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Luminescent silver(I) complexes with pyrazole-tetraphenylethene ligand: turn-on fluorescence due to the coordination-driven rigidification and solvent-oriented structural transformation

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Table S1 Crystal data and structure refinements for Ag complexes.

Compound	**1**	**2**
Formula	$C_{39}H_{30}Cl_2F_{12}N_8P_2Ag_2$	$C_{40}H_{28}F_6N_8O_6S_2Ag_2$
Formula weight	1187.29	1110.56
Crystal system	monoclinic	Triclinic
Space group	*C*2/c	*P*-1
a (Å)	20.5979(11)	10.9590(11)
b (Å)	12.0244(7)	11.9156(12)
c (Å)	17.0561(9)	19.0477(19)
α(º)	90	104.755(3)
β(º)	97.202(2)	91.935(3)
γ(º)	90	105.054(3)
V (Å^3)	4191.1(4)	2309.4(4)
Z	4	2
D_{calc} (g cm^{-3})	1.882	1.597
μ (mm^{-1})	6.925	5.631
F (000)	2344	1104
Reflections collected	15509	31081
Unique reflections	3786	8321
Data/restraints/parameters	3786 / 72 / 349	8321 / 0 / 650
Goodness-of-fit on F^2	1.047	1.016
R_1[a] [I > 2σ(I)]	0.0335	0.0296
wR_2[b] [I > 2σ(I)]	0.0855	0.0840
R_1 [all data]	0.0351	0.0316
wR_2 [all data]	0.0866	0.0857
CCDC#		

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

	3	**4**
Formula	$C_{80}H_{56}Ag_4F_{12}N_{16}O_{12}S_4Ag_4$	$C_{114}H_{84}N_{24}F_{18}P_3Ag_3$
Formula weight	2221.12	2548.59
Crystal system	Triclinic	Cubic
Space group	*P*-1	$I4_132$
a (Å)	14.1282(7)	28.6728(6)
b (Å)	14.4177(7)	28.6728(6)
c (Å)	14.7363(7)	28.6728(6)
α(º)	85.093(2)	90
β(º)	68.925(2)	90
γ(º)	73.243(2)	90
V ($Å^3$)	2681.5(2)	23572.8(15)
Z	1	8
Dcalc (g cm^{-3})	1.375	1.355
μ (mm^{-1})	4.849	3.272
F (000)	1104	9720
Reflections collected	35849	85814
Unique reflections	9433	3619
Data/restraints/parameters	9433 / 0 / 577	3619 / 78 / 237
Goodness-of-fit on F^2	1.19	1.148
R_1[a] [I > 2σ(I)]	0.0869	0.057
wR_2[b] [I > 2σ(I)]	0.2014	0.1528
R_1 [all data]	0.1003	0.0633
wR_2 [all data]	0.2083	0.1597
CCDC#		

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

	6	**7**
Formula	$C_{114}H_{84}N_{27}O_9Ag_3$	$C_{38}H_{28}N_{10}O_6Ag_2$
Formula weight	2299.71	936.44
Crystal system	Cubic	Orthorhombic
Space group	$I4_132$	$P2_12_12_1$
a (Å)	28.4267(7)	9.953(2)
b (Å)	28.4267(7)	13.918(3)
c (Å)	28.4267(7)	25.775(5)
α(º)	90	90
β(º)	90	90
γ(º)	90	90
V (Å^3)	22971.0(17)	3570.5(13)
Z	8	4
D_{calc} (g cm^{-3})	1.294	1.742
μ (mm^{-1})	3.094	1.161
F (000)	9112	1872
Reflections collected	77455	33591
Unique reflections	3545	8197
Data/restraints/parameters	3545 / 0 / 227	8197 / 0 / 505
Goodness-of-fit on F^2	1.112	1.033
R_1[a] [I > 2σ(I)]	0.0478	0.0431
wR_2[b] [I > 2σ(I)]	0.1265	0.0826
R_1 [all data]	0.0491	0.0853
wR_2 [all data]	0.1272	0.1015
CCDC#		

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Selected bond lengths (Å) and angles (°) for Ag complexes.

