Electronic Supplementary Material (ESI) for Materials Advances.

Pyridoxal-based low molecular weight pro-gelator as a new chemosensor for recognition of Ag^{+} and Hg^{2+} under different conditions

Saswati Ghosh Roy[a], Abhishek Kumar[b], Neeraj Misra[b] and Kumaresh Ghosh[*a]

[a]Department of Chemistry, University of Kalyani, Kalyani-741235, Email: ghosh_k2003@yahoo.co.in, kumareshchem18@klyuniv.ac.in
[b]Department of Physics, University of Lucknow, Lucknow-226007, India

Table S1. Results of gelation test of compounds **1** and **2** alone and in presence of metal ions

Solvents	Compound **1**	Compound **2**
Tolune	S	S
Benzene	S	S
1,2 dichlorovenzene	S	S
Petether	S	S
Ethylacetate	S	S
Acetonitrile	S	S
THF	S	S
Dioxane	S	S
DMSO	S	S
DMF	S	S
Methanol	S	S
Dioxane + H_2O (1:1, v/v)	P	P
DMF + H_2O (1:1, v/v)	P	P
DMSO+ H_2O (1:1, v/v)	P	P
Methanol + H_2O (1:1, v/v)	P	P
Acetonitrile + H_2O (1:1, v/v)	P	P
Dioxane + H_2O + Ag^{+}(1:1, v/v)	G	P
DMF + H_2O + Ag^{+}(1:1, v/v)	G	P
DMSO+ H_2O + Ag^{+}(1:1, v/v)	G	P
Methanol + H_2O + Ag^{+}(1:1, v/v)	P	P
Acetonitrile + H_2O + Ag^{+}(1:1, v/v)	Partial Gelation	P

S = Solution; G = Gel (mgc); P = Precipitation. Gelation tests were carried out at a concentration 10 mg/mL in different solvents. Gels were primarily characterized by inversion of vial method after ~5 min of sample preparation.

