

Supramolecular Organogel of Tetrafluoromethylaniline copper (II) nitrate Derivative and its Spectroscopic study

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Article Information

Received : March 11 2021
Revised : April 12 2021
Accepted : April 18 2021
Published : April 30 2021

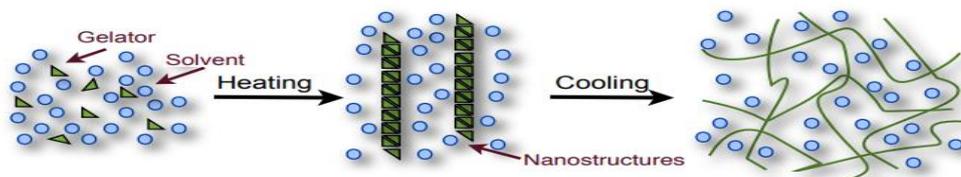
Abstract— Electron-bearing alpha-cyanostyrene removing tetrafluoromethyl groups was produced. Due to the restriction of intramolecular rotations, the alpha-cyanostyrene skeleton supports accumulation improved emission behaviour. Remarkably, similar to its solution state, the cyanostyrenes possessing simple tetrafluoromethyl (CF₃) substituents form stable organogels with improved fluorescence emission. In water, via intermolecular H- bonding, π - π stacking, and cyano substituent associations, the CF₃ substituted self-assembles to an interconnected fibrous nano/microstructures. Using scanning electron microscopy (SEM), infrared microscopy, the morphological characteristics of the aggregates and the gels were substantiated studied, infrared spectroscopy shows multiple functional groups.

Keywords: Organogel, Synthesis, Spectroscopy.

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Graphical abstract for supramolecular gels

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Citation: “Rooshan W. “Supramolecular organogel of tetrafluoromethylaniline copper(II) nitrate derivative and its spectroscopic study”, Journal of Science, Computing and Engineering Research, 2(2), 164-168, 2021.

I INTRODUCTION

π -Conjugated organic fluorophores are also of considerable significance as optoelectronic and biological resources for their own applications [1]. Synthetic feasibility, desired optical characteristics including certain absorption, solution emission, and solid state, and switchable redox functionality can all be improved by applying enough push-pull functional groups [2] Photochemical interconversions are useful for a wide range of optical and biological uses [3]. Furthermore, the use of diarylethylene scaffold-bearing conjugated substances as sensors, photochromic compounds, and cellular imaging has taken on a more streamlined process. [4]. Cyanostilbene derivatives, amongst these materials with this ethylene scaffold, have received much interest to the creation of novel functional materials, especially because of their specific characteristic emission, called Aggregation Induced Enhanced Emission (AIEE), in aqueous media [5].

The inclusion of acceptable push-pull substituents in the cyanostilbene architecture enabled the development of different emission-characteristic luminogens and morphological attributes [6]. In comparison to the weaker emissions in the solution state, such fluorophores show strikingly increased emissions in an aggregated state. The limitation of intramolecular rotation (RIR), the formation of

aggregates of the H- or J-type, charge transfer and other excited state mechanisms are due to this emission activity [7]. The lower molecular weight π -conjugated organic molecules often self-assemble to micro structures apart from their peculiar emission and morphological activity [6]. Such self-assembly of functional organic compounds bearing desirable substituents such as steroidal or alkyl chains, caused by a combination of non-covalent interactions such as H-bonding, π - π stacking, van der Waals force [7].

Organogel frameworks generated from π -conjugated molecular systems have interesting uses as substances that emit white light, sensing and imaging [8]. In this work, we modelled and formed π -conjugated substrates possessing trifluoromethyl (CF₃) substituents of alpha-cyanostyrene. Previous literature studies indicate that the incorporation of CF₃ groups gives the molecular systems excellent gelation properties (low molecular weight organogels: and also results in increased emissions [9]. The architecture and its electronic structure are also considered to be influenced by structural modifications to the π - scaffold. Scanning electron microscopy (SEM) and infrared spectroscopy have characterised the self-assemblies and organogels (FTIR).