1			
Ag(1)-N(1)#1	2.129(3)	Ag(1)-N(4)	2.133(3)
N(1)#1-Ag(1)-N(4)	174.51(9)		
Symmetry transformations used to generate equivalent atoms:			
#1 -x+1,y,-z+1/2;			
2			
Ag(1)-N(5)	2.156(2)	Ag(1)-O(5)	2.578(6)
Ag(1)-N(1)	2.161(2)	Ag(2)-N(4)	2.174(2)
Ag(1)-O(5')	2.581(6)	Ag(2)-N(8)	2.192(2)
N(5)-Ag(1)-N(1)	175.26(8)	N(5)-Ag(1)-O(5)	86.85(15)
N(5)-Ag(1)-O(5')	92.35(16)	N(1)-Ag(1)-O(5)	90.51(15)
N(1)-Ag(1)-O(5')	86.45(16)	N(4)-Ag(2)-N(8)	177.59(8)
3			
Ag(1)-N(1)	2.187(9)	Ag(2)-N(4)	2.195(7)
Ag(1)-N(8)	2.190(8)	Ag(2)-N(5)	2.195(8)
N(1)-Ag(1)-N(8)	175.0(3)	N(4)-Ag(2)-N(5)	169.3(3)
4			
Ag(1)-N(1)	2.385(6)	Ag(1)-N(4)#2	2.402(8)
N(1)#1-Ag(1)-N(1)	88.6(3)	N(4)#2-Ag(1)-N(4)#3	116.0(4)
N(1)-Ag(1)-N(4)#2	90.4(2)	N(1)-Ag(1)-N(4)#3	138.8(3)
Symmetry transformations used to generate equivalent atoms:			
#1 z-3/4,-y+5/4,x+3/4; #2 -y+1/2,-z+1,x+1/2; #3 x-1/4,z+1/4,-y+5/4			
6			
Ag(1)-N(2)#1	2.374(6)	Ag(1)-N(4)	2.385(6)
N(2)#1-Ag(1)-N(2)#2	115.8(3)	N(2)#1-Ag(1)-N(4)	139.5(2)
N(4)#3-Ag(1)-N(4)	88.0(3)	N(2)#2-Ag(1)-N(4)	90.3(2)
Symmetry transformations used to generate equivalent atoms:			
#1 -x+1/2,y,-z; #2 x-1/4,z+1/4,-y+1/4; #3 -x+1/4,-z+1/4,-y+1/4			
7			
Ag(1)-N(8)#1	2.210(5)	Ag(2)-N(2)	2.205(7)
Ag(1)-N(6)	2.217(6)	Ag(2)-O(2)	2.318(7)
Ag(1)-O(4)	2.487(6)	Ag(2)-O(1)	2.550(6)

N(8)#1-Ag(1)-N(6)	146.6(2)	N(2)-Ag(2)-O(2)	157.7(2)
N(8)#1-Ag(1)-O(4)	118.0(2)	N(2)-Ag(2)-O(1)	139.4(2)
N(6)-Ag(1)-O(4)	94.2(2)	O(2)-Ag(2)-O(1)	52.78(19)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,-z+1;