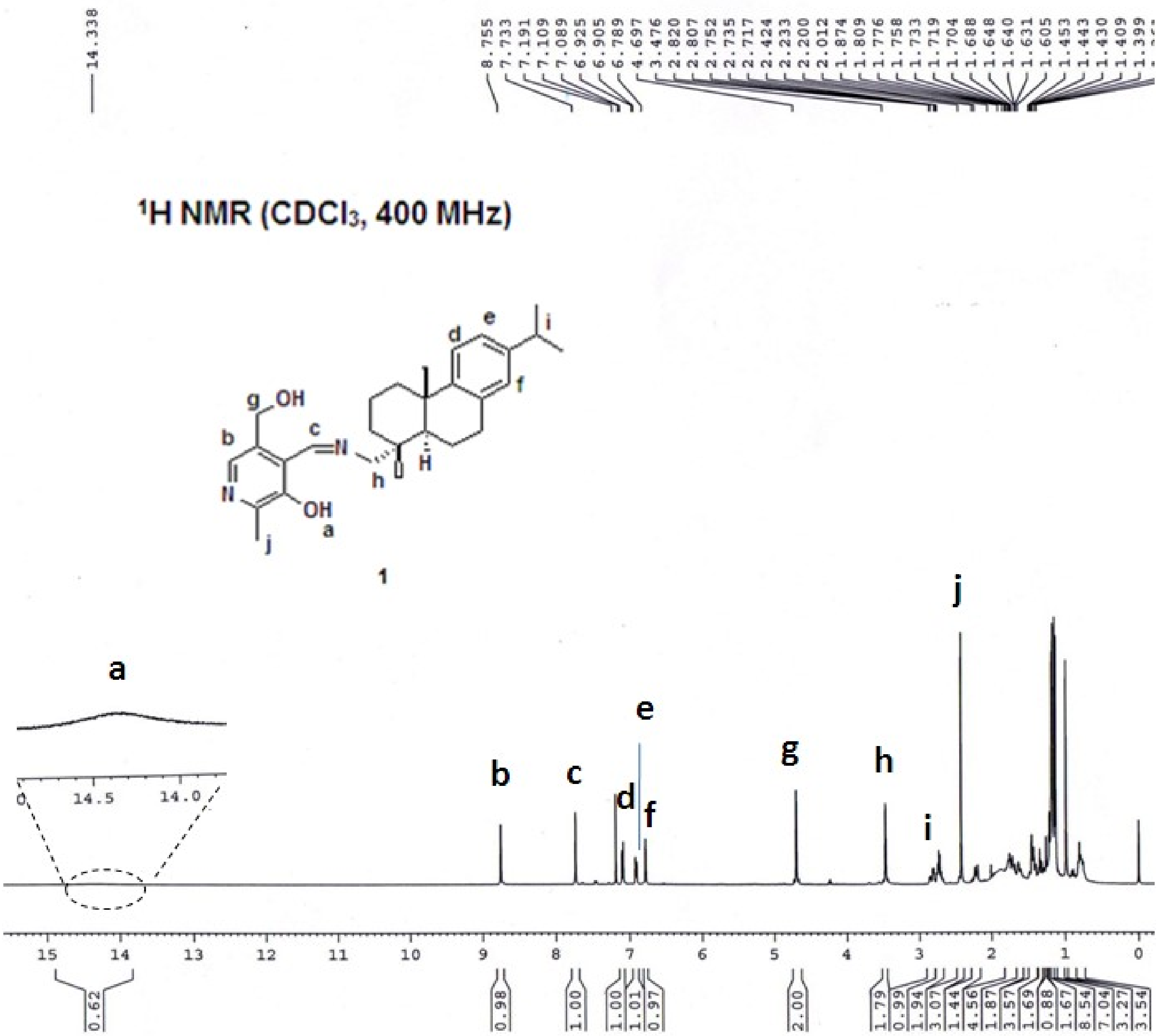


Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

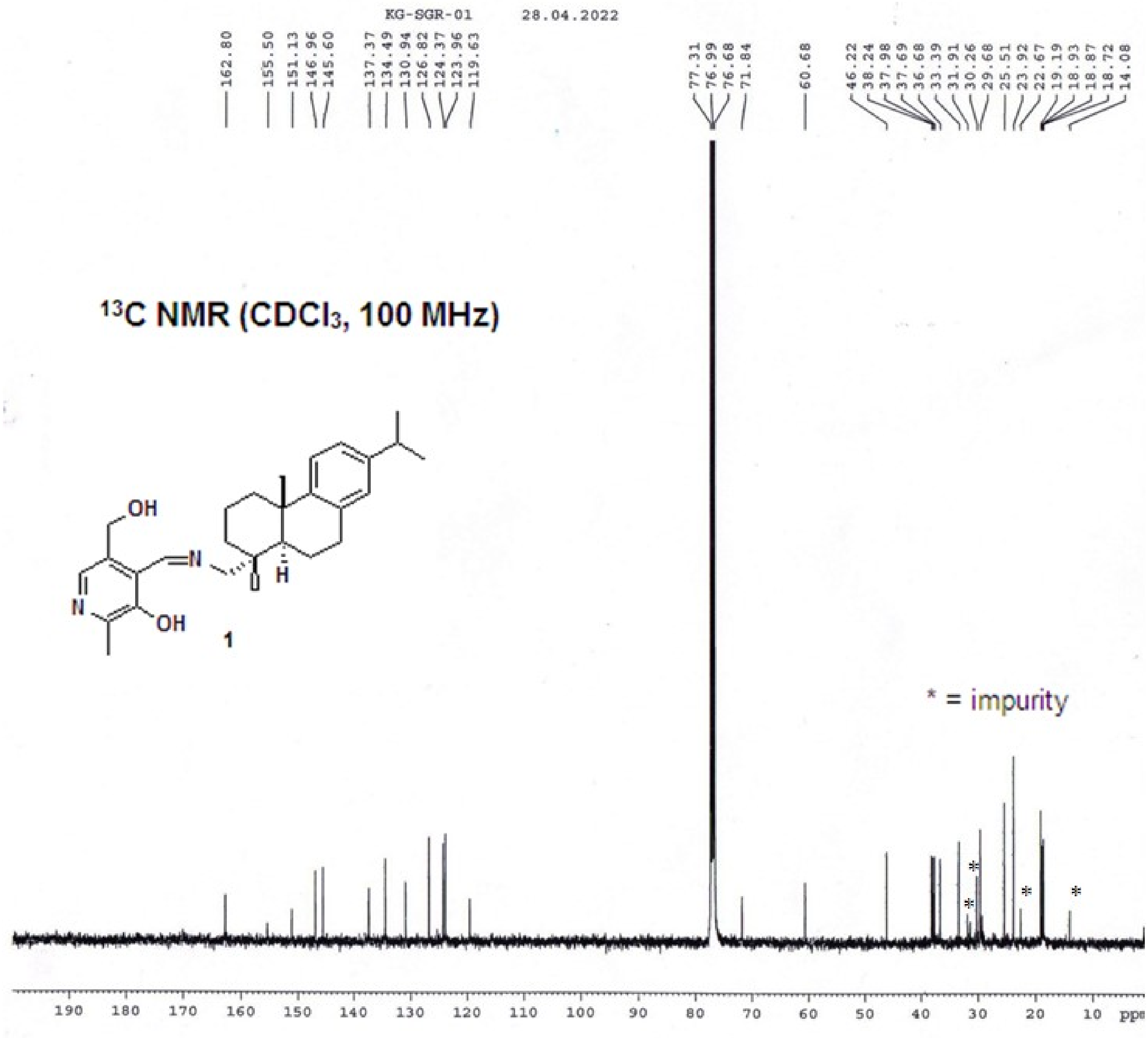


Figure S2. ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

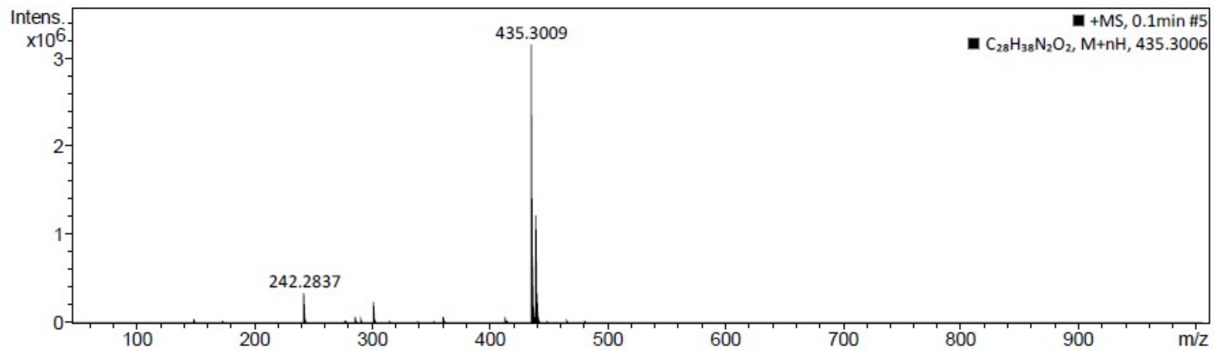


Figure S3. High resolution mass spectrum of compound **1**.Assignment of the main peak: *m*/*z* 435.3009 [M+ H]$^+$ (Calcd. 435.3012).

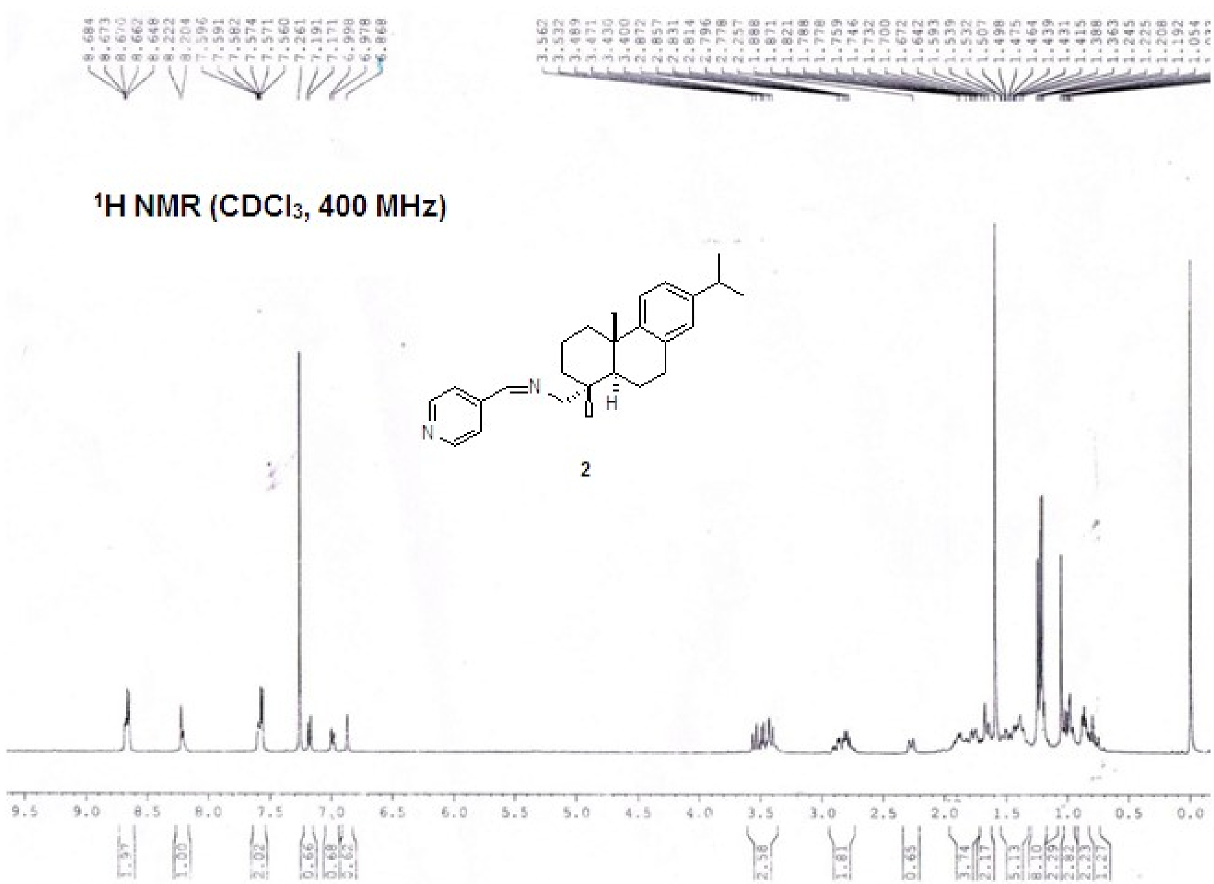


Figure S4.[1]H NMR spectrum of compound **2** in $CDCl_3$.

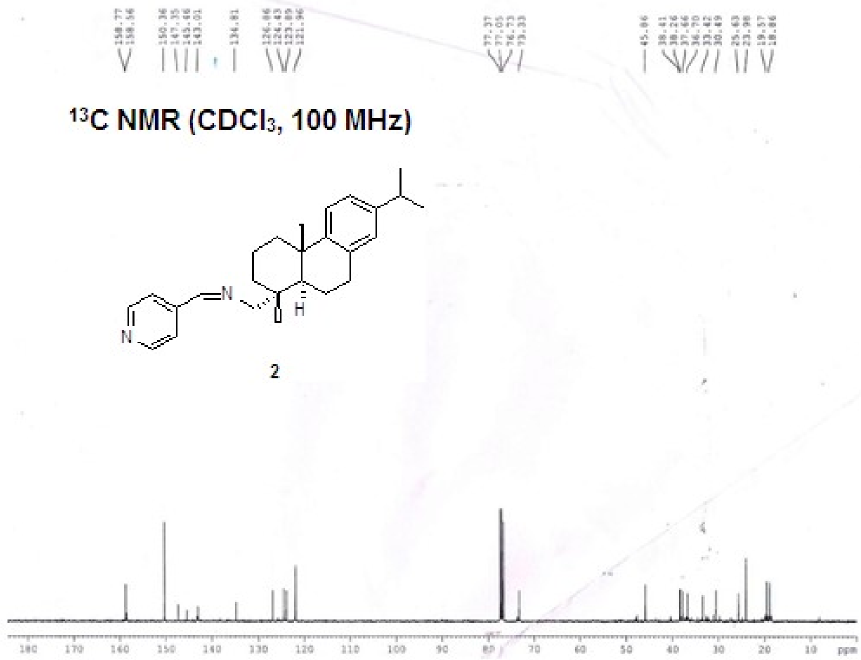


Figure S5.^{13}C NMR spectrum of compound **2** in $CDCl_3$.

