## **Electronic Supporting Information**

# Pyridine coupled mono and bisbenzimidazoles as supramolecular gelators: Selective metal ion sensing and ion conductivity

### Santanu Panja,<sup>a</sup> Subhratanu Bhattacharya,<sup>b</sup> Kumaresh Ghosh<sup>a</sup>\*

<sup>a</sup>Department of Chemistry, University of Kalyani, Kalyani-741235, India, Email: ghosh\_k2003@yahoo.co.in <sup>a</sup>Department of Physics, University of Kalyani, Kalyani-741235, India.

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## Table 1S. Results of gelation test for 1-6.

Solvent	1	2	3	4	5	6
CHCl <sub>3</sub>	Ι	PS	Ι	S	Ι	PS
DCM	Ι	Ι	Ι	S	Ι	Ι
CHCl <sub>3</sub> : MeOH (100:2,v/v)	Ι	S	PS	S	Ι	S
CHCl <sub>3</sub> : MeOH (1:1,v/v)	S	S	S	S	S	S
MeOH	S	S	S	S	S	S
Acetonitrile	Ι	PS	Ι	PS	Ι	Ι
n-Hexane	Ι	Ι	Ι	Ι	Ι	Ι
Diethyl ether	Ι	Ι	Ι	Ι	Ι	Ι
Cyclohexane	Ι	Ι	Ι	Ι	Ι	Ι
Ethylacetate	PS	S	S	S	S	S
THF	PS	S	S	S	S	S
DMF	S	S	S	S	S	S
DMSO	S	S	S	S	S	S
THF: H <sub>2</sub> O (1:1, v/v)	Р	S	Р	S	Р	S
DMF: H <sub>2</sub> O (1:1, v/v)	S	S	Р	S	PG	S
MeOH: H <sub>2</sub> O (1:1, v/v) + $Ag^+$	Р	Р	G	S	PG	Р
MeOH: H <sub>2</sub> O (1:2, v/v)	S	S	Р	S	Р	S
MeOH: H <sub>2</sub> O (1:2, $v/v$ ) + Ag <sup>+</sup>	Р	Р	Р	G	Р	Р
MeOH: H <sub>2</sub> O (1:3, v/v)	G	S	Р	S	Р	S
MeOH: H <sub>2</sub> O (1:6, v/v)	Р	G	Р	Р	Р	Р
DMSO: H <sub>2</sub> O (1:1, v/v) + $Ag^+$	Р	Р	G	S	PG	Р
DMSO: H <sub>2</sub> O (1:2, v/v)	S	S	Р	S	Р	S
DMSO: H <sub>2</sub> O (1:2, v/v) + $Ag^+$	Р	Р	Р	G	Р	Р
DMSO: H <sub>2</sub> O (1:3, v/v)	G	S	Р	S	Р	S
DMSO: H <sub>2</sub> O (1:6, v/v)	Р	G	Р	Р	Р	Р
S = solution; I = insoluble; G = gel (minimum gelatination concentration for 1 = 3.8 mg/mL, 2 = 5 mg/mL, $3 = 4.9$ g/mL, $4 = 4.5$ g/mL); P = precipitation; PS = partially soluble.						



Fig. S1. Pictorial representation of the thermo reversibility of the DMSO: H<sub>2</sub>O gels of (a) 1 and (b) 2.



Fig. S2. Variation of gel melting temperature (Tg) with increasing concentration of gelators from DMSO:  $H_2O$  solvent system.



Fig. S3. Comparison of FTIR spectra of (A) 1 and (B) 2 in amorphous (a) and gel (b) states.



Fig. S4. Comparison of emission spectra of 1 (a) and 2 (b) in sol and gel states.



**Fig. S5.** Chemical responsiveness of the gel of **1** [8 mg/ mL in DMSO: H<sub>2</sub>O (1:3, v/v)] on successive addition of (a) Ag<sup>+</sup> (c = 0.2 M) and Cl<sup>-</sup> (b) Cu<sup>2+</sup> (c = 0.2 M) and ethylene diamine.



Fig. S6. Photograph showing the pH dependency of the DMSO: H<sub>2</sub>O gels of 1 (a) and 2 (b).



Fig. S7. Pictorial representation of thermo reversibility of the  $Ag^+$ -induced gel of (a) 3 and (b) 4 in DMSO:  $H_2O$ .



**Fig. S8.** Variation of gel melting temperature  $(T_g)$  with increasing concentration of gelators **3** and **4** in DMSO: H<sub>2</sub>O solvent in presence of 2 equiv. amounts of Ag<sup>+</sup>.