II MATERIALS AND METHODS

A. Materials

All the chemicals, reagents needed for the synthesis of anthracene derivatives were bought from Sigma-Aldrich, all the synthesized samples were characterized as an internal standard using Bruker Avance 500 MHz NMR spectrometer using ^1H NMR in CDCl_3 with Tetramethylsilane (TMS). Using Analytic Jena specord 210, UV-Vis absorption spectra were published. Scanning electron microscopy (SEM) experiment was undertaken by field emission SEM (JSM 7600F JEOL). For this reason, with the aid of a double sided adhesive carbon tape, one drop of the sample [$\sim 10^{-6}$ M solution in water] were deposited on a Si-wafer placed on an Aluminum stub. In order to ensure complete elimination of any residual water, the samples were heat-dried at 35°C for 12 h and vacuum-dried for 30 min and coated with platinum before being evaluated. The rheological properties of gels are evaluated using the Anton Paar MCR 302 rheometer, regulated by strain and stress. A standard cone and plate geometry with a cone diameter of 25 mm and a substrating angle of 2° with a distance of 0.10^5 mm is used at a constant temperature of 20°C , and rheological parameters are estimated of the small amplitude oscillatory frequency sweep and high amplitude oscillatory sweep.

B. Methodology

1. Synthesis of Schiff base ligand

Salicylaldehyde (1.07 mL, 10.00 mmol) was refluxed with 2, 5-difluoromethylaniline (1.10 g, 10.00 mmol) in ethanol for 3-4 hours and the precipitated which was orange in colour was form. Filtration of the precipitated product was done under suction, washed with ethanol and recrystallized from ethanol. The product obtained was dried over silica gel in a desiccator [10].

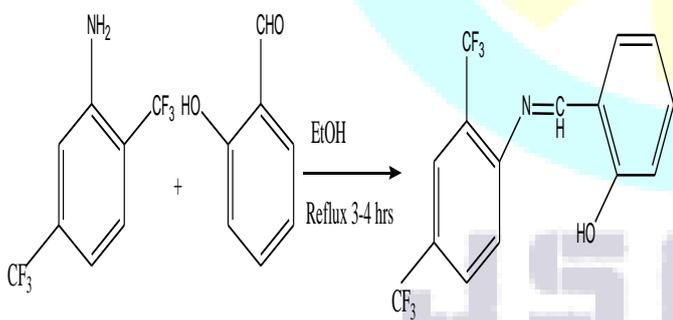


Figure 1 synthesis of Schiff base ligand

2. Synthesis of metal complex

Copper nitrate, (0.123 g, 0.617 mmol) was completely dissolved in ethanol (10 mL) and (0.30 g, 1.23 mmol) ethanolic solution of the synthesized ligand was added dropwise with vigorous stirring. A green precipitated of the product was form which was suction filtered, washed with ethanol and dried in a desiccator [10].