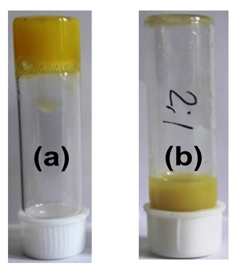


Figure S6. Gelation study of compound **1** (5 mg/mL) in DMSO-H_2O (v/v, 1/1) in presence of $AgNO_3$: (a) in presence of 1 equiv. of Ag^+ (**1** : Ag^+ = 1:2) and (b) 0.5 equiv. of Ag^+ ion (**1** : Ag^+ = 2:1).

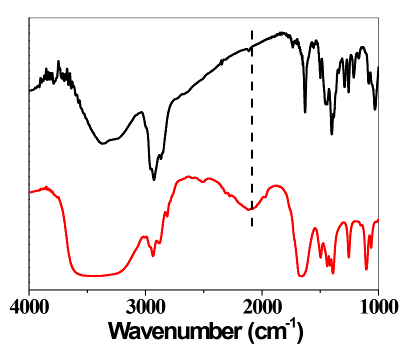


Figure S7. FT IR spectra of compound **1** in amorphous (black line) and gel state (red line).

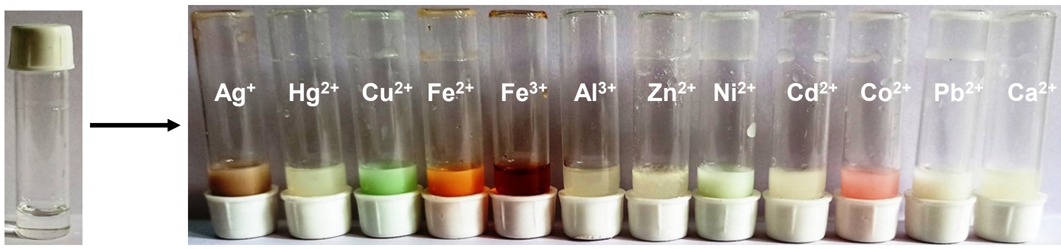


Figure S8. Photograph showing the interaction of **2** (c = 0.023 mmol) upon addition of 1 equivalent amount of various metal analytes (c = 1×10^{-3} mmol) in DMSO/H_2O (1:1, v/v). All metal salts were taken as their nitrate salts (NO_3^-), and Hg^{2+}, Fe^{2+} and Al^{3+} were taken as their perchlorate salts (ClO_4^-).

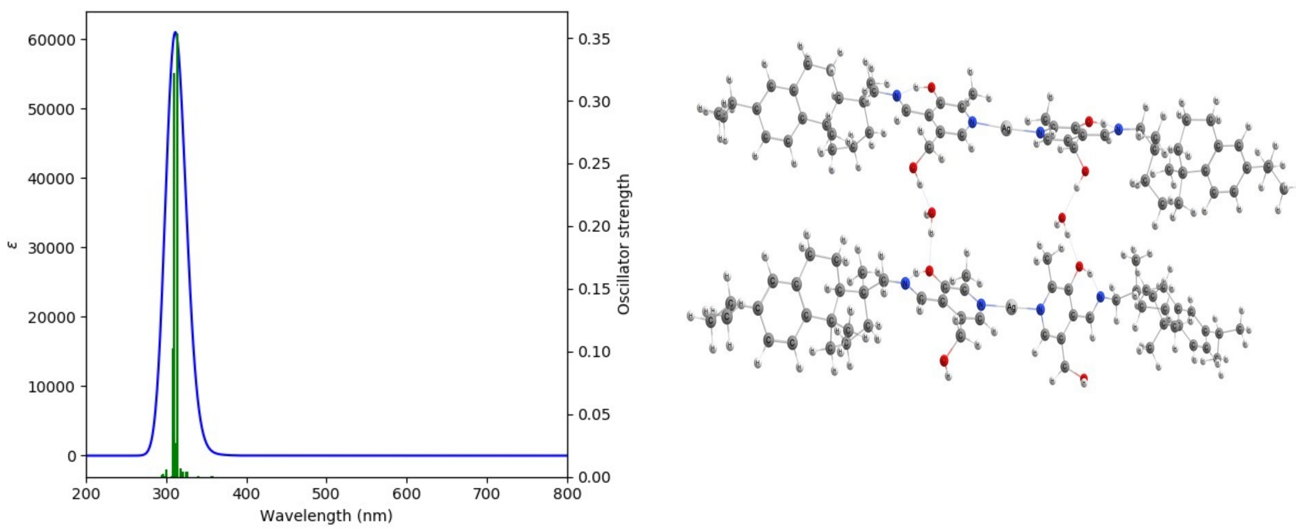


Figure S9. UV-Vis spectra of the aggregated form (shown at the right side) in DMSO-water.

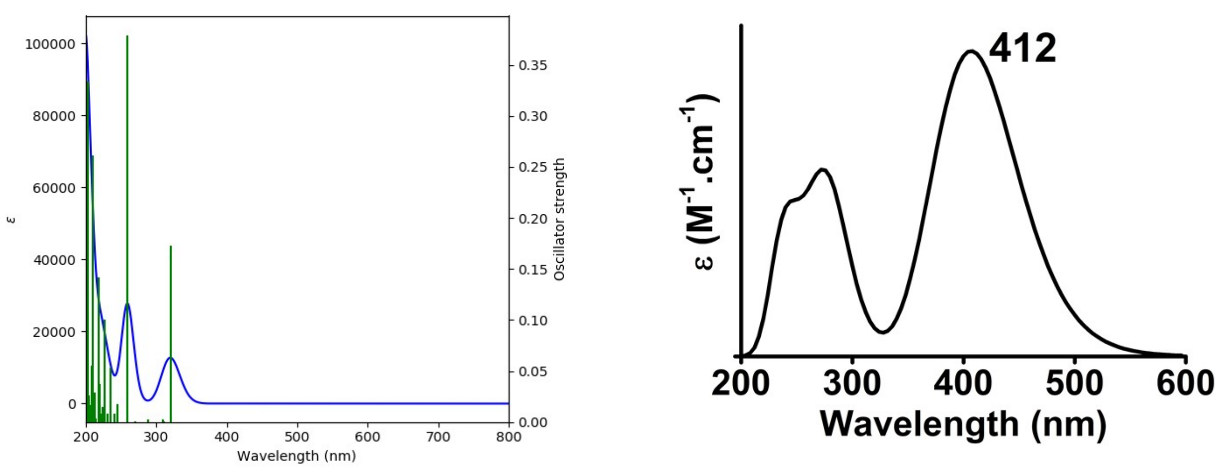


Figure S10. UV-Vis spectra of the form **1** (left) and its phenoxide form (right) in DMSO.

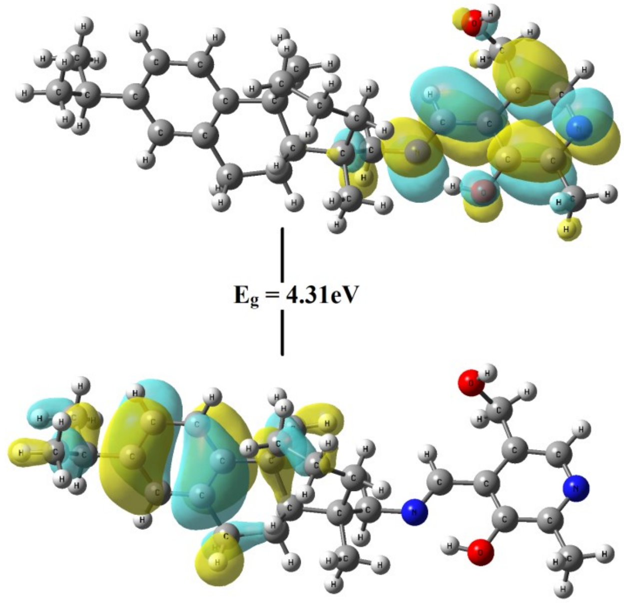


Figure S11. HOMO-LUMO plot of compound **1**.

