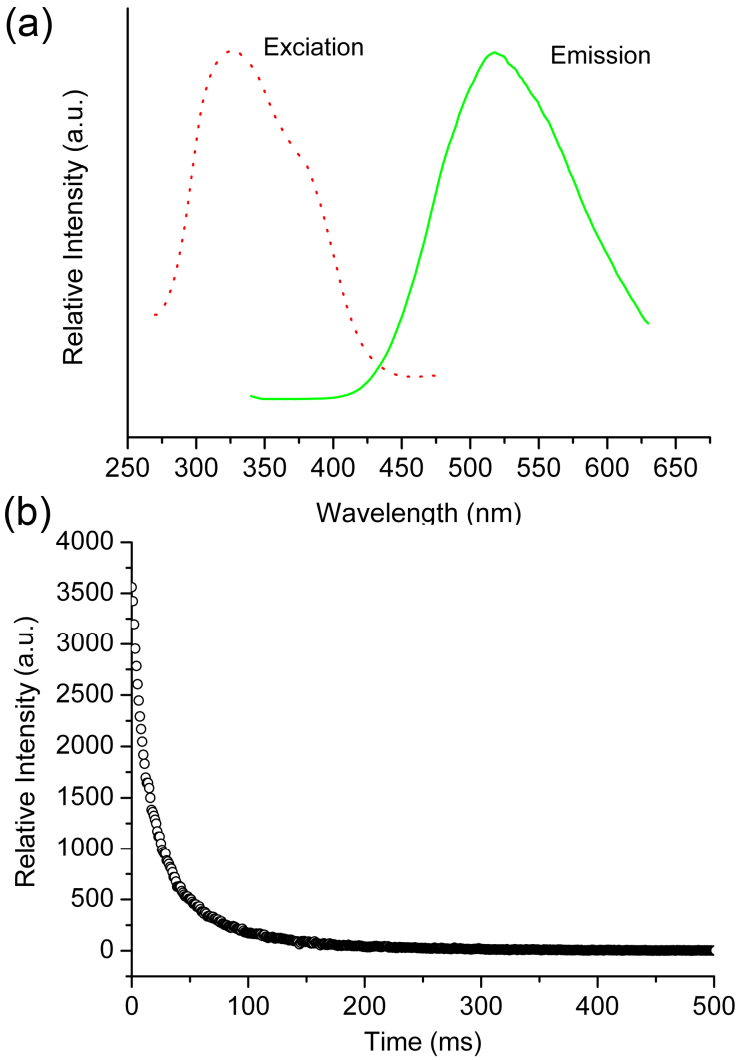


Table S1. Selected bond distances and angles for **1-3**

1

Ag1−N1	2.269(4)	Ag1−C5(N4)	2.140(5)
Ag1−N2^{i}	2.196(4)	Ag2−N3	2.074(4)
Ag2−N3^{ii}	2.074(4)		
N1−Ag1−C5(N4)	115.21(16)	N2^{i}−Ag1−C5(N4)	130.40(18)
N1−Ag1−N2^{i}	113.62(14)		

Symmetry code: i :3/2-x,3/2-y,1-z; ii: 2-x,-y,1-z

2

Ag1−N1	2.075(6)	Ag2−N2	2.232(6)
Ag2−N4	2.204(6)	Ag2−N8	2.292(6)
Ag3−N3	2.206(7)	Ag3−N5^{i}	2.172(6)
Ag3−N9^{i}	2.279(6)	Ag4−N6	2.076(6)
Ag4−N7^{ii}	2.070(6)		
N2−Ag2−N4	131.5(2)	N2−Ag2−N8	108.4(2)
N4−Ag2−N8	119.2(2)	N3−Ag3−N5^{i}	136.9(2)
N3−Ag3−N9^{i}	106.0(2)	N5^{i}−Ag3−N9^{i}	116.9(2)
N6−Ag4−N7^{ii}	174.2(2)		

Symmetry code: i: 1-x,1-y,-z; ii: -1+x,1+y,z

3

Ag1−N1	2.096(5)	Ag2−N2	2.144(6)
Ag2−N3^{i}	2.132(5)		
N1−Ag1−N1^{ii}	167.2(3)	N2−Ag2−N3^{i}	151.6(2)

Symmetry code: i: -1+y,1-x,z; ii: -1/2+y,1/2+x,2-z