Metal-ion Induced Low Molecular Weight Gel

M.Sc. Thesis

By JONU YADAV



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY, 2016

Metal-ion Induced Low Molecular Weight Gel

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree **of**

Master of Science

by JONU YADAV



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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Metal-ion induced low molecular weight gel** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from JULY, 2014 to JULY, 2016 under the supervision of Dr. Apurba K. Das, Associate Professor, Discipline of chemistry, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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M.Sc. II year Discipline of Chemistry IIT INDORE

Dedicated to my grandfather (baba) and my family

Abstract

We report molecular state of self-assembly of a amino acid based discotic molecule using spectroscopic and microscopic techniques. Discotic moiety containing phenylalanine forms a metallogel using LiOH at room temperature. The hydrogen bonding and π - π stacking are responsible for the formation of self-assembled metallogel, which is confirmed by FTIR, wide angle X-ray scattering and fluorescence spectroscopic study. SEM revels that the gelator molecules self-assemble into left-handed helical nano-fiber like structure. The viscoelastic nature of the metallogel was investigated by rheological experiments.

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NOMENCLATURE

| θ | Angle |
|----|------------|
| λ | Wavelength |
| Å | Angstrom |
| nm | Nanometer |
| cm | Centimeter |
| π | pi |

ACRONYMS

Abbreviations used for compounds, substituents, reagents, etc. are largely in accordance with the recommendations of the IUPAC. Additional abbreviations used in this thesis are listed below.

| SEM | Scanning Electron Microscopy |
|---------------------|---|
| CDCl ₃ | Chloroform-d |
| DMSO-d ₆ | Dimethyl Sulfoxide-d ₆ |
| d | Doublet |
| DMF | Dimethyl Formamide |
| EtOH | Ethanol |
| EtOAc | Ethyl Acetate |
| ESI-MS | Electrospray Ionization Mass Spectrometry |
| HCl | Hydrochloric Acid |
| MeOH | Methanol |
| LiOH | Lithium Hydroxide |
| NMR | Nuclear Magnetic Resonance |
| S | Singlet |
| t | Triplet |
| THF | Tetrahydrofuran |
| TLC | Thin Layer Chromatography |
| UV-Vis | UV-Visible Spectroscopy |

_____{ i }____

Chapter 1: Introduction and Reaction Scheme:

1.1 Introduction:

The self-assembly is a spontaneous process in which molecules combine into ordered nanostructures and deliver a bottom-up approach to obtain the structural regularity of various morphologies such as fibers^[1], helix^[2] and rectangles.^[3] A large amount of organic solvent or water could entrap into these self-assembled nanostructure forming supramolecular organogels or hydrogels.^[4-10] As name suggest, organogel represents the gelator molecules that immobilize organic solvents while hydrogel represents the molecules that immobilize water. These gels are commonly recognized by their flow characteristics, despite being mainly liquid in composition (usually 99% by weight of the gel is liquid) they afford solid like appearance and do not flow. Supramolecular organogels or hydrogels can be formed through the involvement of non-covalent interactions such as hydrogen bonding, π - π stacking, van der Waals and electrostatic interactions. Owing to the weak character of these forces, supramolecular gels can change their physical or chemical behavior, often reversibly, when they acted upon by some external stimuli such as sound, light, field.[11-16] redox and chemicals, temperature, magnetic pН, Supramolecular gels can be used in chemosensors^[17], pollutants capturing</sup> and removal, drug delivery and several other applications.^[18-23] Synthetic peptides also form gel as usually they self-assemble to form various supramolecular structure such as hollow fibers^[24], tapes^[25] and tubes.^[26]

Metallogels are one such class of supramolecular gels in which metal ions incorporates into the ordered nanostructure of gelator molecule and forms gel.^[27-52] LMWGs containing metal ion have various non-covalent interactions but they also have strong coordination-interaction between gelator moiety and metal ions. These coordination-interaction play a key role in the formation of gel fiber network.^[53-55] Several complexes^[56],