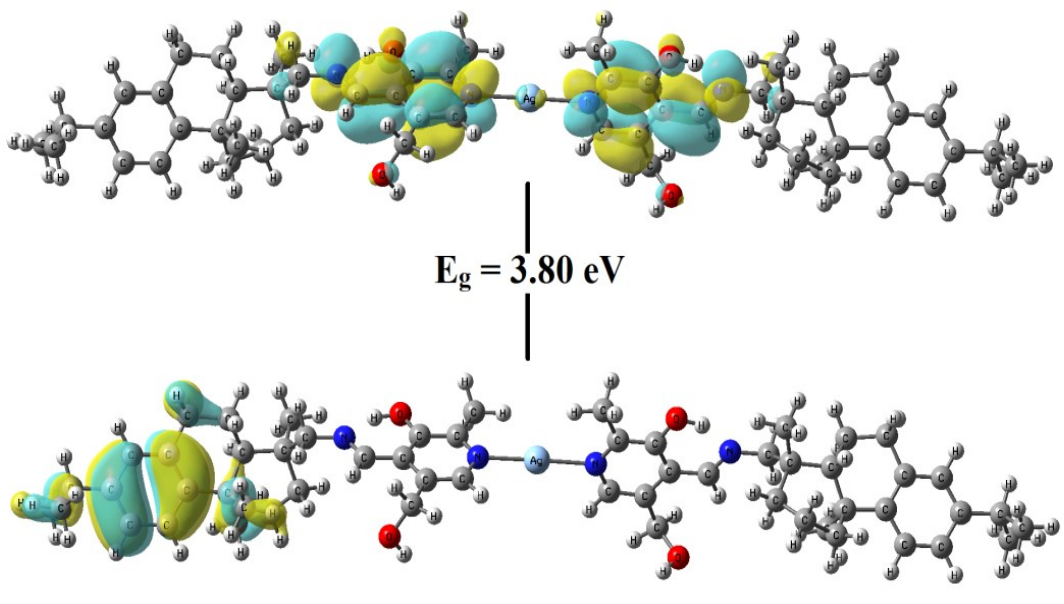


Figure S12. HOMO-LUMO plot of dimer of compound **1** with silver ion.

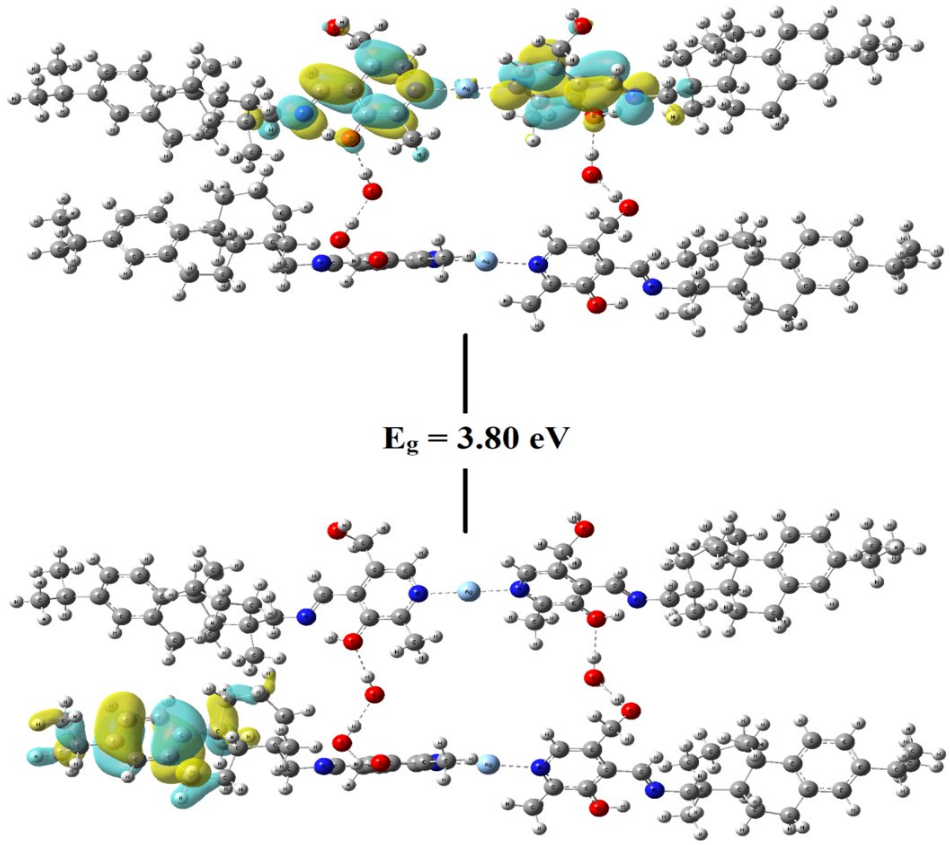


Figure S13. HOMO-LUMO plot of tetramer of compound **1** with two silver ion.

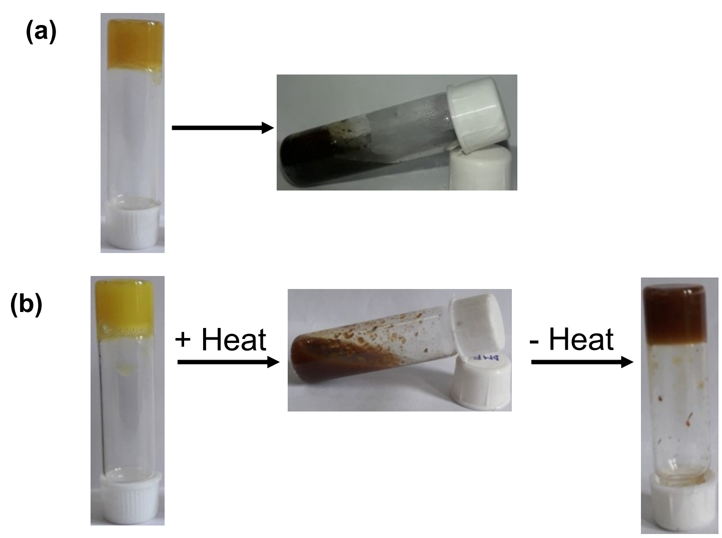


Figure S14. Temperature induced gel to sol transition of compound **1** in presence of Ag^+ in (a) DMF/H_2O and in (b) $DMSO/H_2O$ system.

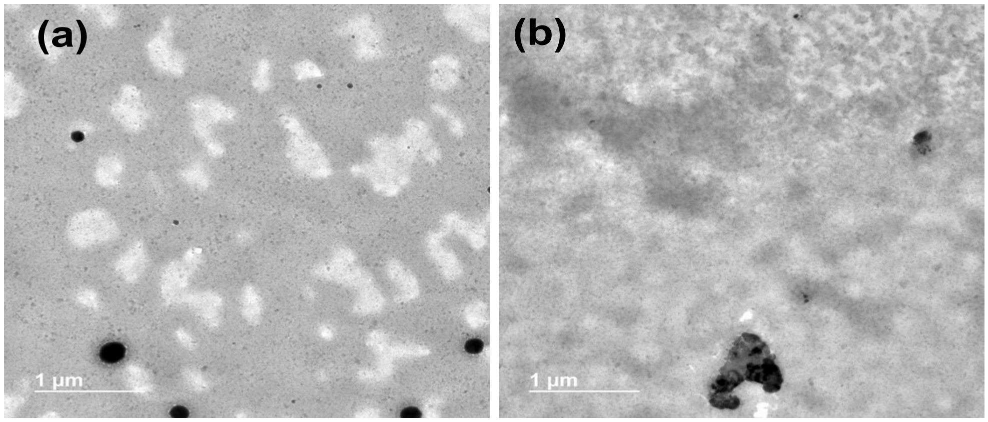


Figure S15. Transmission electron microscopy (TEM) images of xerogel of compound **1** prepared in DMSO/H_2O (1:1, v/v) in presence of 2 equivalent amounts of Ag^+ ion.