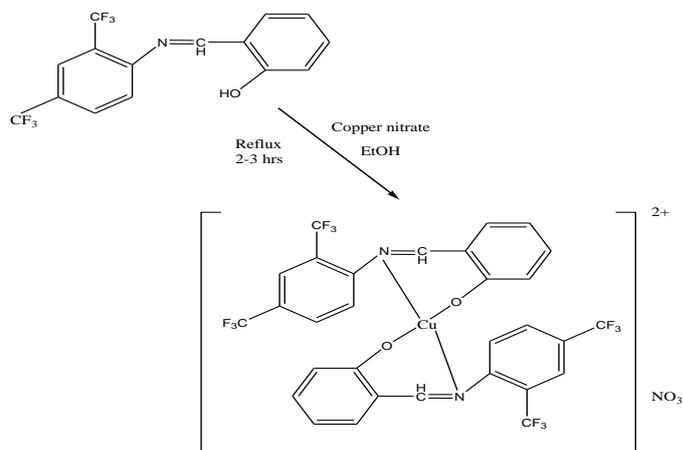


Figure 2 synthesis of nitrate complex

3. CD measurements

In the desired solvent, a gel was prepared at the mgc. Then the gel solvent was extracted to obtain the xerogel under vacuum. Samples were prepared by mixing xerogels in an agate mortar at approximately $0.020\text{-}0.025$ mmol g^{-1} with KBr (1.2-1.6 wt. percent) and pressing the mixture for 10 minutes. Translucid discs were acquired using a JASCO-715 spectropolarimeter and the CD spectra were reported and analyzed using the associated software. In order to obtain representative data, data recording was repeated at 15-20 times rotating the thin film 120° in each.

III RESULTS AND DISCUSSIONS

1. UV-visible spectroscopy

The substituted tetrafluoromethyl was synthesized and studied in the solution and solid state for its absorption activity. The compound has the tetrafluoromethyl (CF_3) group and the effect on the emission properties caused by aggregation has been studied. The absorption does not display any major changes following the incorporation of CF_3 groups with a maximum absorption range of between 386 nm and 411 nm in different solvents. Only a meagre effect on the absorption spectrum is replacement by heavy electron removing CF_3 group and solvent polarity. However, broader bands with a slight red-shift absorption effect have been found in water [11].

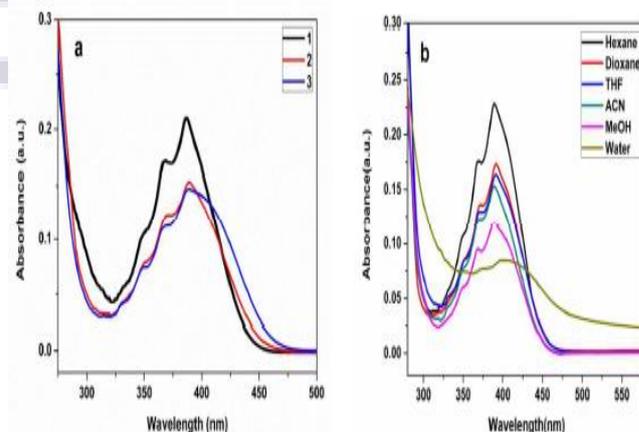


Figure 3 Absorption spectra in (a) CAN (b) different organic solvents

With the increase in solvent polarity, solvatochrome emission shifts (+ 59 nm) were noted in the UV-visible spectra of a synthesised ligand (Figure 4) emitting at ~430 nm in heptane. Similarly, complex emits at ~435nm in heptane and displays similar solvatochrome changes (+56nm) in higher polarity solvents with peaks at 474-490 nm. CF₃ does not play a role in enhancing solvatochromic properties despite its electron withdrawing power [11]. This is likely because there is no resonance effect due to the absence of orbitals or electron pairs that may overlap with those of the aromatic ring. Nevertheless, we reported major emission changes in water (+16-23 nm) with emission bands at 505 nm for ligands, 513 nm for complexes. This unique aqueous media emission activity is due to the exquisite phenomenon known as increased emission caused by aggregation or the product of intramolecular rotation restrictions that block the non-radiative decay pathway [11].

Table I: Absorption and emission of compounds in organic solvents and water

Compds	Solvents	λ_{abs} (nm)	λ_{em} (nm)	Stokes Shift (cm^{-1})	Quantu m yield (ϕ_f)
Ligand	Heptane	386	430	2650	0.00243
	Dioxane	388	461	4081	0.00365
	THF	388	473	4631	0.0098
	Acetonitrile	386	450	3684	0.00187
	Methanol	389	489	5257	0.00345
	Water	388	505	5971	0.0037
					0.0444
Complex	Heptane	389	435	2718	0.0024
	Dioxane	391	457	3693	0.0027
	THF	391	474	4478	0.0039
	Acetonitrile	388	450	3550	0.0020
	Methanol	393	490	5037	0.0046
	Water	402	513	5382	