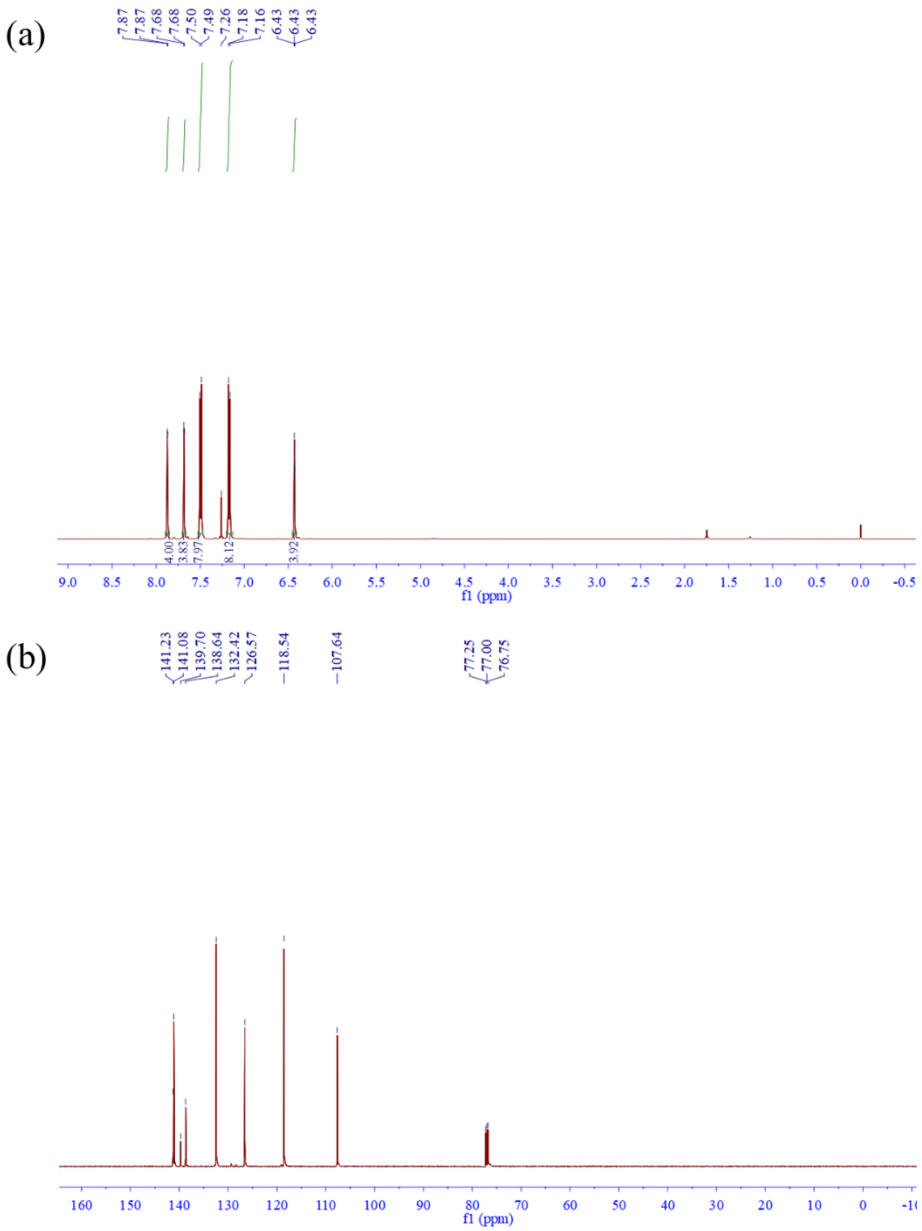

Fig. S1 ^{1}H NMR (a) and ^{13}C NMR spectra (b) of ligand **L** in $CDCl_3$.