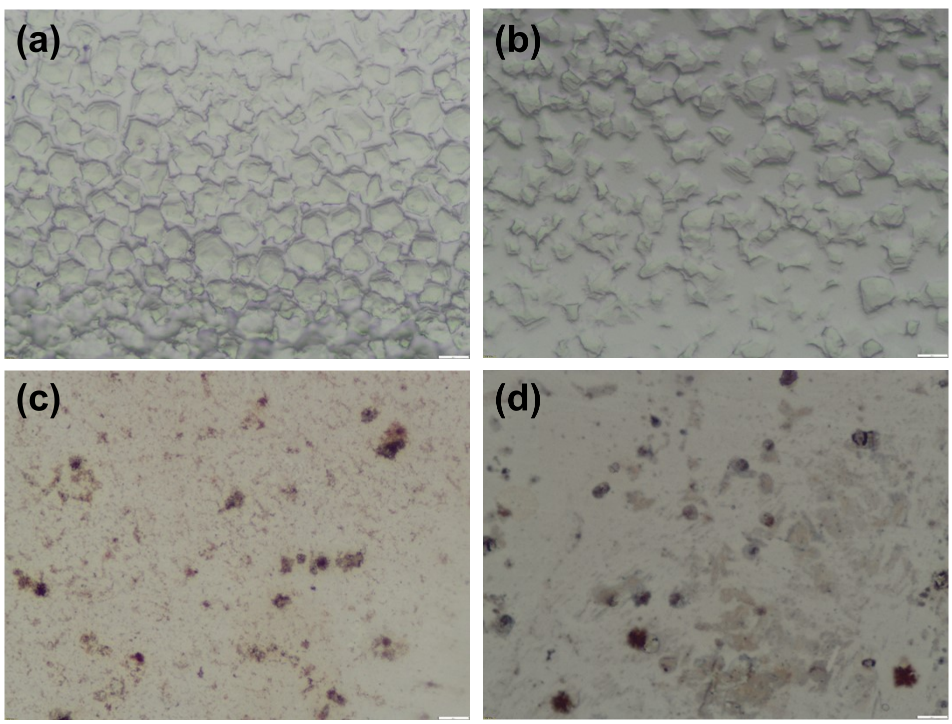


Figure S16. Optical image of solution of compound **1** prepared in (a) DMF (b) DMF-H_2O (v/v, 1/1) (c) DMF-H_2O in presence of 1 equiv. of Ag^+ and (d) DMF-H_2O in presence of 2 equivalent amount of Ag^+ ion.

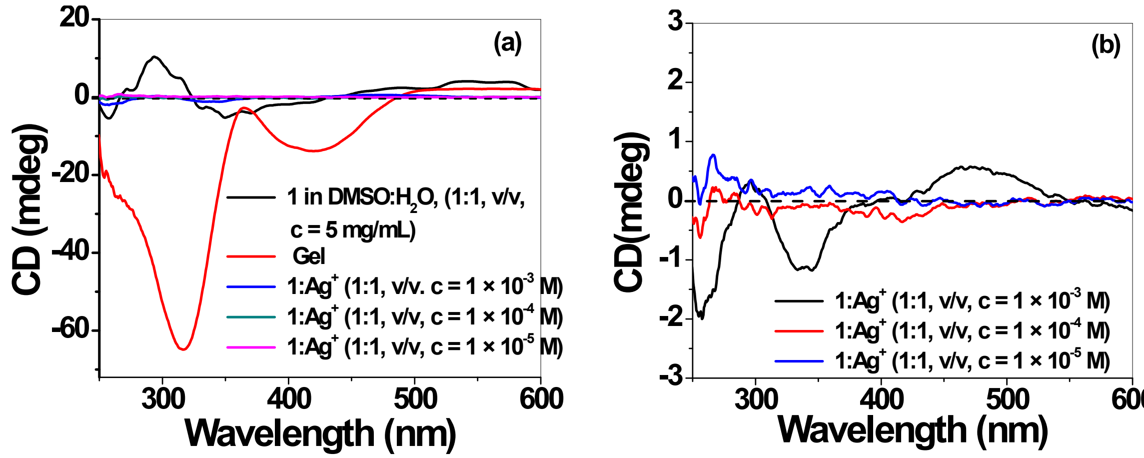


Figure S17. CD spectra of compound **1**: (a) at different concentrations of compound **1** (5 mg/mL) in DMSO:H_2O (1:1,v/v) in absence of Ag^+ ion, gel and in presence of Ag^+ ion with decreasing concentration from 1×10^{-3} to 1×10^{-5} M and (b) Expanded CD spectra of the same in small scale of Y-axis.

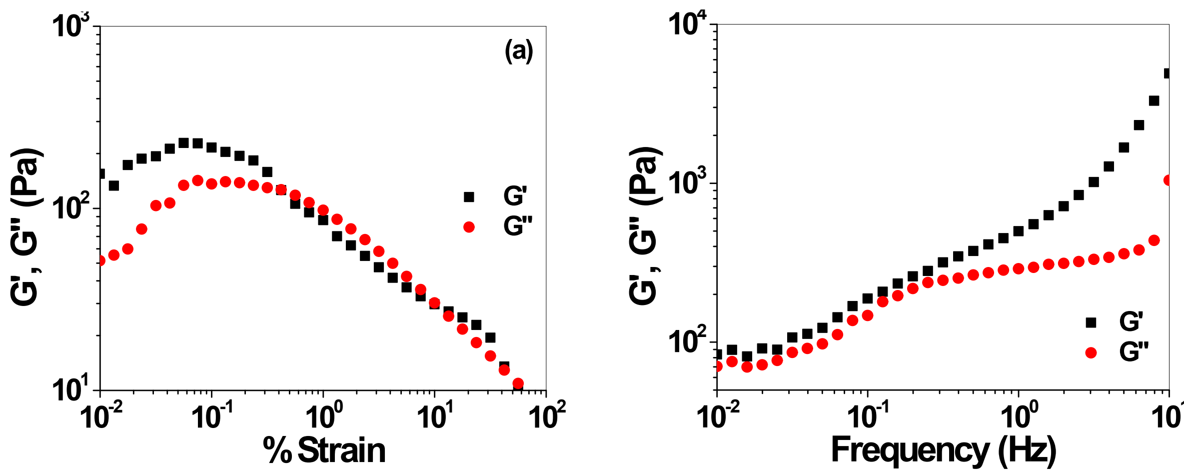


Figure S18. Rheological behaviour of supramolecular gel of **1** in presence of silver acetate (AgOAc): (a) Storage modulus G' and loss modulus G'' of gel on strain sweep prepared in DMSO/H_2O (1:1, v/v), and (b) storage modulus G' *versus* frequency sweep (strain: 0.1 %) of gel in DMSO/H_2O (1:1, v/v).