2. FT-IR studies

In FT-IR spectra of ligand, the 1606 cm^{-1} stretching mode allocated to (C = N) in the Schiff base ligand indicates that the 2,4-difluoroaniline group was converted to the azomethine group. At 1281 cm^{-1} band, the aniline stretching vibration was moved to 1149 cm^{-1} , supporting the aniline oxygen atom complexation [12]. The appearance of the band allocated to (OH) in free Schiff base ligand at 3431 cm^{-1} stretching mode indicate that the hydroxyl group was presence in the Schiff base ligand. Similarly, in FTIR spectra of copper (II) nitrate (Table 2), the free Schiff base ligand with a band at 3431 cm^{-1} allocated to (OH) group was shifted to a lower absorption frequency of 3436 cm^{-1} , which showed that it was coordinated to the metal atom. The azomethine band changed from 1606 cm^{-1} to the lower absorption band of 1616 cm^{-1} in the complex suggests that the (C=N) group was coordinated to the metal atom. Thus, the ligand is known as bidentate [12].

Table II. FTIR spectra of Schiff base ligand and copper nitrate

Functional groups	Frequency of Ligand cm^{-1}	Frequency of Complex cm^{-1}
OH	3431	3436
C-H	1848	1962
C=N	1606	1616
C-O	1281	1187
Cu-N	-----	578
Cu-O	-----	464

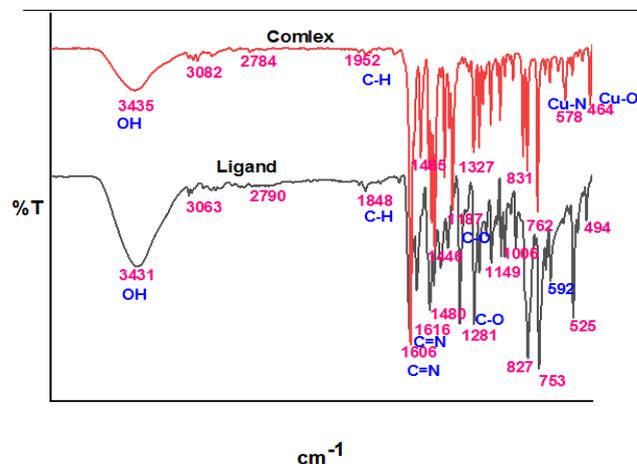


Figure 4 FTIR spectra of the synthesized ligand and its complex

3. Morphology

The microstructures of the gel networks were examined through SEM techniques to obtain a visual insight into the morphologies of the molecular aggregation mode. As shown in Fig. 5. The DMF complex microstructures form normal belts of 1 to 3 μm in width and tens of micrometers in length. The morphologies of the aggregates shown in the SEM images can be rationalized by taking into account a widely understood principle that intermolecular interactions are highly directional. Favors the development of belt structures such as hydrogen bonding or π - π interactions [13].

