Insights Into the Gelation of Biphenyl Coupled Pyridyl Bisamides

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Abstract Biphenyl coupled isomeric pyridyl bisamides **1**–**4** have been synthesized and their gelation properties have been thoroughly investigated. In spite of having a pyridine center, capable of forming water linking network and hydrogen bonding amide functionality, all the compounds behave as non-gelator in organic and semi aqueous solvents. However, in presence of Ag⁺ ions, only compound **1** forms gel and validates its visual sensing over other metal ions. The nongelation behaviour of other derivatives **2**, **3** and also *meta* derivative **4** highlights the effect of positional role of the pyridine ring nitrogen with respect to the biphenyl ring as well as endorse the isomeric substitution in biphenyl ring, respectively. Spectroscopic studies confirm that the metal coordination as well as the hydrogen bonding involving the amide NHs of **1** plays a pivotal role in establishing the gel network in solution. Not only through gelation, compound **1** also selectively recognizes Ag⁺ ions fluorimetrically in a turn-on mode in solution state and correlates the gel phase observations.

Keywords supramolecular gels, biphenyl-linked bispyridine amide, stimuli responsiveness, Ag⁺ sensing, fluorometric detection

Introduction

Supramolecular gels are incredibly important in many areas from medicine to material science.^[1–17] These gels are formed when small monomeric units combine to form a larger structure under the influence of various noncovalent forces like hydrogen bonding, π -stacking, electrostatic, hydrophobic interactions, etc. In general, to bring about self-assembly, usually a trigger like pH, temperature, irradiation, ions, redox, and so on, is applied to the suspension or solution of the gelator.^[6–8,12,13,15,18–30] As a result, the solubility of the molecules in solution decreases and self-aggregation occurs. Of various stimuli, metal ion coordination draws attention for visual detection through the conversion a sol state into a metal-organic gel state.^[19,21,31–36] Apart from visual detection, the metallogels are widely applicable in catalysis, optoelectronics and medicines.^[1,7,13,16,21,31,33,37–46] Metallogels are synthesized based on strong metal-ligand interactions.^[21,31,33,35,42,47–57] Metal coordination allows two or more molecules to come closer and simultaneously influences other non-covalent interactions to encourage the growth of assembly in a directional way. However, if the metal-ligand interactions are strong enough, it could lead to precipitation or crystallization.^[2,33,35,47–49,52,54] Therefore, a delicate balance between different intermolecular interactions is required to get a metallogel. To explore this, the study on correlation between the gelling behaviour and structural parameters of gelators is being increasingly important by designing new functional architectures.^[14,21,38,39,41,42,48,52,58,59]

The literature survey reveals that pyridine-containing compounds are promising materials for constructing metallogels.^[21,38,39,48–50,59–91] In such compounds, the pyridine moieties are coupled to different spacers through various functional groups like amide, urea, imidazole, imine, etc. Despite information available, it is still unclear why some molecules form gel and some are not. Moreover, in many cases, the bulk phase interactions are found to be dramatically

different from that of the microscopic level (in 10^{−5} M).^[39,92,93] Thus, there is enough scope to deal with new molecular systems that are simple and can be easily synthesized for task-specific applications.

In this work, we intend to investigate the structure-property relationship of some isomeric pyridyl bisamides. For this purpose, we synthesized compounds **1**–**4** by placing different pyridyl motifs around a common biphenyl spacer through amide bond (Figure 1). All the compounds possess pyridine nitrogen and amide functionality for intermolecular hydrogen bonding interaction. They are expected to exhibit different conformations and hydrogen bonding attributes in solution due to the change in position of the pyridine ring nitrogens (**1**, **2** and **3**) as well as change in spacer (**1** and **4**). In reality, the compounds behaved differently in self-aggregation. Of the bisamides **1**–**4**, only compound **1** is established as a potential gelator that forms gel in presence of Ag⁺ ions and validates its visual sensing.