**Fig. S9.** Chemical responsiveness of the gels of (a) **3** [4.9 mg/ mL] and (b) **4** [4.5 mg/ mL] in DMSO: H<sub>2</sub>O on successive addition of 2 equiv. amounts of Cl<sup>-</sup> (c = 0.2 M) and Ag<sup>+</sup> (c = 0.2 M) ions, respectively. The Cl<sup>-</sup>-induced disrupted gel was recovered by adding Ag<sup>+</sup> solution after 4h and 2h for **3** and **4**, respectively.



Fig. S10. Suggested modes of interaction of (a) 3 and (b) 4 involving  $Ag^+$  ions to form the networks responsible for gelation.



**Fig. S11**. FTIR spectra representing the change in stretching frequency in amorphous and gel states for (a) **3** and (b) **4**.



Fig. S12. Comparison of absorption spectra of 3 (a) and 4 (b) in the sol and gel states.



Fig. S13. Comparison of emission spectra of 3 (a) and 4 (b) in the sol and gel states.



**Fig. S14.** MMX calculations: (A) Hydrogen bonded dimmers of **4** (E = 78.76 kcal/mol, a = b = 2.00Å), **2** (E = 62.90 kcal/mol; Hydrogen bond: distance: 2.19 Å) and **6** (E = 67.77 kcal/mol; Hydrogen bond distance: 1.97 Å); (B) water assembled dimmers of **2** (E = 49.12 kcal/mol; a = 2.08, b = 1.93, c = 1.97, d = 1.72; all are in Å) and **6** (E = 51.83 kcal/mol; a = 1.94, b = 1.82, c = 1.74; all are in Å) [Calculation was done using PC model, version 9.2, serena software].

#### Change in emission of 1 with metal ions



**Fig. S15.** Change in fluorescence ratio ( $\lambda_{ex} = 330 \text{ nm}$ ) of **1** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) at 442 nm upon addition of 10 equiv. amounts of metal ions ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v).



#### Change in emission of 1 in DMSO: H<sub>2</sub>O (1:9, v/v).

**Fig. S16.** Change in emission of 1 ( $c = 2.5 \times 10^{-5}$  M) upon addition of 10 equiv. amount of (a) Pb<sup>2+</sup>, (b) Mg<sup>2+</sup>, (c) Co<sup>2+</sup>, (d) Ni<sup>2+</sup>, (e) Zn<sup>2+</sup>, (f) Cd<sup>2+</sup>, (g) Fe<sup>2+</sup> and (h) Hg<sup>2+</sup> ( $c = 1.0 \times 10^{-3}$  M) ) in DMSO: H<sub>2</sub>O (1:9, v/v).



**Fig. S17.** Job plots of receptor 1 ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>+</sup> and (b) Cu<sup>2+</sup> from fluorescence.



**Fig. S18.** Non liner binding constant curves for 1 ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>+</sup> and (b) Cu<sup>2+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v) from fluorescence.



**Fig. S19.** Detection limits of **1** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>+</sup> and (b) Cu<sup>2+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v) from fluorescence.



**Fig. S20.** Fluorescence response of **1** (c =  $2.50 \times 10^{-5} \text{ M}$ ) upon addition of 10 equiv. amounts of Ag<sup>+</sup> ions to the solution of **1** containing other metal ions in 10 equiv. amounts in DMSO: H<sub>2</sub>O (1:9, v/v).

#### Change in emission of 2 with metal ions



**Fig. S21.** Change in fluorescence ratio ( $\lambda_{ex} = 300 \text{ nm}$ ) of **2** ( $c = 2.5 \text{ x } 10^{-5} \text{ M}$ ) at 382 nm upon addition of 20 equiv. amounts of metal ions ( $c = 1.0 \text{ x } 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v).

## Change in emission of 2 in DMSO: H<sub>2</sub>O (1:9, v/v).





**Fig. S22.** Change in emission of **2** ( $c = 2.5 \times 10^{-5}$  M) upon addition of 20 equiv. amount of (a) Pb<sup>2+</sup>, (b) Mg<sup>2+</sup>, (c) Co<sup>2+</sup>, (d) Ni<sup>2+</sup>, (e) Zn<sup>2+</sup>, (f) Cd<sup>2+</sup>, (g) Fe<sup>2+</sup>, (h) Hg<sup>2+</sup>, (i) Cu<sup>2+</sup>, (j) Ag<sup>+</sup> ( $c = 1.0 \times 10^{-3}$  M) ) in DMSO: H<sub>2</sub>O (1:9, v/v).



**Fig. S23.** Job plots of receptor **2** ( $c = 2.5 \times 10^{-5}$  M) with (a) Ag<sup>2+</sup>, (b) Cu<sup>2+</sup> and (c) Hg<sup>2+</sup> from fluorescence.