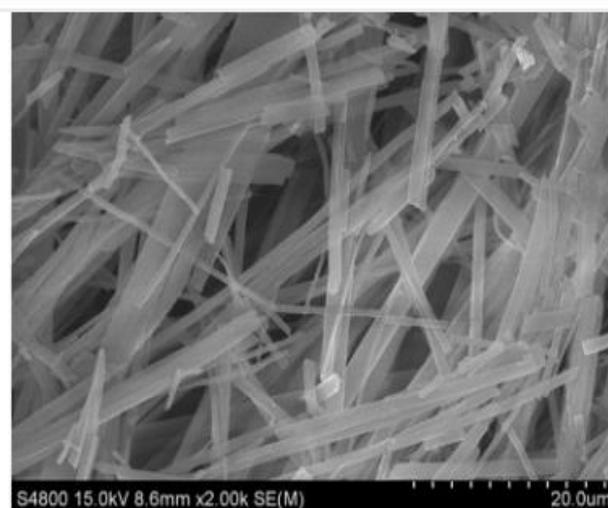


Figure 5 SEM image of the synthesized complex

4. Gelation and Rheology studies

We examined the synthesis of low molecular weight organogelators with compounds (ligand & complex) incorporating tetrafluoromethyl substituents, encouraged by the peculiar emission in aqueous media and the tendency of CF₃ substituted compounds to form organogels. Ligand and complex were dissolved in t-butanol (1.8% wt) in a glass vial heated to 70 °C to obtain a transparent solution in order to research the gelation properties. Whenever the hot solutions of ligand & complex in t-BuOH were stored for ~5 min in the refrigerator and then left for 30 min at room temperature, organic fibers/ribbons eventually established in the solution by assembling through non-covalent interactions (H-bonding and hydrophobic interactions). The hot t-BuOH liquid is preceded by a sonic solution and then cooled in the refrigerator for five minutes. The warming of the room temperature solution lead to the formation of a viscous gel. Even after alternation of the vial showing its overall stability, the gel thus produced has no gravitational flow. This gel formation, with heating (~70 °C) and cooling cycles, was also thermo-reversible. Analysis of its emission shows a bathochromic change in wavelength as applied to the solution, with a concomitant rise in emission rate. In toluene and 1, 2-dichloroethane the gelation was also effective, but here we report the studies of gels with t-butanol as a solvent.



Figure 6. The thermo-reversible sol-gel transitions of the gels of ligand and complex

To ascertain the formation of gels and assess the stability and viscoelastic properties of ligand & complex, rheological properties were characterized by the time, frequency and amplitude sweep measurements. The samples were equilibrated for 5 minutes before starting the rheological experiments and further subjected to an oscillatory strain (γ) = 0.1% and angular frequency (ω) of 100 – 0.1 rad/s. Such conditions ensure that, in the linear viscoelastic (LVE) regime, the storage modulus (G') and loss modulus (G'') are determined. Oscillatory strain sweep measurements calculate the non-linear response of the samples at a fixed rate of 6.28 rad/s in the range of $\gamma = 0.01$ percent - 100 percent. Our data indicate that the storage moduli (G') is very higher than the loss moduli (G'') indicating low $\tan \delta$ ($\tan \delta = G''/G'$) values obtained for both gel samples ligand and complex which disclose their gel nature. As shown in Figure 8 and 9, the G' values for both gel ligand and complex were irrespective of experimental time and frequency range. Furthermore, the figures show that the G' obtained for gel ligand is in the order of 10^3 Pa, while the G' measured value for gel complex is in the order of 10^4 Pa, which implies a higher gel complex

strength compared to gel ligand. Although the strong π - π stacking interactions between the rigid segments provide the basic driving force for gelation, the presence of two CF₃ groups in the gel complex can be understood as the comparatively greater strength of the gel complex. These CF₃ moieties play a key role in the development of stronger gel networks by non-covalent strengthening. Interactions 26, as opposed to gel ligands consisting of a single group of CF₃s. The gel begins to form liquid with an increase in strain amplitudes by a steep decrease in the values of both moduli and the reversal of the viscoelastic signal ($G'' > G'$). The contribution of CF₃ groups through non-covalent interactions to the formation of gels is widely known

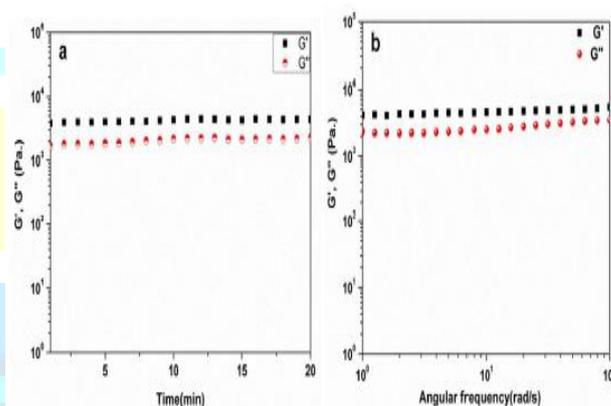


Figure 7 Time sweep measurement (b) Frequency sweep measurement of gel ligand in t-BuOH.