Notably, the nongelation behaviour of the derivatives **2** and **3** highlights the positional role of pyridine ring nitrogen with respect to the biphenyl ring during self-aggregation in the presence of Ag⁺ ions. In relation to this, different behaviours of the *ortho* and *meta* derivatives **1** and **4**, respectively, towards gelation in presence of Ag⁺ ions endorse that the gelation abilities of these molecules significantly depend on the orientation of hydrogen bonding moieties around the spacers used.

Compound **1** further selectively interacts with Ag⁺ ions (as verified by fluorescence and UV-vis) in solution and shows a correlation with the gel phase behavior. Fluorometric sensing of metal ions draws considerable attention due to their environmental and physiological relevance.^[94–102] Of various metal ions, Ag⁺ ion is of great importance as it is associated with bioaccumulation and toxicity.^[95,102,103] Additionally, it has considerable applications in photography and imaging industry, organic synthesis, electronics, and so on.^[95,103] Thus, selective recognition of Ag⁺ ions is of utmost interest.

Figure 1 (Left) Structures of compounds 1–4. (Right) Schematic representation of the mode of aggregation of 1 in presence of Ag^+ in solution.

Experimental

Materials and methods

Reagents and solvents were purified using standard techniques. All solvents used in the synthesis were purified, dried and distilled following standard procedure. Solvents for spectroscopic measurements were of spectroscopic or HPLC grade. Solvents used in NMR experiments were obtained from Aldrich. Thin layer chromatography was performed on Merck precoated silica gel 60-F₂₅₄ plates. ^1H NMR and ^{13}C NMR spectra were recorded using Bruker 400 MHz instrument using TMS as internal standard. High resolution mass data were acquired by the electron spray ionization (ESI) technique on XEVO GS-2 QTOF Waters mass spectrometer. FTIR measurements of all the compounds and dried gels (xerogels) were carried out using a Perkin-Elmer L120-00A spectrometer (ν_{max} in cm^{-1}) using KBr cell and KBr pellets, respectively. Scanning electron microscopy (SEM) images were obtained on EVO LS-10 ZEISS instrument. Fluorescence and UV-vis studies were performed using Horiba Fluoromax 4C spectrofluorimeter and Shimadzu UV-2450 spectrophotometer, respectively.

Synthesis

$N^2, N^{2'}$ -di(pyridin-3-yl) biphenyl-2,2'-dicarboxamide (1)

To a stirred solution of biphenyl-2,2'-dicarboxylic acid (0.87 g, 3.59 mmol) in dry CH_2Cl_2 (20 mL), SOCl_2 (0.77 mL, 7.18 mmol) was added and the reaction mixture was refluxed for 10 h. On removal of excess SOCl_2 under reduced pressure, compound 5 was obtained as solid mass, which was directly used in the next step. The symmetrical bisamide 1 was obtained by coupling of 3-aminopyridine (1.09 g, 10.77 mmol) with biphenyl-2,2'-dicarbonyl dichloride 5 in 60 mL dry CH_2Cl_2 followed by addition of triethylamine (2.5 mL) under nitrogen atmosphere. The reaction mixture was stirred for 12 h. After completion of the reaction, solvent was removed under vacuum. The residual mass was extracted with $\text{CHCl}_3/\text{CH}_3\text{OH}$ mixture (30 mL $\times$ 3). The organic layer was washed with NaHCO_3 solution (15 mL $\times$ 3) and dried over anhydrous Na_2SO_4 and