coordination polymers^[57-59] or cross-linked coordination polymers^[60] also form gel fibers through molecular self-assembly. Non-coordinated metal and metallic nanoparticals may also be incorporated into the gel matrices.^[61,62] With the involvement of metal ion in the gel structures, metallogels have acquire unique and interesting properties, which could hardly be achieved by organic compounds alone. Thus, metallogels can be turned to imparts redox, magnetic, catalytic and spectroscopic properties.^[63-69] Similarly, "tuning" of gel behavior by metal ion and anion binding is also become very active area of research.^[70-76] Although synthesis of all metallogels are almost same, depend on the self-assembly of gelator molecules in the appropriate conditions but they differ mainly in the metal ion used, which directly influences their functions. Over the years, many transition metals effectively incorporate into the gelator moiety and formed beneficial metallogels. Among numerous metals ions that are used, metallogel of gold ion appears as a red-luminescent gel, which formed by Au(I) in trinuclear gold(I) pyrazolate complexes with long akyl chains and hydro-metallogel of gold ion appear as a transparent hydrogel, which formed by Au(III) and glutathione.^[77] Due to high affinity to bind with nitrogen, silver metal ion also formed stable supramolecular metallogels.^[78] However, copper ion have a unrestricted nature that allows them to bind with several kind of ligands, which readily form stable metallogels with several distinct properties. Metallogels formed by copper ion with bipyridines can lead to research about the coordination of copper ion to DNA base pair.^[78] Copper ion can easily binds with oxalic acid dihydrate, which can be used as proton conductor.^[79] One of the recent studies in copper hydrogels that shown self-healing properties in which metallogel formed through coordination with glyme.^[80] Therefore, formation of metallogels with different types of metal ions are very active area of interest from early decades to date.[55,81-83]

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Fig. 1: Schematic representation of self-assembly into metallogel.

So, we require a perfect moiety for our desire interest for the formation of new class of metallogel. Benzene-1,3,5-tricarboxamide (BTA) moiety plays an important role in the formation of supramolecular metallogel.^[84] They have three amide groups which are not only capable of intermolecular hydrogen bond formation but also effectively coordinate with metal ion turn out to be highly beneficial in immobilizing solvent molecules.^[85]

The nature of the side chain the BTA molecules also play an important role in the potential application. For example, BTAs comprising bulky, aliphatic side chains are high melting crystalline solids, which crystallize as fiber-like needles, long alkyl side chains induce thermotropic liquid crystalline behavior and branched alkyl side chains result in organogel behavior.^[86] Inspiring from these various important applications of BTA based compounds, we have selected L-phenylanaline as side chain and by coupling it with trimesic acid, we have prepared 2-[3,5-Bis-(1-methoxycarbonyl-2-phenyl-ethylcarbamoyl)-benzoylamino]-3-phenyl-propionic acid methyl ester.



1.2 Reaction Scheme:



Reagents: (i) distilled SOCl₂, dry MeOH ; (ii) (3) HOBt, DIPC, dry DMF ; (iii) 1 (N) LiOH, dry THF.

Chapter 2: Experimental sections:

2.1 Materials:

Amino acid, diisopropylcarbodiimide (DIPC), and 1-hydroxybenzotriazole (HOBt) were purchased from Sigma-Aldrich, India. All the solvents, which were used in the reactions and for column chromatography were properly dried and distilled. All the synthesized products were dried under high vacuum pump before sample characterizations (¹H NMR, ESI-MS). Milli-Q water was used for reaction purposes.

2.2: Synthesis of compounds:

2.2.1 Synthesis of methyl ester of L-phenylalanine:

20 mL dry methanol was taken in 250 mL round bottom flask stirring with a magnetic bar. Methanol was cooled in ice bath for 10 min. Thionyl chloride (2.65 mL) was added dropwise in cooled methanol. Then, Lphenylalanine (3 g, 18.16 mmol) was added to the reaction mixture. The reaction mixture was stirred for overnight. The reaction mixture was evaporated using rotavapor. Then, the reaction mixture was washed with diethyl ether. The compound was dried on a vacuum pump.