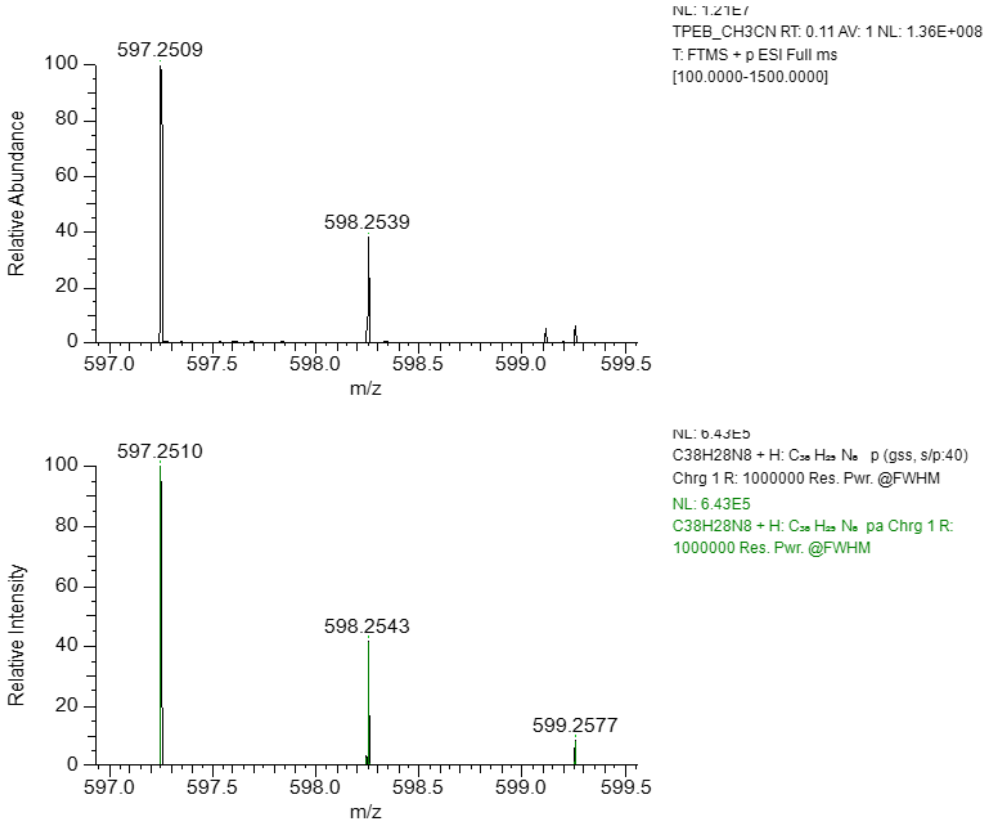

Fig. S2 High resolution mass spectrum of ligand **L** in acetonitrile (upper) and simulated ion $[C_{38}H_{28}N_8 + H]^+$ (below).

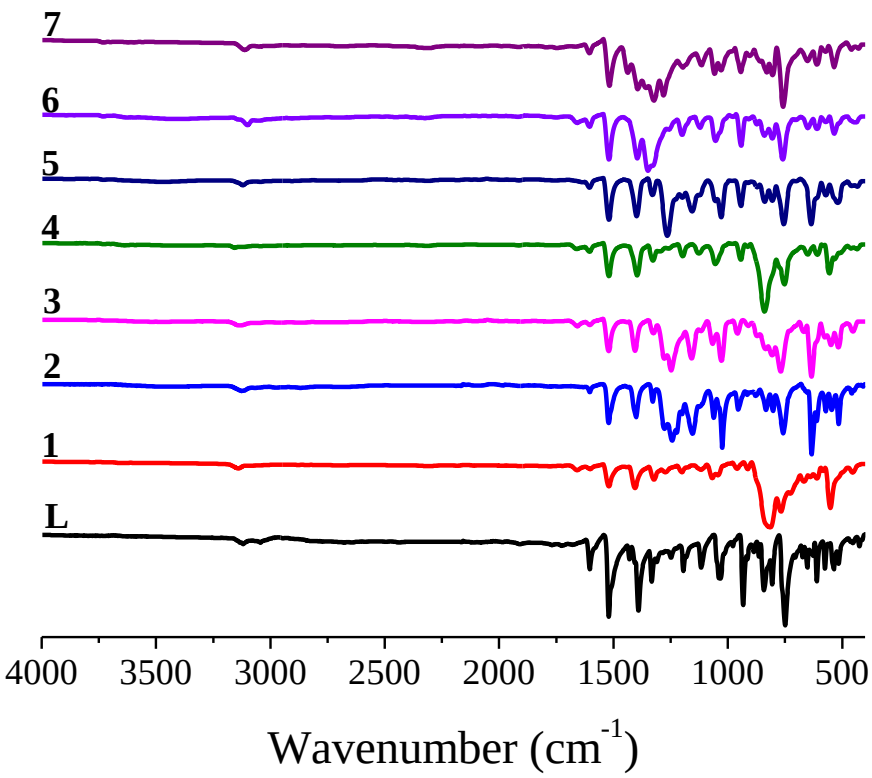

Fig. S3 FT-IR spectra of ligand **L** and Ag complexes.