filtered. The filtrate was concentrated under reduced pressure. The crude mass was purified by column chromatography over silica gel using ethyl acetate : pet ether (8 : 1, V/V) as eluent to afford the desired diamide 1 in 64% yield (0.9 g), m.p. 92 $^\circ\text{C}$. ^1H NMR (CDCl_3 containing few drops of d_6 -DMSO, 400 MHz) δ : 10.45 (s, 2H), 8.47 (s, 2H), 8.16 (d, 2H, J = 4 Hz), 7.93–7.90 (m, 2H), 7.62–7.60 (m, 2H), 7.34–7.30 (m, 4H), 7.11–7.06 (m, 4H); ^{13}C NMR (CDCl_3 containing few drops of d_6 -DMSO, 100 MHz) δ : 169.1, 144.9, 144.5, 138.9, 135.8, 135.3, 130.1, 129.5, 127.9, 127.6, 127.1, 123.4; FTIR (KBr) ν_{max} : 3233, 3173, 3117, 3052, 1654, 545, 1482 cm^{-1} ; HRMS (TOF MS ES $^+$): Calcd for (M+H) $^+$: 395.1508, Found: 395.1506.

$N^2, N^{2'}$ -di(pyridin-2-yl) biphenyl-2,2'-dicarboxamide (2)

To a stirred solution of biphenyl-2,2'-dicarboxylic acid (0.87 g, 3.59 mmol) in dry CH_2Cl_2 (20 mL), SOCl_2 (0.77 mL, 7.18 mmol) was added and the reaction mixture was refluxed for 10 h. On removal of excess SOCl_2 under reduced pressure, compound 5 was obtained as solid mass, which was directly used in the next step. The symmetrical bisamide 2 was obtained by coupling of 2-aminopyridine (1.09 g, 10.77 mmol) with biphenyl-2,2'-dicarbonyl dichloride 5 in 60 mL dry CH_2Cl_2 followed by addition of triethylamine (2.5 mL) under nitrogen atmosphere. The reaction mixture was stirred for 12 h. After completion of the reaction, solvent was removed under vacuum. The residual mass was dissolved in 10 mL of acetone followed by the addition of 100 mL of water and stirred for 30 min. The pH of the medium was adjusted to 8–9 by adding NaHCO_3 . Then, the precipitation was separated by filtration to have crude compound 2, which was purified by column chromatography over silica gel using ethyl acetate : pet ether (6 : 1, V/V) as eluent to afford the desired diamide 2 in 62% yield (0.87 g), m.p. 176 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 400 MHz) δ : 9.61 (s, 2H), 8.16 (d, 2H, J = 8 Hz), 8.08 (d, 2H, J = 4 Hz), 7.32–7.71 (m, 2H), 7.64–7.59 (m, 2H), 7.41–7.39 (m, 4H), 7.26–7.21 (m, 2H), 6.94 (dd, 2H, J_1 = 8 Hz, J_2 = 4 Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 168.6, 151.6, 147.6, 139.0, 138.2, 135.8, 130.3, 129.7, 128.0, 127.6, 119.6, 114.4; FTIR (KBr) ν : 3235, 1676, 1575, 1524, 1430, 1366 cm^{-1} ; HRMS (TOF MS ES $^+$): Calcd for (M+H) $^+$: 395.1508, Found: 395.1526.

***N*²,*N*^{2'}-di(pyridin-4-yl) biphenyl-2,2'-dicarboxamide (3)**

To a stirred solution of biphenyl-2,2'-dicarboxylic acid (0.87 g, 3.59 mmol) in dry CH₂Cl₂ (20 mL), SOCl₂ (0.77 mL, 7.18 mmol) was added and the reaction mixture was refluxed for 10 h. On removal of excess SOCl₂ under reduced pressure, compound **5** was obtained as solid mass, which was directly used in the next step. The symmetrical bisamide **3** was obtained by coupling of 4-aminopyridine (1.09 g, 10.77 mmol) with biphenyl-2,2'-dicarbonyl dichloride **5** in 60 mL dry CH₂Cl₂ followed by addition of triethylamine (2.5 mL) under nitrogen atmosphere. The reaction mixture was stirred for 12 h. After completion of the reaction, solvent was removed under vacuum. The residual mass was extracted with CHCl₃/CH₃OH mixture (30 mL × 3). The organic layer was washed with NaHCO₃ solution (15 mL × 3) and dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure. The crude mass was purified by column chromatography over silica gel using 10% MeOH in ethyl acetate as eluent to afford the desired diamide **3** in 72% yield (1.01 g), m.p. 258 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 9.78 (s, 2H), 8.36 (d, 4H, *J* = 8 Hz), 7.68–7.65 (m, 2H), 7.42–7.37 (m, 8H), 7.13–7.09 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ: 169.6, 150.1, 145.5, 138.7, 135.3, 130.5, 129.6, 128.2, 127.5, 113.9; FTIR (KBr) ν: 3285, 1658, 1592, 1528, 1415, 1366 cm⁻¹; HRMS (TOF MS ES⁺): Calcd for (M+H)⁺: 395.1508, Found: 395.1507.