**Fig. S24.** Non liner binding constant curves for **2** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>2+</sup>, (b) Cu<sup>2+</sup> and (c) Hg<sup>2+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v) from fluorescence.



**Fig. S25.** Detection limits of **2** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>2+</sup>, (b) Cu<sup>2+</sup> and (c) Hg<sup>2+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O(1:9, v/v) from fluorescence.



**Fig. S26.** Job plot of receptors **3** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with Ag<sup>+</sup> from (a) fluorescence and (b) UV.



**Fig. S27.** Non liner binding constant curves for **3** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with Ag<sup>+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v) from (a) fluorescence and (b) UV.



**Fig. S28.** Job plots of receptor 4 ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with Ag<sup>+</sup> from (a) fluorescence and (b) UV.



**Fig. S29.** Non liner binding constant curves for 4 ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with Ag<sup>+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v) from (a) fluorescence and (b) UV.



**Fig. S30.** Detection limit of **3** ( $c = 2.5 \times 10^{-5}$  M) with Ag<sup>+</sup> ( $c = 1.0 \times 10^{-3}$  M) in DMSO: H<sub>2</sub>O (1:9, v/v) from fluorescence.



**Fig. S31.** Detection limit of **4** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with Ag<sup>+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v) from fluorescence.





**Fig. S32.** Change in absorbance of **1** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) upon addition of 6 equiv. amount of (a) Pb<sup>2+</sup>, (b) Mg<sup>2+</sup>, (c) Co<sup>2+</sup>, (d) Ni<sup>2+</sup>, (e) Zn<sup>2+</sup>, (f) Cd<sup>2+</sup>, (g) Fe<sup>2+</sup>, (h) Hg<sup>2+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v).



**Fig. S33.** Job plots of receptor 1 ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>+</sup> and (b) Cu<sup>2+</sup> from UV.



**Fig. S34.** Non liner binding constant curve for 1 ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>+</sup> and (b) Cu<sup>2+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v) from UV.







**Fig. S35.** Change in absorbance of **2** ( $c = 2.5 \times 10^{-5}$  M) upon addition of 10 equiv. amount of (a) Pb<sup>2+</sup>, (b) Mg<sup>2+</sup>, (c) Co<sup>2+</sup>, (d) Ni<sup>2+</sup>, (e) Zn<sup>2+</sup>, (f) Cd<sup>2+</sup>, (g) Fe<sup>2+</sup>, (h) Hg<sup>2+</sup>, (i) Cu<sup>2+</sup>, (j) Ag<sup>+</sup> ( $c = 1.0 \times 10^{-3}$  M) in DMSO: H<sub>2</sub>O (1:9, v/v).



**Fig. S36.** Job plots of receptor 2 ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>+</sup>, (b) Cu<sup>2+</sup> and (c) Hg<sup>2+</sup> from UV.



**Fig. S37.** Non liner binding constant curves for **2** ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with (a) Ag<sup>2+</sup>, (b) Cu<sup>2+</sup> and (c) Hg<sup>2+</sup> ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v) from UV.

**Table S2.** Non liner binding constant data for 1-4 ( $c = 2.5 \times 10^{-5} \text{ M}$ ) with respective metal ions ( $c = 1.0 \times 10^{-3} \text{ M}$ ) in DMSO: H<sub>2</sub>O (1:9, v/v).

Metal- ligand	Binding constant	Binding constant values ( M <sup>-1</sup> )			
complex	From florescence titration data	From UV titration data			
<b>1</b> - Ag <sup>+</sup>	$\mathbf{K} = (2.78 \pm 0.45) \ge 10^4$	$\mathbf{K} = (2.13 \pm 0.48) \ge 10^3$			
<b>1</b> - Cu <sup>2+</sup>	$K = (1.88 \pm 0.28) \times 10^4$	$K = (1.04 \pm 0.15) \text{ x } 10^4$			
<b>2</b> - Ag <sup>+</sup>	$K_1 = (1.05 \pm 0.15) \; x \; 10^4$	$K = (3.60 \pm 0.57) \ge 10^3$			
	$K_2 = (9.75 \pm 4.01) \; x \; 10^2$				
<b>2</b> - Cu <sup>2+</sup>	$K_1 = (9.02 \pm 2.44) \; x \; 10^3$	$\mathbf{K} = (4.67 \pm 0.25) \ge 10^3$			
	$K_2 = (6.57 \pm 1.58) \; x \; 10^3$				
<b>2</b> - Hg <sup>+</sup>	$K_1 = (6.01 \pm 0.28) \ x \ 10^3$	$\mathbf{K} = (9.25 \pm 2.53) \ge 10^3$			
	$K_2 = (2.07 \pm 0.04) \ x \ 10^3$				
<b>3</b> - Ag <sup>+</sup>	$K = (1.30 \pm 0.31) \ x \ 10^6$	$K = (9.47 \pm 1.07) \ x \ 10^4$			
<b>4</b> - Ag <sup>+</sup>	$K = (4.98 \pm 0.98) \ x \ 10^4$	$K = (2.46 \pm 0.66) \ge 10^4$			