2.2.2 Synthesis of 2-[3,5-Bis-(1-methoxycarbonyl-2-phenylethylcarbamoyl)-benzoylamino]-3-phenyl-propionic acid methyl ester:

0.5 g (2.37 mmol) of benzene-1,3,5- tricarboxylic acid was dissolved in a mixture of 1.5 mL of dry N,N-dimethyl formamide (DMF) and cooled in an ice-water bath. NH₂-Phe-OMe was isolated from 1.983 g (9.2 mmol) of the corresponding methyl ester hydrochloride by neutralization with saturated sodium carbonate, subsequent extraction with ethyl acetate. This was added to the reaction mixture, followed immediately by 1.2 mL (3.3

mmol) of N,N'-diisopropylcarbodiimide (DIPC) and 0.966 g (3 mmol) of HOBt. The reaction mixture was allowed to cool down at room temperature and stirred for 24 h. DMF was evaporated, and the residue was taken in ethyl acetate. N, N'-diisopropylurea was filtered off. The organic layer was washed with 1N HCl (3×20 mL), brine water (3×20 mL), 1N sodium carbonate (3×20 mL) solution. Then the organic layer was dried over anhydrous sodium sulphate and evaporated under vacuum to yield 1.2 g of compound **2** (73.00%). ¹H NMR (400 MHz, CDCl₃, TMS, r.t).) δ 8.14 (s, 3H, ArH), 7.08-7.25(m, 15H, Phe), 6.80 (d, 3H, -NH), 3.11-3.23 (m, 6H, -CH₂), 4.98-5.03 (q, 3H, -CH), 3.70 (s, 9H, -OCH₃) ppm; ¹³C NMR (100 MHz, CDCl₃); δ 172.33, 165.23, 136.01, 134.64, 129.21, 128.71, 127.24, 54.17, 52.58, 37.87 ppm; MS (ESI) m/z for C₃₉H₃₉N₃O₉ calcd.: 693.2, found: 716.2 [M+Na]⁺.

2.2.3. Synthesis of 2-[3,5-Bis-(1-carboxy-2-phenylethylcarbamoyl) benzoylamino]-3-phenyl-propionic acid:

A solution of 2-[3,5-Bis-(1-methoxycarbonyl-2-phenyl-ethylcarbamoyl)benzoylamino]-3-phenyl-propionic acid methyl ester (200 mg, 0.288 mmol) in 20 mL of dry THF was allowed to react with 1M LiOH solution. The progress of the reaction was monitored by thin layer chromatography (TLC). The reaction mixture was stirred for 2 h. Then, THF was removed under vacuum. The residue was taken in water and washed with diethyl ether (2 x 20 mL). The pH of aqueous layer was adjusted to 2 using 1 M HCl and it was extracted with ethyl acetate (3 x 30 mL). The ethyl acetate layer was dried over anhydrous sodium sulfate and evaporated under vacuum to yield the desired product. Yield = 120 mg (63%); ¹H NMR (400 MHz, DMSO-d6): δ 8.96 (d, 3H, -NH), 7.15-7.30 (m, 15H, Phe), 4.62-4.67 (q, 3H, -CH), 3.04-3.21 (m, 6H, -CH₂), 8.30 (s, 3H, ArH) ppm; MS (ESI) *m/z* for C₃₆H₃₃N₃O₉ calcd.: 651.6., found: 652.6 [M+H]⁺.

2.2.4 Preparation of Gel:

A solution of 2-[3,5-Bis-(1-methoxycarbonyl-2-phenyl-ethylcarbamoyl)benzoylamino]-3-phenyl-propionic acid methyl ester (60 mg, 0.086 mmol) in 5 mL of dry THF was allowed to react with 1M LiOH (300 μ L) solution. The progress of the reaction was monitored after every 15 minutes by thin layer chromatography (TLC). The reaction mixture was stirred for 90 minutes and the gel was formed.

2.3 General methods:

All the chemicals and reagents were obtained commercially. All NMR spectra were recorded at 400 MHz Bruker Advance III 400 NMR. Compounds concentrations were in the range of 1-10 mmol in (CD₃)₂SO and CDCl₃. Mass spectra were recorded on Bruker micrOTOF-Q II by positive mode electrospray ionizations.

2.3.1 Rheology:

Rheological measurements were carried out using an Anton Paar Physica MCR 301 rheometer with parallel plate of geometry (25 mm in diameter, 0.200 μ m gap). 200 μ L of gel was prepared in glass vial and transferred onto the plate of the instrument using microspatulla. The temperature was kept at 25 °C by using an integrated temperature controller. To investigate the rheological properties of gel, we measure dynamic frequency sweep as function of frequency in the range of 0.05-100 rad s⁻¹ with constant strain value 0.1%. To determine the exact strain for frequency sweep, the linear viscoelastic (LVE) regime were performed at a constant frequency of 10 rad s⁻¹.