Biphenyl-3,3'-dicarboxylic acid bis-pyridin-3-ylamide (4)

To a stirred solution of biphenyl-3,3'-dicarboxylic acid (0.87 g, 3.59 mmol) in dry CH₂Cl₂ (20 mL), SOCl₂ (0.77 mL, 7.18 mmol) was added and the reaction mixture was refluxed for 8 h. On removal of excess SOCl₂ under reduced pressure, compound **6** was obtained as solid mass, which was directly used in the next step. The symmetrical bisamide **4** was obtained by coupling of 3-aminopyridine (1.09 g, 10.77 mmol) with biphenyl-3,3'-dicarbonyl dichloride **6** in 60 mL dry CH₂Cl₂ followed by the addition of triethylamine (2.5 mL) under nitrogen atmosphere. The reaction mixture was stirred for 12 h. After completion of the reaction, solvent was removed under vacuum. The residual mass was extracted with CHCl₃/CH₃OH mixture (30 mL × 3). The organic layer was washed with NaHCO₃ solution (15 mL × 3) and dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure. The crude mass was purified by column chromatography over silica gel using ethyl acetate as eluent to afford the desired diamide **4** in 58% yield (0.81 g), m.p. 266 °C. ¹H NMR (d₆-DMSO, 400 MHz) δ: 10.64 (s, 1H), 10.53 (s, 1H), 8.90–8.88 (m, 2H), 8.49 (s, 1H), 8.28–8.26 (m, 3H), 8.18–8.11 (m, 4H), 7.97–7.94 (m, 2H), 7.75 (t, 1H, *J* = 8 Hz), 7.64 (t, 1H, *J* = 8 Hz), 7.38–7.34 (m, 2H); ¹³C NMR (d₆-DMSO, 100 MHz) δ: 165.7, 165.0, 151.6, 144.7, 144.6, 142.0, 139.6, 135.7, 135.6, 135.0, 130.8, 130.3, 129.8, 129.3, 127.5, 127.2, 126.1, 125.6, 123.5, 121.9 (appears unsymmetrical and some carbons overlap); FTIR (KBr) ν: 3299, 1679, 1655, 1557, 1519, 1482, 1333 cm⁻¹; HRMS (TOF MS ES⁺): Calcd for (M+H)⁺: 395.1508, Found: 395.1505.

General procedure for gelation test

The required amount of the compounds was firstly taken in pure organic solvents (1 mL), slightly warmed to dissolve and then cooled to room temperature to allow gelation. For semi aqueous solvents, compounds were firstly dissolved in the organic solvent and then water was added to it. Analyte-responsive behaviour of the compounds was investigated following the same method. In that case, all the guest analytes were taken in water. All the gels were tested *via* the usual inversion of vial method after ~1 h of sample preparation. Samples of gel for SEM image was dried under vacuum and

then coated with a thin layer of gold metal. The gel-to-sol transition temperature (*T*_g) was determined by the dropping ball method.

General procedures of UV-vis and fluorescence titrations

Stock solutions of the compounds were prepared in respective solvents in the concentration of ~10⁻⁵ M. Stock solutions of the metal ions were also prepared in the same solvents in the concentration of ~10⁻³ M. Solution of each compound (2 mL) was taken in the cuvette and to this solution different ions were individually added in different amounts. Upon addition of metal ions, the change in emission of the compound was recorded. The same stock solutions were used to perform the UV-vis titration experiment in the same way.