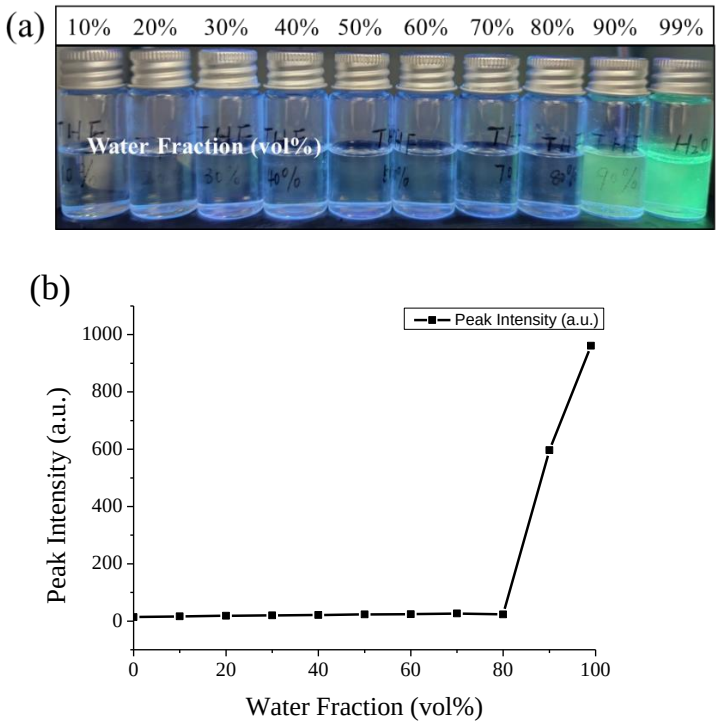

Fig. S4 (a) Images of **L** in THF with the increasing water fraction under UV light. (b) Plots of fluorescence intensity in mixtures of THF/water by varying H_2O content in the range of 0–99%.

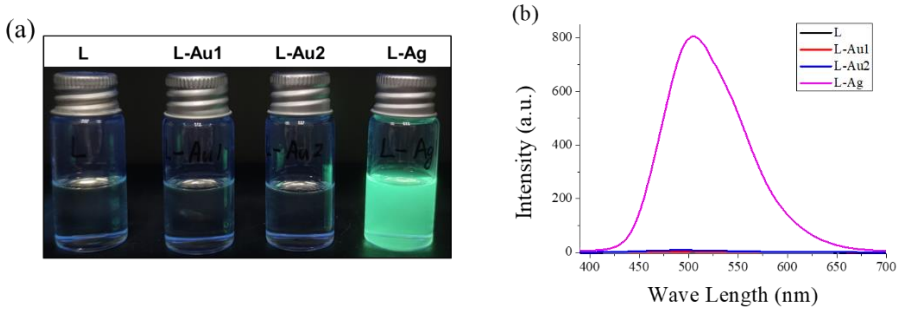

Fig. S5 (a) Images of **L** in CH_2Cl_2 (2 mg/5 mL) with addition of 2 equivalents chloro(dimethylsulfide)gold(I) (Me_2SAuCl, **Au1**), chloro(triphenylphosphine)gold(I) (Ph_3PAuCl, **Au2**) and $AgCF_3SO_3$ under UV light. (b) Fluorescence spectra of **L** in CH_2Cl_2 in absence and presence of **Au1**, **Au2** and $AgCF_3SO_3$ (λ_{ex} = 367 nm).