Table S2. Rheology data for Ag(OAc) gel

Solvent system (1:1, v/v)	Critical strain (%)	Crossover (% strain)	G'_{av}(Pa)	G''_{av} (Pa)	Tan δ (G''_{av}/G'_{av})
DMSO-H_2O	0.13	0.45	112	91	0.74

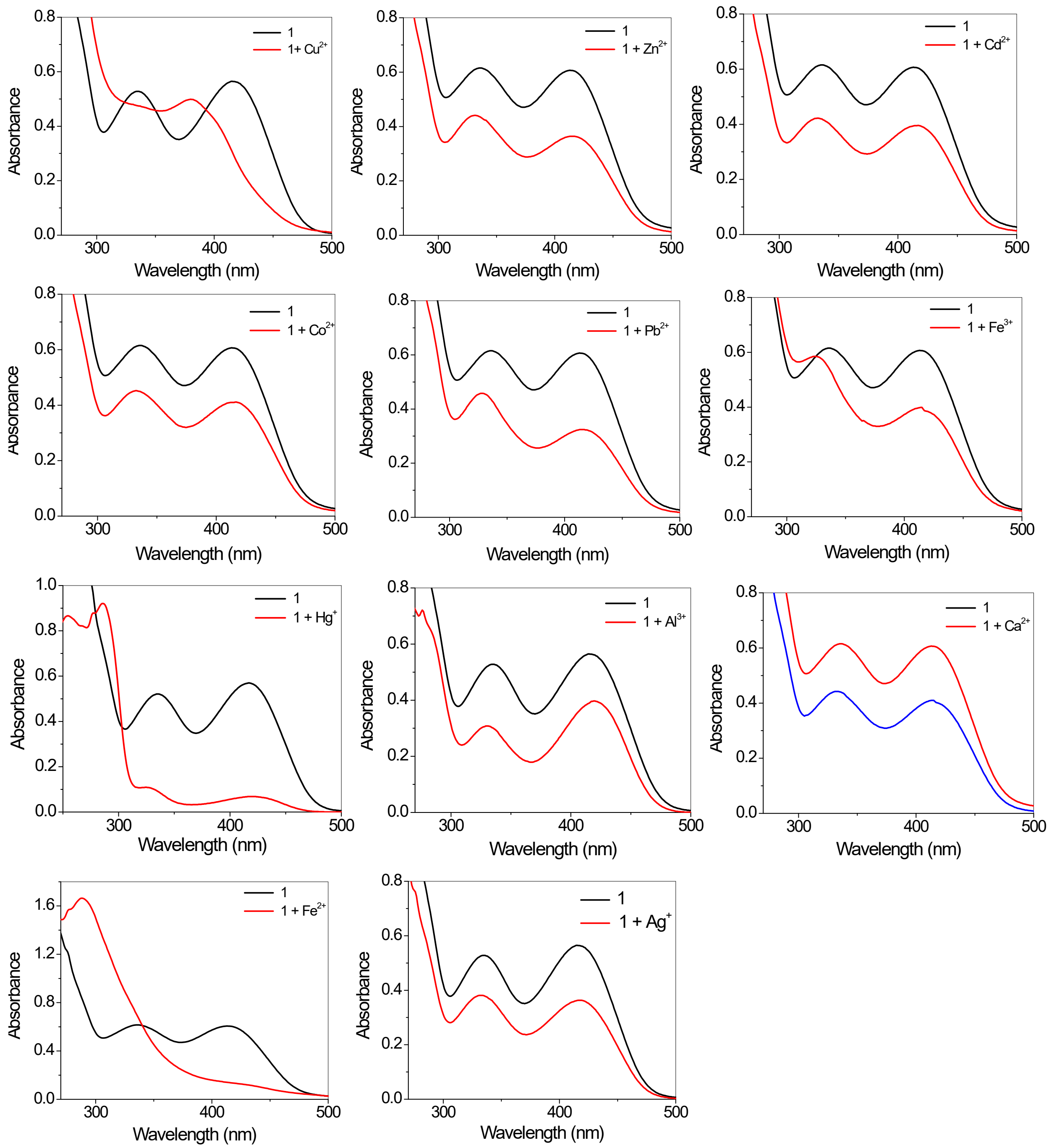


Figure S19. Change in absorption spectra of compound **1** (c = 2.5×10^{-4} M) in presence of 3 equivalent of (a) Cu^{2+}, (b) Zn^{2+}, (c) Cd^{2+}, (d) Ni^{2+}, (e) Co^{2+}, (f) Pb^{2+}, (g) Fe^{3+}, (g) Hg^{2+}, (i) Al^{3+}, (j) Ca^{2+}, (k) Fe^{2+}, (l) Ag^{+} metal ions (c = 1×10^{-3} M) in DMSO/H_2O (v/v, 1/1).

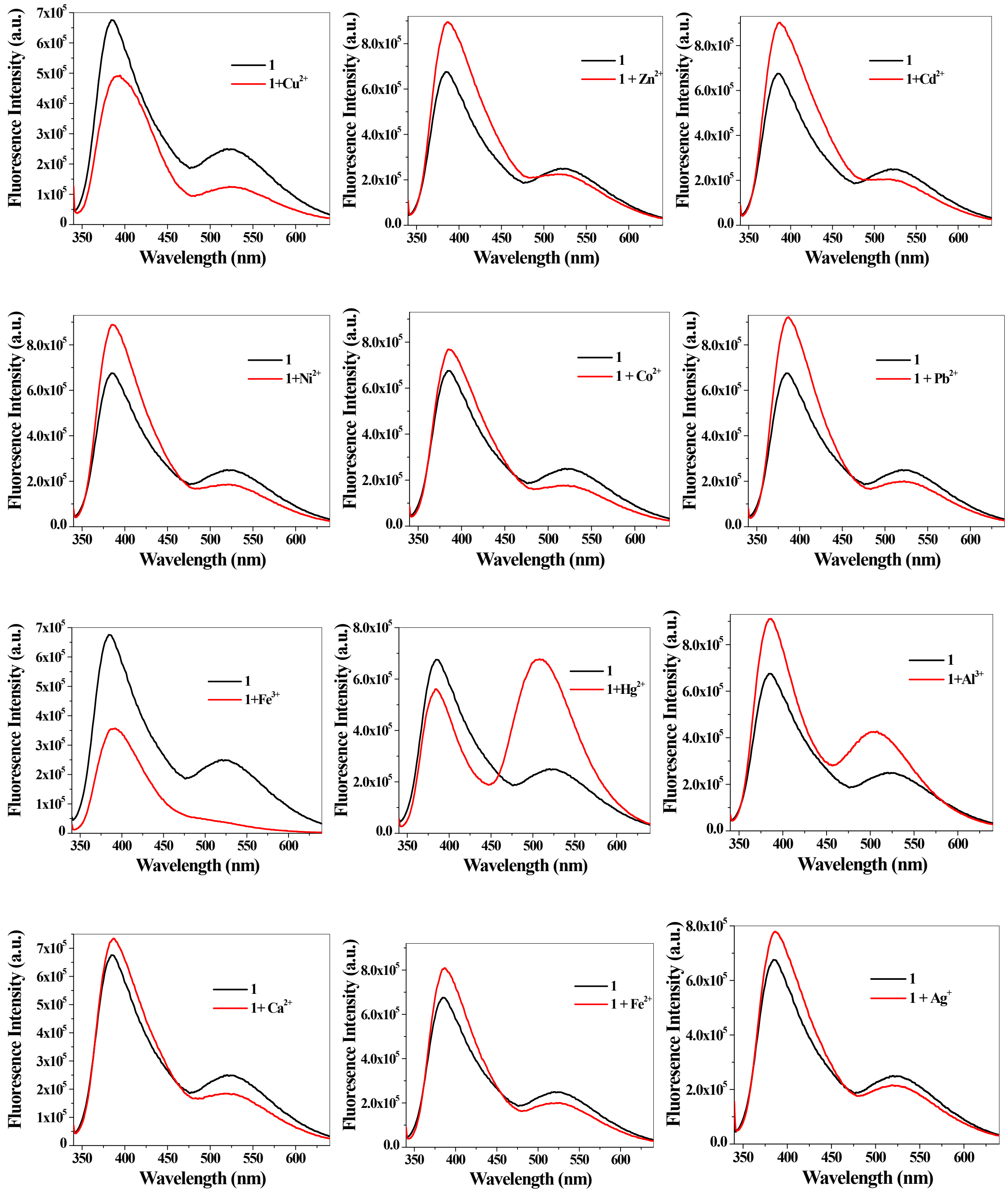


Figure S20. Change in emission spectra of compound **1** (c = 2.5×10^{-4} M) in presence of 3 equivalent of (a) Cu^{2+}, (b) Zn^{2+}, (c) Cd^{2+}, (d) Ni^{2+}, (e) Co^{2+}, (f) Pb^{2+}, (g) Fe^{3+}, (g) Hg^{2+}, (i) Al^{3+}, (j) Ca^{2+}, (k) Fe^{2+}, (l) Ag^{+} metal ions (c = 1×10^{-3} M) in DMSO/H_2O (v/v, 1/1).