Method for Job plot^[104]

The stoichiometry was determined by the continuous variation method (Job plot). In this method, solutions of host and guests of equal concentrations were prepared in respective solvent. Then host and guest solutions were mixed in different proportions maintaining a total volume of 3 mL of the mixture. The related compositions for host: guest (V/V) were 3:0, 2.8:0.2; 2.5:0.5, 2.2:0.8, 2:1, 1.8:1.2, 1.5:1.5, 1:2, 0.8:2.2, 0.5:2.5, 0.2:2.8. All the prepared solutions were kept for 1 h with occasional shaking at room temperature. Then emission and absorbance of the solutions of different compositions were recorded. The concentration of the complex, *i.e.*, [HG] was deduced using the equation [HG] = Δ*I*/*I*₀ × [H] or [HG] = Δ*A*/*A*₀ × [H], where Δ*I*/*I*₀ and Δ*A*/*A*₀ indicate the relative emission and absorbance intensities, respectively. [H] corresponds the concentration of pure host. Mole fraction of the host (*X*_H) was plotted against concentration of the complex [HG]. In the plot, mole fraction of the host, at which the concentration of the host-guest complex concentration [HG] is maximum, means the stoichiometry of the complex.

Calculation of detection limit^[103]

The detection limit was calculated from fluorescence titration data. The emission of compound **1** was measured 5 times to measure the standard deviation of the blank. To have the slope, fluorescence intensities at 370 nm were plotted as concentrations of Ag⁺. The detection limit was calculated using the equation: detection limit = 3σ/*k*, where σ is the standard deviation of blank measurement and *k* is the slope.

Results and Discussion

Compounds **1**–**4** were obtained according to the Scheme 1. Simple coupling of biphenyl-2,2'-diacid dichloride **5** with 3-, 2- and 4-aminopyridines in the presence of Et₃N in dry CH₂Cl₂ at room temperature resulted in formation of compounds **1**, **2** and **3**, respectively (Scheme 1). Whereas, under similar reaction conditions, treatment of biphenyl-3,3'-diacid dichloride **6** with

Scheme 1 Synthesis of compounds **1**–**4**

Reagents and conditions: (i) SOCl₂, dry CH₂Cl₂, reflux, 10 h; (ii) 2-, 3-, or 4-amino pyridine, Et₃N, dry CH₂Cl₂, r.t., 12 h; (iii) 3-amino pyridine, Et₃N, dry CH₂Cl₂, r.t., 12 h.

3-aminopyridine introduced compound **4** in appreciable yield. All the compounds were characterized by usual spectroscopic techniques.

Structural analysis reveals that compounds **1–4** possess bispyridyl amide motifs around the aromatic biphenyl spacer that imparts rigidity and conformational flexibility.^[39] In the structures, while the amide NHs act as hydrogen bond donors, the pyridyl motifs serve as hydrogen bond acceptors. Therefore, the molecules may assume different conformations and as such, different hydrogen bonding characteristics in solution.^[38,39] Considering such different attributes, initially the gelation abilities of the compounds **1–4** were examined in a wide range of protic and aprotic solvents with different polarities and coordination abilities. The results are summarized in Table 1S. It was observed that all the compounds showed non-gelation behaviours and remained either as soluble or produced precipitation in most of the solvents. However, in THF, 1,4-dioxan, DMF and DMSO, compound **1** formed white coloured gel in the presence of aqueous Ag^+ ion. In DMSO : H_2O (1 : 2, V/V), it formed gel with lower minimum gelation concentration of 3.9 mg/mL (Figure 2). Under identical conditions, the rest of the compounds behaved as a non gelator. Hence, comparison of aggregation behaviours of compounds **1–3** highlights the positional role of pyridine ring nitrogen with respect to the biphenyl ring, which controls the self-aggregation of the molecules in the presence of Ag^+ ions. Moreover, the contrasting behaviours of compounds **1** and **4** in presence of Ag^+ ions emphasize that the gelation abilities of these molecules depend significantly on the hydrogen bonding interactions of the amide moieties, coupled to the isomeric spacers.