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2.3.2 Morphology (SEM):

Field-emission Gun-scanning electron microscopic study was done by using Jeol Scanning Microscope-JSM-7600F. The gel sample was dried on a glass cover slip and coated with gold.

2.3.3 Wide angle X-ray scattering:

The Wide angle X-ray scattering measurements were performed using Rigaku Smart Lab, Automated Multipurpose X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of the X-ray was 1.54 Å (Cu K-alpha). The X-rays were detected using a linear counting detector based on silicon strip technology (Scintillator NaI photomultiplier detector).

2.3.4 FT-IR:

Fourier transform infrared (FTIR) spectra of compound **2** and gel were recorded on Bruker (Tensor 27) FTIR spectrophotometer. FTIR of compound **2** was performed with KBr pellet technique. In case of gel, the gel sample was placed between ZnSe windows and scanned between 700 and 3600 cm⁻¹ over 16 scans at a resolution of 4 cm⁻¹ and an interval of 1 cm⁻¹.

2.3.5 UV-Vis spectroscopy:

UV-Vis absorption spectrum of gel (20 mmol L⁻¹) was recorded using a Varian Cary100 Bio UV-Vis spectrophotometer.

2.3.6 Fluorescence spectroscopy:

Fluorescence emission spectrum of gel (20 mmol L^{-1}) was recorded on a Horiba Scientific Fluoromax-4 spectrophotometer with a 1 cm path length quartz cell at room temperature. The slit width for the excitation and emission was set at 2 nm and 1 nm data pitch. Excitation of sample was performed at 335 nm and the data range was in between 345 to 650nm.

Chapter 3: Results and discussion:

3.1. Synthesis of compounds:

A metallogel containing discotic moiety having an amino acid was prepared for the molecular state of self-assembly study. Gel was formed from 2-[3,5-Bis-(1-carboxy-2-phenyl-ethylcarbamoyl)-benzoylamino]-3phenyl-propionic acid (1), which was synthesized according to reaction scheme described above. Starting from commercially available Lphenylanaline which was treated with thionylchloride in dry MeOH medium followed by esterification to the synthesis of compound (3)according to the reported method.^[39] Then, coupling of compound (3) with benzene-1,3,5-tricarboxylic acid in presence of coupling reagents N,N'diisopropylcarbodiimide (DIPC), hydroxybenzotriazole (HOBt) in dry N,N-dimethyl formamide (DMF) medium 2-[3,5-bis-(1-methoxycarbonyl-2-phenyl-ethylcarbamoyl)-benzoylamino]-3-phenyl-propionic acid methyl ester (2) was synthesized. Compound (1) was synthesized by base catalyzed hydrolysis of compound (2). The self-assembly of the gel was studied by rheology, fluorescence, SEM, FT-IR and wide angle X-ray scattering. Compounds **1-3** were characterized by ESI-MS, ¹H NMR.

3.1.1: Rheology study of gel:

Rheological measurements (Fig. 2 and Fig. 3) demonstrate the viscoelastic properties of gel. Viscoelastisity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. To investigate the rheological properties of gel (20 mmol L^{-1}), we measure dynamic frequency sweep as a function of frequency in the range of 0.05-100 rad s⁻¹ with constant strain value 0.1%. To determine the exact strain

for frequency sweep, the linear viscoelastic (LVE) regime were performed at constant frequency of 10 rad s⁻¹. The values of the storage modulus (G[']) (that describes the elastic properties) exceeded those of the loss modulus (G^{''}) (that describes the viscous properties) by an order of magnitude, which indicates the formation of strong and rigid gel.^[87]



Fig. 2: Rheological measurement: LVE of gel at a constant frequency 10 rad s⁻¹.



Fig. 3: Dynamic frequency sweep of gel at a constant strain 0.1%.

3.1.2: Morphological study of gel:

SEM was performed to investigate the self-assembled morphological diversity of gel. We performed scanning electron microscopy to study the morphological features. As shown in the SEM image (Fig.4), a left-handed helical nano-fiber like structure was observed for the gel formed by compound 2 with an average width of the helix 50 nm.



Fig. 4: SEM image indicating helical nano-fiber like structure of gel.