**Fig. S38.** <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO) of (a) compound **1** (c = 1.50 x 10<sup>-2</sup> M) and (b) **1** with equiv. amount of AgClO<sub>4</sub>.



**Fig. S39.** <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO) of (a) compound **3** (c = 1.07 x 10<sup>-2</sup> M) and (b) **3** with equiv. amount of AgClO<sub>4</sub>.

Table S3: List of metal ion responsive pyridine tied benzimidazoles as supramolecular gelators

Structure	Solvent	Metal ion (phase transformation)	Ref.
	МеОН	Ag <sup>+</sup> (Sol to gel)	<i>Chem. Commun.</i> 2013, 49, 4181
-0,О HOОН	MeOH:H <sub>2</sub> O (1:1, v/v)	Ag <sup>+</sup> (Sol to gel)	Supramol. Chem. 2014, 26, 39
	MeOH	$Cu^{2+}$ , $Cd^{2+}$ (Sol to gel)	Chem. Mater., 2012, 24, 1165
	МеОН	Cu <sup>2+</sup> (Sol to gel)	<i>CrystEngComm</i> , 2013, 15, 9769
	CH3CN	Co <sup>2+</sup> , Zn <sup>2+</sup> , La <sup>3+</sup> , Eu <sup>3+</sup> (Sol to gel)	J. Am. Chem. Soc., 2003, 125, 13922
	DMF	Zn <sup>2+</sup> , Ni <sup>2+</sup> (Sol to gel)	J Porous Mater, 2016, 23, 663
$R = C_{6}H_{2} \cdot (OC_{12}H_{23})_{1} \cdot 3.4.5$	CHCl <sub>3</sub>	Sol to gel	<i>Chem. Eur. J.</i> , 2014, 20, 9930
$\left[\overbrace{\begin{matrix} & & \\ & & $	CH3CN	Sol to gel	Chem. Eur. J., 2009, 15, 1853
a; $R = n-C_{16}H_{33}$ ; X=Br b; $R = n-C_{16}H_{33}$ ; X=I			





# Mass spectrum of 1.







## Mass spectrum of 2.



![](_page_25_Figure_1.jpeg)

## <sup>13</sup>C NMR (*d*<sub>6</sub>-DMSO, 100 MHz)

![](_page_26_Figure_1.jpeg)

## Mass spectrum of 3.

![](_page_27_Figure_1.jpeg)

![](_page_28_Figure_1.jpeg)

![](_page_29_Figure_1.jpeg)

# Mass spectrum of 4.

G Bernental Composition	- 0 X
Re Edit View Process Help	
Single Mass Analysis Telescore 10.0 PPM / DEC min = 1.5, max = 50.0 Element preficience 0.0 Element p	
Mana Cate Mana — Ang PMM2 (2015) Ferminals — 14917   1-071 Norm / 24 Canof %. C   14 N   196-0479 - 196-0479 = 0.3 - 1.3 - 9.3 - C(2 1-09 NU - 54.6 - n/a - n/a - 1.2 - 1.9 - 3 	
KLYNS, 51 153 17 877, 442 (44 30000 0.555 28.0 00 LS 10); Cm (151 153) 190	10F MD E5- 3.07#-04
s-	
	4 197.0010
192 4190 468.0718 1/6 9766 178.0691 191.0443 192.0870 199.0651 192.4564 195.0870 192.5 195.0 197.5 170.0 172.5 175.0 177.5 190.0 192.5 195.0 197.5 190.0 192.5 1	198.0948 202.0831 206.0869 210.1924 216.8845 221.8965 224.0424 228.9552 230.1919 234.9860.215.9450 6.0 1975 200.0 2025 205.0 2075 210.0 212.5 215.0 217.5 220.0 222.5 225.0 227.5 220.0 212.5 235.0 217.5

![](_page_31_Figure_1.jpeg)

![](_page_32_Figure_1.jpeg)

Mass spectrum of 5.

![](_page_33_Figure_1.jpeg)

![](_page_34_Figure_1.jpeg)

![](_page_35_Figure_1.jpeg)

# Mass spectrum of 6.

![](_page_36_Figure_1.jpeg)