Figure 2 Photograph showing the phase changes of **1** (3.9 mg/mL) in DMSO : H_2O (1 : 2, V/V) in presence of 2 equiv. amounts of different metal ions [$c = 0.4 \text{ M}$ in H_2O as perchlorate salt] after 1 h.

We also investigated the effect of other metal ions on gelation of **1** (Figure 2). Interestingly, except Ag^+ , other metal ions considered in the study were found to be futile in bringing gelation. The presence of other metal ions like Cu^{2+} , Hg^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Mg^{2+} and Fe^{2+} under similar conditions produced either precipitate or solution. These results indicated the metal responsive behaviour of **1** and validated the visual sensing of Ag^+ . In the study, minimum 2 equiv. amounts of Ag^+ ion was necessary to form the thick gel at a gelator concentration of 3.9 mg/mL.

The gel was thermo reversible and upon heating was transformed into clear solution, which upon cooling again to room temperature caused reappearance of the gel (Figure 3a). The thermal stability of the gel was studied in DMSO : H_2O solvent system. At minimum gelation concentration of 3.9 mg/mL, the gel melting temperature (T_g) was recorded as 52°C and a sharp increase in T_g value was observed with increase in gelator's concentration (Figure 3b). Similar gel-to-sol phase transformation was noticed in presence of silver chelating agent (Figure 1S). Initially, the silver metallogel of **1** was treated with external chemical stimuli like Cl^- ion. The addition of 2 equiv. amounts of KCl (in water) on the top of the gel at room temperature scavenged the interlinked Ag^+ ions from the gel matrix

Figure 3 (a) Pictorial representation of the thermo reversibility of the DMSO : H_2O (1 : 2, V/V) gels of **1** (3.9 mg/mL) in presence of Ag^+ (2 equiv.). (b) Variation of gel melting temperature (T_g) with increasing concentration of gelator **1** in DMSO : H_2O (1 : 2, V/V) in presence of 2 equiv. amounts of Ag^+ .

and ruptured the gel to sol (within 1 h) with white precipitate of AgCl . Further addition of Ag^+ to the Cl^- -induced broken gel resulted in reappearance of the gel after 30 min.

The viscoelastic properties of Ag^+ -gel of **1** was characterised by rheological measurements, in which the storage modulus G' and the loss modulus G'' were measured as a function of strain and frequency (Figures 4a and 4b). In strain sweep, a nonlinear response of both G' and G'' was observed with the applied strain amplitude at a fixed frequency ($\omega = 10 \text{ rad/s}$). With gradual increase in the applied stress, both G' and G'' were deviated from linearity at 10% of strain (critical strain) indicating that the gel started to collapse, after which a sharp fall of both G' and G'' values was observed. The gel was completely destroyed beyond a strain of 24% (crossover point). In a frequency sweep experiment, at a fixed strain of 1%, both G' and G'' were frequency invariant over the entire range studied and the values of G' were around seven times greater than G'' at any frequency, signifying dominant elastic character of the metallogel.

The morphology of the metallogel was studied by SEM images that exhibited layer by layer stacking of closely spaced flakes like matrices (Figures 4c and 4d). To our belief, molecules of compound **1** under the influence of intermolecular hydrogen bonding of the amide groups and silver coordination involving two pyridyl units of two different gelator molecules adopt a linear binding geometry that undergoes stacking as proposed in Figure 5.

To support our proposition of interaction, FTIR spectra of compound **1** in its amorphous and gel states were analyzed. Compound **1** in amorphous state showed the stretching for amide $\text{C}=\text{O}$ at 1684 cm^{-1} as sharp signal and it was shifted to

Figure 4 (a) Strain and (b) frequency sweeps of the Ag^+ -gel of **1** (3.9 mg/mL) prepared from DMSO : H_2O (1 : 2, V/V). In both cases, the black symbols represent G' , red symbols G'' . (c) and (d) represent the SEM images of xerogel of compound **1** (3.9 mg/mL) with Ag^+ prepared from DMSO : H_2O (1 : 2, V/V). In all cases, $[\text{Ag}^+] = 2$ molar equiv. with respect to **1**.