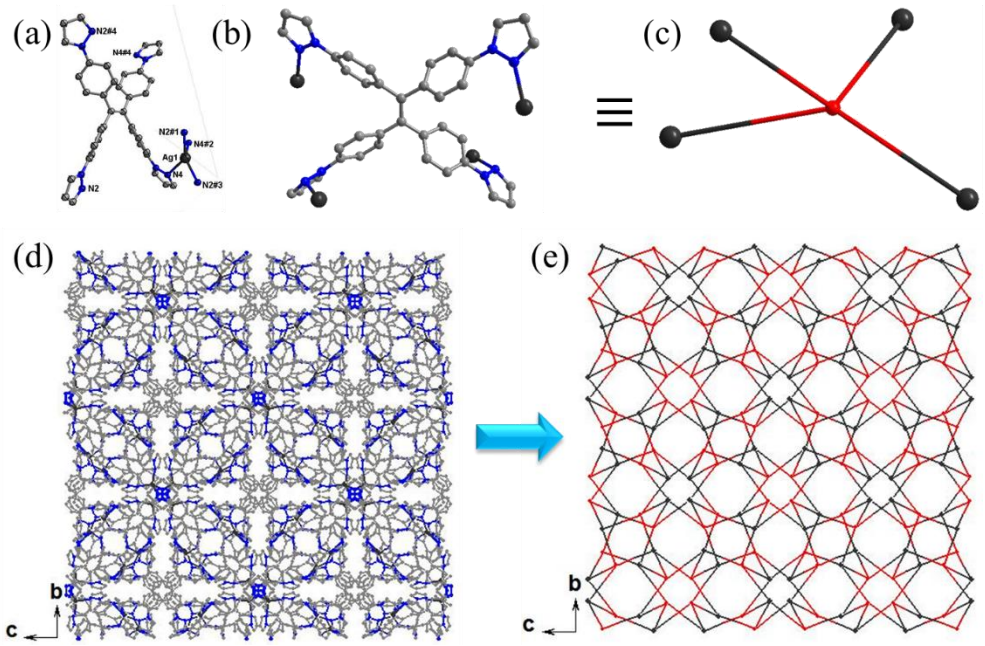

Fig. S6 Crystal structures and simplified schematic diagram of **6**.