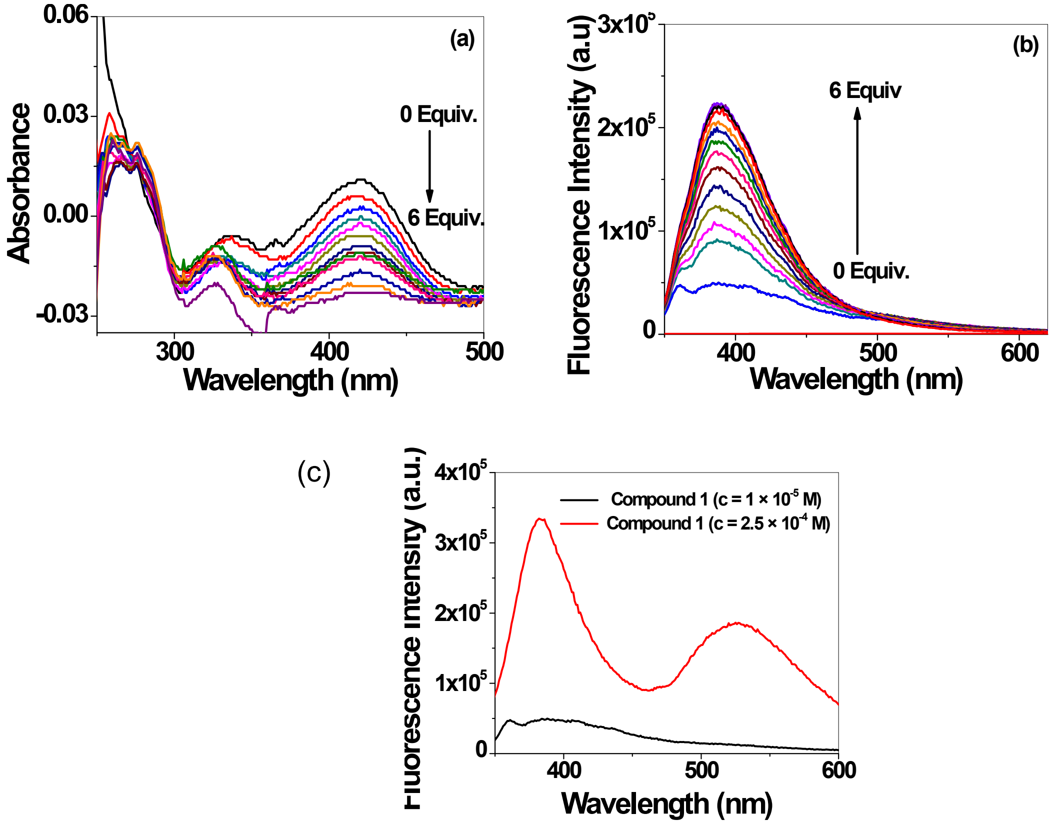


Figure S21. (a) Absorption, (b) emission titration spectra of compound **1** in DMSO/H_2O (1:1, v/v) (c = 1×10^{-5} M) in presence of Hg^{2+} ion (c = 1×10^{-3} M) ($Hg^{2+}$is taken as $HgClO_4$), and (c) Fluorescence spectra of compound **1** in different concentrations.

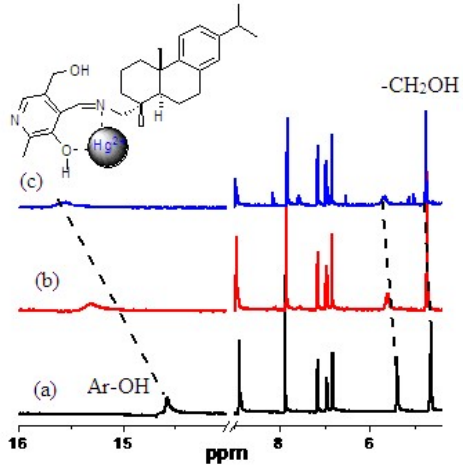


Figure S22. Partial ^1H NMR spectra of receptor **1** (c = 2.5 × 10^{-3}M) (a) in absence and in presence of (b) 1 equiv. and (c) 2 equiv. of Hg^{2+} ion in d_6-DMSO.

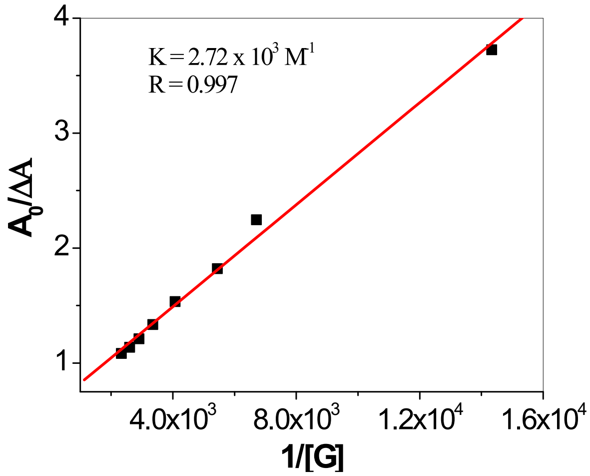


Figure S23.UV-Vis Benesi-Hildebrand plot for **1** (c = 2.5 × 10^{-4} M) with Hg^{2+} (c = 1 × 10^{-3} M) at 420 nm.

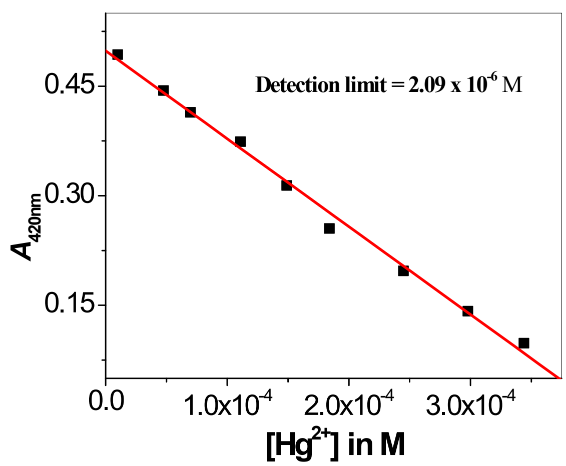
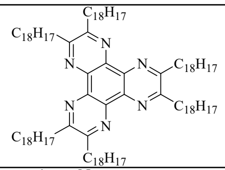
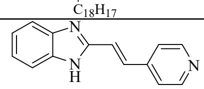
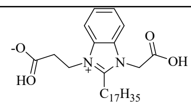
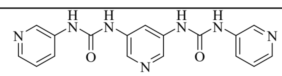
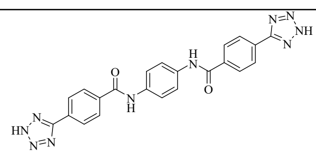
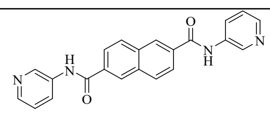
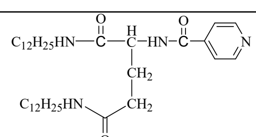
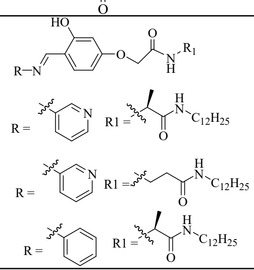
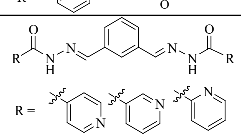
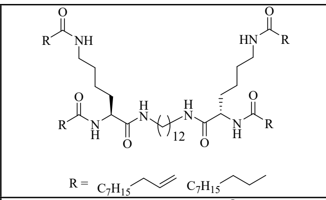
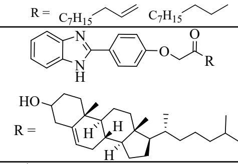
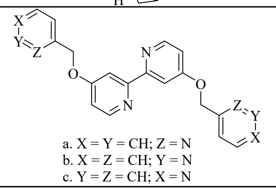
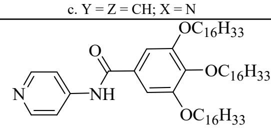
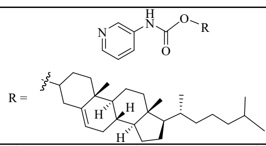
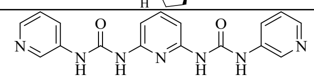
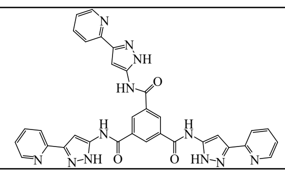
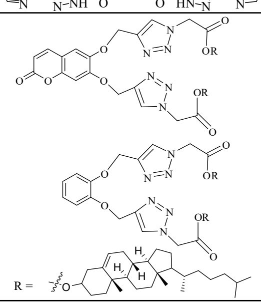
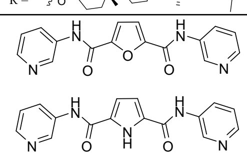
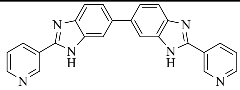
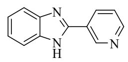
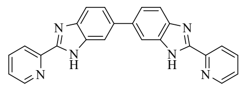
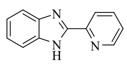
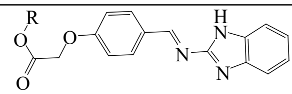
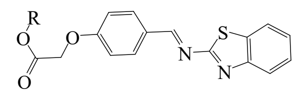
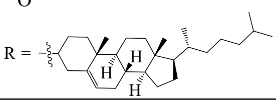
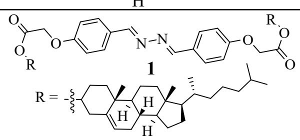
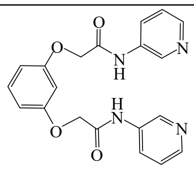
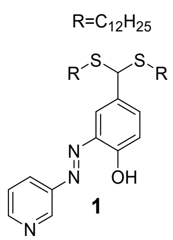