Figure 5 Suggested mode of interaction of compound **1** with Ag^+ to form 3D-network in solution.

1646 cm^{-1} with broadening in the gel state (Figure 6a). Moreover, stretching frequency of the amide NH of compound **1** moved to the higher region by 188 units in the gel states. These findings undoubtedly corroborate the important roles of metal chelation and hydrogen bonding during gelation, respectively. In order to understand the metal ligand interactions in detail, we further recorded ^1H NMR of compound **1** itself and with Ag^+ in CDCl_3 containing few drops of d_6 -DMSO (Figure 2S). In general, metal ion coordination leads to downfield chemical shift of the aromatic ring protons.^[39,48,58,103] However, this is not always true for metal ion-induced self-assembled systems.^[21,30,38,56,59] In case of metallogels, the chemical shift of the protons depends entirely upon the self-assembly pattern established after metal coordination. In addition, metal ion coordination is not the only determining factor for showing the chemical shift of the corresponding ring protons, other non-covalent interactions like

Figure 6 Partial FTIR spectra of **1** in (i) amorphous and (ii) gel states. Comparison of UV-vis (b) and fluorescence (c) spectra of compound **1** in the sol and gel states; [Inset: emission spectra of compound **1** in gel state]. In all cases, concentration of **1** is 3.9 mg/mL. The gel was prepared with Ag⁺ (2 molar equiv. with respect to **1**). Solvent is DMSO : H₂O (1 : 2, V/V).

hydrogen bonding, aromatic stacking, and so on, which regulate the growth of the assembly, while working tandem also influences chemical shift of the protons.^[21,30,38,56,59] In ¹H NMR of compound **1** with 2 equiv. amounts of Ag⁺, the upfield chemical shift of the amide NH_a ($\Delta\delta$ 0.04) including all aromatic protons ($\Delta\delta$ 0.04–0.06) indicated metal-ligand interaction (Figure 2S).^[30,38] These results signify that, for ligand **1**, metal binding followed by intermolecular hydrogen bonding simultaneously plays a crucial role during gelation.

To examine the key role of π - π stacking interactions exerted by biphenyl units, UV-vis and emission spectra of compound **1** in sol and gel states were compared. A strong absorption band at 300 nm in UV-vis spectrum of compound **1** in the gel state (Figure 6b) with respect to the sol state corroborated the aggregation-induced planarization of the biphenyl unit that extends the effective π -conjugation length.^[39,105] On the other hand, in emission spectra, it exhibited aggregation-induced quenching, where 32 nm red shifted band in the gel state as compared to sol state was observed (Figure 6c). Additionally, the gel state showed a new band at 500 nm with slightly higher intensity. This indicated that the gel formation occurred not only due to metal coordination but also the π - π stacking of the biphenyl units^[39,105] played a significant role during aggregation process.

In order to correlate the selective gelation of compound **1** by Ag⁺, solution phase interactions studies were conducted. We performed UV-vis and fluorescence titrations of **1** ($c = 2.5 \times 10^{-5}$ M) in DMSO : H₂O (1 : 9, V/V). In fluorescence, compound **1** initially showed emission band at 370 nm upon excitation at 290 nm. Figure 7a represents the change in fluorescence ratio of compound **1** at 370 nm in the presence of 6 equiv. amounts of metal ions and highlights the sensitivity towards Ag⁺ over the other metal ions taken in the study. During titration, while intensity of the emission at 370 nm underwent significant enhancement only in the presence of Ag⁺ ions (Figures 7b and 3S), other metal ions gave a negligible effect on emission of compound **1**.