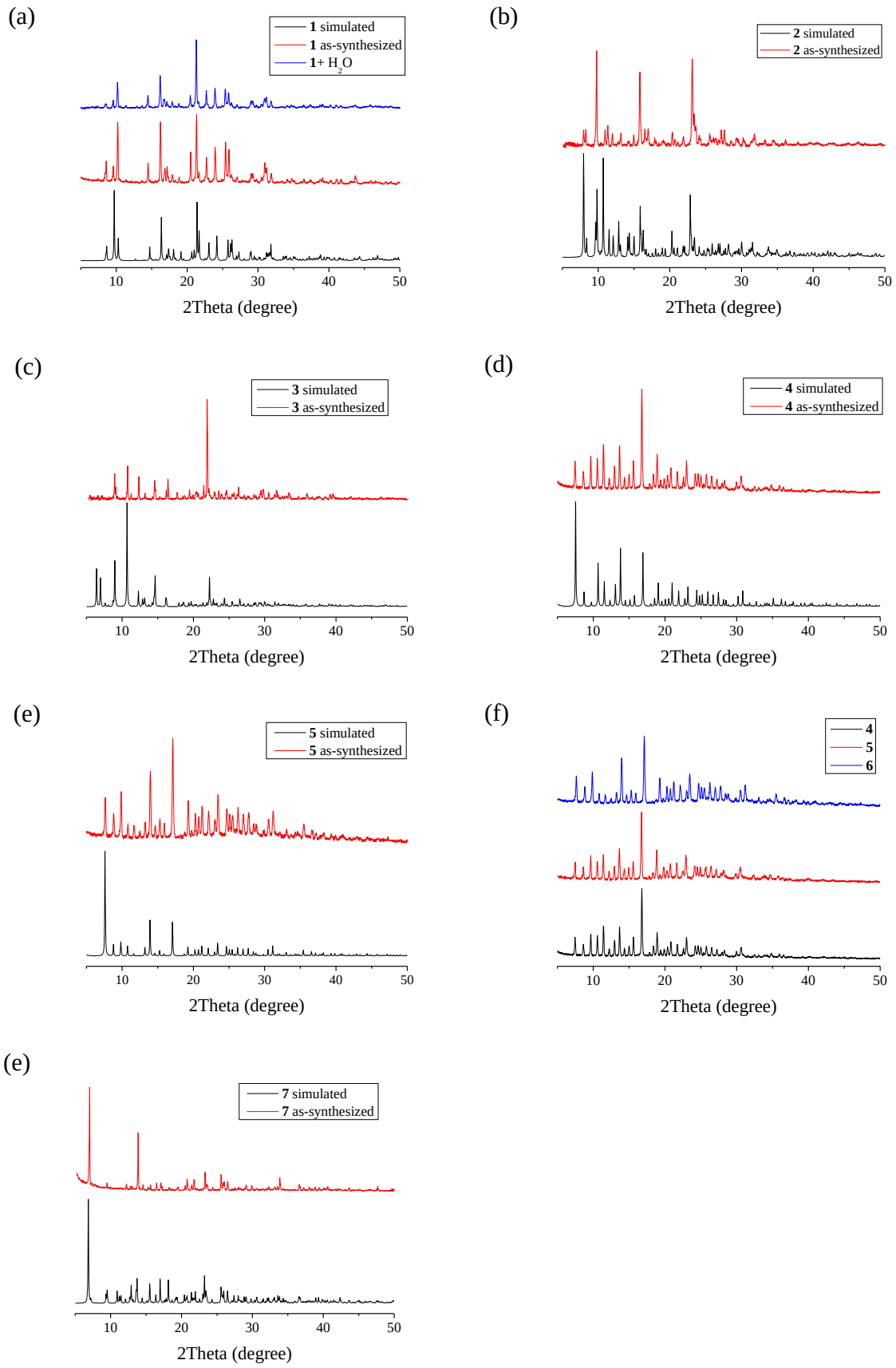

Fig. S7 PXRD patterns of Ag complexes.

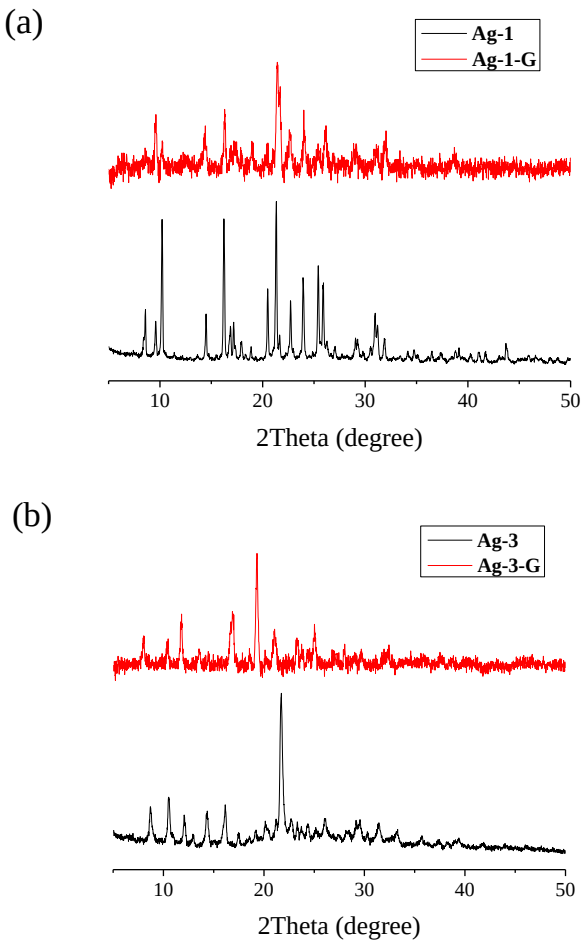

Fig. S8 (a) PXRD patterns of **1** before and after grinding. (b) PXRD patterns of **3** before and after grinding.

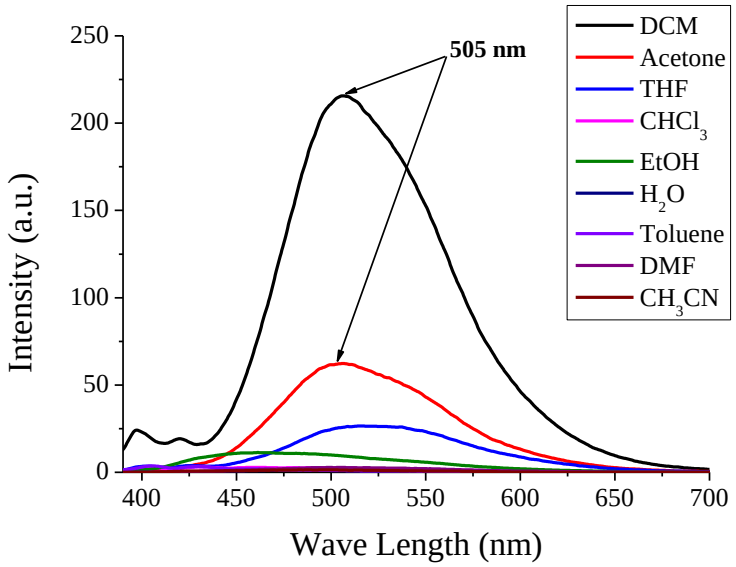

Fig. S9 Emission spectra of the filtered solutions for **1** dispersed in different solvents (2 mg/5 mL).