3.1.3 Wide angle X-ray scattering study of gelator molecule and dried gel:

To attain the structural features of the gel formed by compound **2**wide angle X-ray scattering was performed. (Fig. 5) For dried gel, the scattering patterns appeared at $2\theta = 18.134$ and 20.932 with corresponding d spacing of 4.87 Å and 4.23 Å respectively. 4.23 Å peak suggests the presence of intermolecular π - π stacking interactions between two aromatic groups in the gelator molecule.^[88] For compound **2**, the scattering patterns appeared at $2\theta = 15.199$, 17.200, 19.601, 20.800, 25.463 and 26.796 with the corresponding d spacing values of 5.824 Å, 5.167 Å, 4.529 Å, 4.277 Å, 3.500 Å and 3.347 Å respectively. The reflection peaks appeared at 4.2, 3.5 and 3.347 Å suggest the presence of intermolecular π - π stacking interactions between two aromatic groups of compound **2**.^[89]



Fig. 5: Wide angle X-ray scattering of dried gel and compound 2

3.1.4 FT-IR study of gelator molecule and gel:

FT-IR study of compound **2** (Fig. 6) and gel (Fig. 7) were performed to get more idea about the secondary structural arrangement of the supramolecular metallogel. N-H stretching bands observed at 3228 and 3264 cm⁻¹ for compound **2** and gel respectively, indicate strong hydrogen bonding interaction in both cases. In solid compound **2**, peak appeared at 1642 cm⁻¹ corresponding to the C=O stretching vibration of amide, along with an absorption band at 1545 cm⁻¹ corresponding to the N–H bending vibration. In gel state, peak appeared at 1678 cm⁻¹, along with a peak at 1558 cm⁻¹, which indicates that the gel self-assembled through hydrogen bonding interaction into a helical nanofiber like structure. In solid gelator molecule, a peak appeared at 1747 cm⁻¹, which indicates the presence of ester group, However in gel state the peak is shifted to 1729 cm⁻¹ that clearly indicates that ester is converted into carboxylate ion in gel state.



Fig. 6: FTIR spectrum of compound 2



Fig.7: FTIR spectrum of gel

3.1.5: Absorption and emission spectra of gel:

To get more detailed information of the molecular arrangement of gel, absorption and emission spectra of gel were acquired. The characteristic peak in absorption spectrum for gel (20 mmol L⁻¹) appears at 335 nm (Fig. 8). This intense absorption peak was corresponds to the π to π^* transition of the carbonyl group. In emission spectrum, the characteristic emission peaks for gel (20 mmol L⁻¹) appears at 380 and 420 nm in the solution (Fig. 9). Excitation wavelength for sample was 335 nm and the data range was in between 345 to 650 nm. The fluorescence emission spectrum reveals that π - π stacking interactions play an important role towards the formation of higher ordered self-assembled structures in the self-assembly process. The emission peak at 380 nm corresponds to the π - π stacking interaction between the two aromatic groups during the self-assembly process in the gelator compound.



Fig. 8: Absorption spectrum of gel



Fig. 9: Fluorescence emission spectrum of gel ($\lambda ex = 335$ nm).

Chapter 4: Conclusion:

In this project, we reported molecular state of self-assembly of an α -amino acid based discotic molecule using spectroscopic and microscopic techniques. Li⁺¹ ion induced metallogel was achieved via mixing the phenylalanine incorporated discotic moiety with 1N LiOH solution in THF at room temperature. The self-assembled supramolecular metallogel matrix was formed through hydrogen bonding, π - π stacking and van der Waals interactions. These supramolecular interactions were investigated via FTIR, wide angle X-ray diffraction and fluorescence spectroscopic studies. Scanning electron microscopic studies reveal the gelator molecules self-assemble into a left-handed helical nano-fiber like structures that formed a self-supporting supramolecular metallogel. The rheological experiments demonstrated the strength of the metallogel as gel was strong and rigid enough by external forces.

Appendix A: ¹H NMR, ¹³C NMR and Mass spectra of compounds: NMR Spectra:



Fig. 10: 400 MHz ¹H NMR spectrum of compound 2 in CDCl₃



Fig. 11: 100 MHz ¹³C NMR spectrum of compound 2 in CDCl₃



Fig. 12: 400 MHz ¹H NMR spectrum of compound 1 in CDCl₃

ESI-MS spectra:



Fig. 13: ESI-MS spectrum for compound 2



Fig. 14: ESI-MS spectrum for compound 1

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