Ag⁺-induced greater enhancing of emission at 370 nm even in the presence of other metal ions corroborated the selectivity of compound **1** towards silver ions (Figure 8a), where other metals in the study were found to be noninterfering. In this process, the detection limits^[103] for Ag⁺ was determined to be 2.64×10^{-6} M (Figure 4S). The binding constant^[106] values were found to be $K_1 = (1.25 \pm 0.48) \times 10^4 \text{ M}^{-1}$ and $K_2 = (4.94 \pm 1.83) \times 10^4 \text{ M}^{-1}$, respectively, with 1 : 2 (**1** : Ag⁺) stoichiometries^[104] (Figures 5S and 6S).

In UV-vis titration of compound **1**, in presence of Ag⁺ ion, the intensity of the absorption peak at 290 nm was increased

Figure 7 (a) Change in fluorescence ratio ($\lambda_{\text{ex}} = 290 \text{ nm}$) of compound **1** ($c = 2.5 \times 10^{-5} \text{ M}$) at 370 nm upon addition of 6 equiv. amounts of metal ions ($c = 1.0 \times 10^{-3} \text{ M}$) and (b) change in emission of compound **1** ($c = 2.5 \times 10^{-5} \text{ M}$) upon addition of 6 equiv. amount of Ag^+ in $\text{DMSO} : \text{H}_2\text{O}$ (1 : 9, V/V).

Figure 8 (a) Fluorescence response of compound **1** ($c = 2.50 \times 10^{-5} \text{ M}$) upon addition of 6 equiv. amounts of Ag^+ ions to the solution of **1** containing other metal ions in 6 equiv. amounts in $\text{DMSO} : \text{H}_2\text{O}$ (1 : 9, V/V). (b) Change in absorbance of compound **1** ($c = 2.50 \times 10^{-5} \text{ M}$) upon addition of 6 equiv. amount of Ag^+ ($c = 1.0 \times 10^{-3} \text{ M}$) in $\text{DMSO} : \text{H}_2\text{O}$ (1 : 9, V/V).

significantly, where other metal ions resulted in negligible change in the absorption spectra (Figures 8b and 7S). From Job method,^[104] 1 : 2 ligand-metal interaction was confirmed, and the binding constant values^[106] were calculated to be $K_1 = (5.02 \pm 3.81) \times 10^3 \text{ M}^{-1}$ and $K_2 = (1.02 \pm 0.76) \times 10^5 \text{ M}^{-1}$, respectively (Figures 5S and 6S).

Conclusions and Perspectives

In conclusion, a series of pyridyl bisamides coupled to biphenyl skeleton have been designed and synthesized. Out of the bisamides **1**–**4**, only the compound **1** is established as a potential gelator that forms gel in presence of Ag^+ ions and validates its visual sensing. The nongelation behaviour of other derivatives **2** and **3** highlights the positional role of pyridine ring nitrogen with respect to the biphenyl ring during self-aggregation in the presence of Ag^+ ions. In relation to this, different behaviours of the *ortho* and *meta* derivatives **1** and **4**, respectively, towards gelation in presence of Ag^+ ions is interesting. The findings signify that the gelation abilities of these molecules depend significantly on the hydrogen bonding interactions of the amide moieties around the isomeric biphenyl spacers. Spectroscopic studies confirm that the metal coordination as well as the hydrogen bonding involving the amide NHs of compound **1** play a crucial role in establishing the gel network in solution. Compound **1** also selectively recognizes Ag^+ ions fluorimetrically in a *turn-on* mode in solution. Exploration of biphenyl-based gelators in selective metal ion recognition is rare (as most of them suffered interference from other metal ions) in the literature (Table 2S), and hence, compound **1** draws attention.

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Author Contributions

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Supporting Information

Figures show the changes in emission and absorption spectra, binding curves, detection limit, NMR and mass studies, copies of ^1H NMR, ^{13}C NMR and HRMS spectra.

Conflict of Interest

The authors declare no conflict of interest.

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