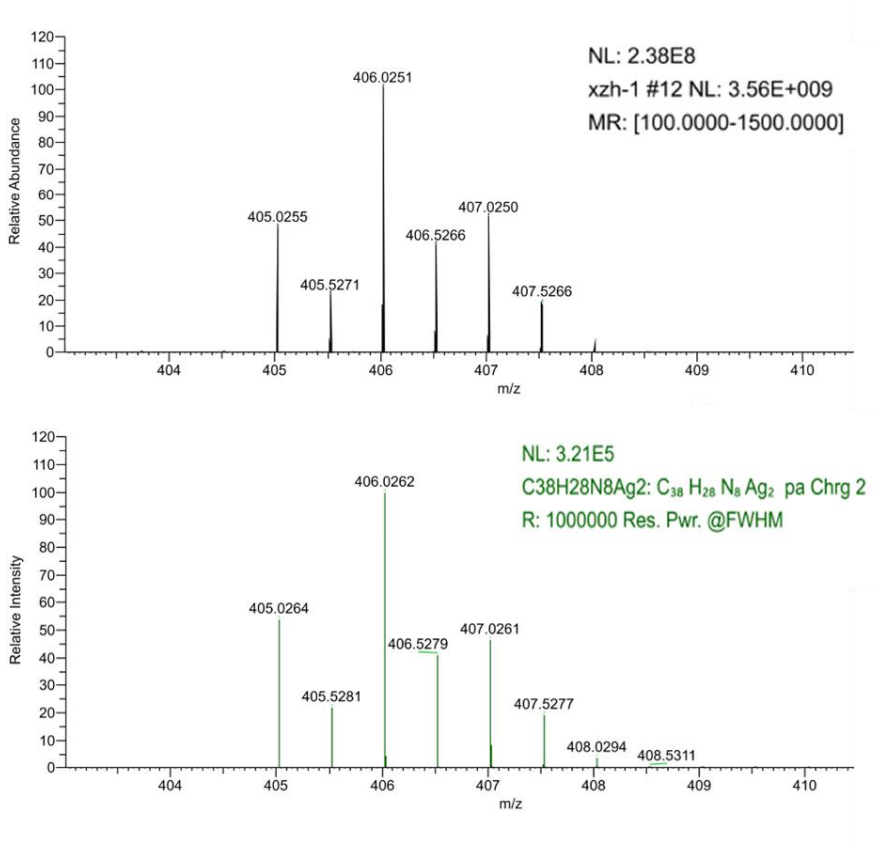

Fig. S10 High resolution mass spectrum of **1** in acetonitrile (upper) and simulated ion $[Ag_2(L)]^{2+}$ (below).

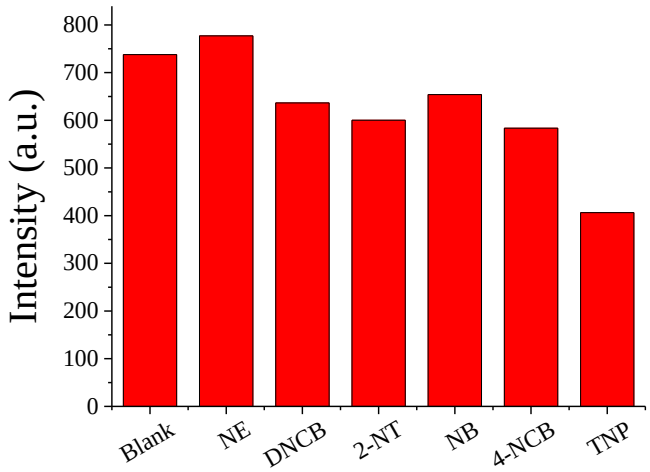

Fig. S11 Fluorescence intensity of the CH_2Cl_2 solution of **1** (2 mg/5 mL) upon addition of CH_2Cl_2 solution of different nitro-compounds (400 μL, 5 mM).