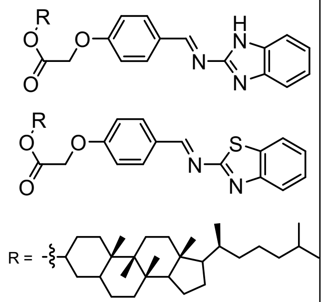
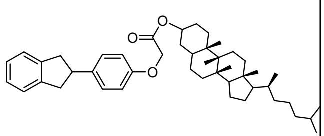
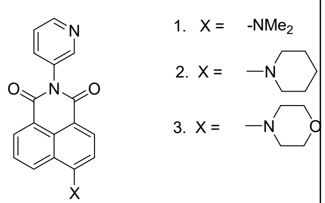
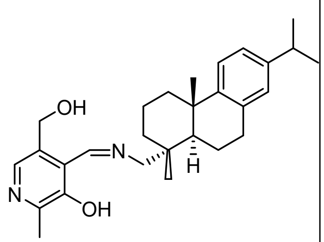
Figure S24. Detection limit for receptor **1** (c = 2.5 × 10^{-4} M) with Hg^{2+} (c = 1 × 10^{-3} M) at 420 nm.

Table S3. List of different Ag^+ ion responsive supramolecular gelators

Entry	Structure	Solvent	Phase transformation in presence of Ag^+ ions	Interfering metal ions	Detection limit for Ag^+ (M)	Ref.
1		EtOH	Gel to sol	-	-	*Tetrahedron Lett*. 2012, **53**, 1840.
2		MeOH	Sol to gel	-	-	*Chem. Commun*. 2013, **49**, 4181.
3		MeOH:H_2O (1:1, v/v)	Sol to gel	-	-	*Supramol. Chem*. 2014, **26**, 39.
4		THF/ H_2O	Sol to gel	-	-	*Soft Matter*, 2011, **7**, 2412.
5		H_2O	Sol to gel	-	-	*Soft Matter*, 2012, **8**, 6557.
6		DMF: H_2O (2:3, v/v)	Sol to gel	-	-	*Cryst. Growth Des*. 2015, **15**, 4635.
7		CH_2Cl_2, $CHCl_3$, THF	Sol to gel	-	-	*Langmuir*, 2012, **28**, 27.
8		Toluene: EtOH (99:1, v/v)	Sol to gel	-	-	*Chem. Commun*. 2015, **51**, 13929.
9		DMF, DMF/ H_2O, DMSO/ H_2O	Sol to gel	-	-	*Cryst. Growth Des*. 2015, **15**, 5360.

10		EtOAc	Gel to sol	Li^{+}	-	*Chem. Commun.* 2012, **48**, 2767.
11		DMF : H_2O (1:1, v/v)	Sol to gel	-	4.31 x 10^{-5}	*ChemistrySelect*, 2017, **2**, 959.
12		DMSO: H_2O	Sol to gel	-	-	*Dalton Trans.*, 2017, **46**, 2793.
13		Toluene/ethanol (10:1, v/v)	Sol to gel	-	-	*Langmuir,* 2007, **23**, 8217.
14		Diphenyl ether	Sol to gel	-	-	*Chem. Lett.*, 2003, **32**, 12.
15		THF-H_2O (3 : 2)	Sol to gel	-	-	*New J. Chem.*, 2010, **34**, 2261.
16		H_2O	Sol to gel	-	-	*New J. Chem.*, 2014, **38**, 2470.
17		$CHCl_3$:CH_3OH (2:1, v/v)	Gel to Sol	Cu^{2+}, Hg^{2+}	-	*New. J. Chem.*, 2016, **40**, 3476.
18		DMSO: H_2O (1:1, v/v)	Sol to gel	Cu^{2+} -	- -	*New. J. Chem.*, 2018, **42**, 6488.

19	   	DMSO: H_2O DMSO: H_2O DMSO: H_2O DMSO: H_2O	Gel to sol Gel to sol Sol to gel Sol to gel	Cu^{2+} Cu^{2+}, Hg^{2+} - -	3.69 x 10^{-6} 3.34 x 10^{-6} 1.93 x 10^{-7} 1.28 x 10^{-6}	*Mater. Chem. Front.*, 2018, **2**, 385.
20	  	1,4-dioxane-MeOH (1:1, v/v) 1,4-dioxane-H_2O (1:1, v/v)	Gel to sol Sol to gel	- -	3.27 x 10^{-5} 9.27 x 10^{-5}	*New J. Chem.*, 2019, **43**, 5139
21		$CHCl_3/CH_3OH$ (3:1, v/v)	Visual detection through sol-to-gel transition	Fe^{3+}	9.35 x 10^{-6}	*Mater. Chem. Front.,*2018, **2**, 2286
22		DMSO-H_2O (1:2, v/v)	Visual detection through sol-to-gel transition	-	5.95 x 10^{-5}	*New J. Chem.*, **2019**, *43*, 934
23		DMSO-H_2O (1:1, v/v)	Sol-to-Gel transition	Ag^{+} (Different modes of interaction, Hg^{2+} and Ag^{+} ions are discriminated with the aid of different chelating agents)	1.1 x 10^{-6}	*ChemistrySelect*, **2019**, *4*, 11564.

24		1,4-dioxane-MeOH (1:1, v/v) 1,4-dioxane-H2O (1:1,v/v)	Gel to sol Sol to gel	- -	3.27×10^{-5} 9.27×10^{-5}	*New J. Chem.*, 2**019,** *43*, 5139.
25		Nitrobenzene	Gel to Sol	-	-	*New J. Chem.*, 2**019,** *43*, 10509.
26		DMF-H_2O (1 : 1, v/v)	Sol to gel	-	-	*ChemistrySelect*, **2021**, *6*, 11696.
27		DMF-H_2O (1 : 1, v/v) DMSO-H_2O (1 : 1, v/v) Dioxan-H_2O (1 : 1, v/v)	Sol to gel	-	-	Present work