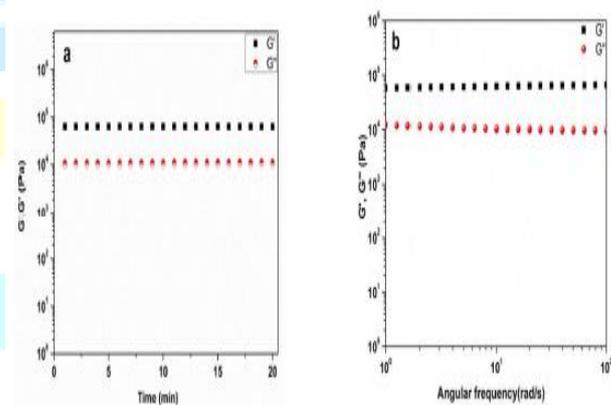


Figure 8 Time sweep measurement (b) Frequency sweep measurement of gel complex in t-BuOH

For further insight on aggregation morphology of ligand and complex, a dried organogel sample was transferred onto a silicon wafer and subjected to the scanning electron microscopy (SEM) observation. The SEM images in Figure 7 suggest that ligand and complex form entangled three-dimensional networks consisting of the bundles of fibrous aggregates, which must be responsible for the observed gelation.

5. Circular dichroism

Due to their low solubility in methanol, which is a widely used solvent for compounds containing these chromophores, CD spectra of the ligand and complex in solution have not

been reported. The CD spectra of xerogels obtained by drying the respective gels in toluene are shown in Figure 10.

IV CONCLUSION

Gel of tetrafluoromethylaniline copper (II) nitrate have been synthesized for the first time and investigated as low molecular weight organogel (LMWOGs) concluding that there was a clear influence of the ring size on their hierarchical supramolecular organization and on their properties as organogelators. SEM images display spherical and disordered fibers and also suggest that the ligand and complex form entangled three-dimensional networks consisting of the bundles of fibrous aggregates, which must be responsible for the observed gelation. The FTIR spectrum shows multiple functional groups with a little shift from ligand to the complex, circular dichroism (CD) shows different supramolecular arrangements. UV-visible adsorptions does not display any major changes following the incorporation of CF₃ groups in different-solvents.

ACKNOWLEDGMENT

The authors wish to acknowledge the provision of research facilities by the Universiti Teknologi Malaysia. Further acknowledgement goes to Higher Education Development Programme (HEDP) for scholarship funding via Baghlan University Afghanistan, to pursue MSc programmed.

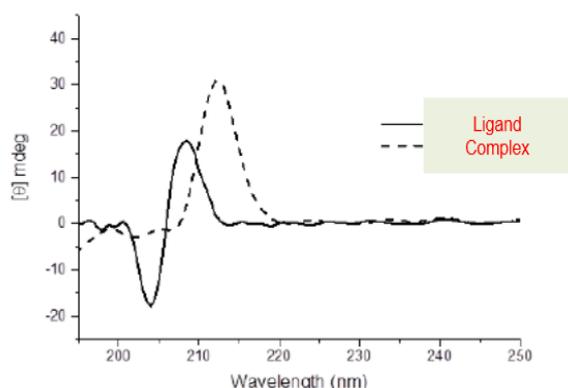


Figure 10. CD spectra of ligand and complex in KBr ($c = 0.02$ mmol g⁻¹) at 25°C

A bisignate cotton effect is presented by the ligand, while the complex shows a band, indicating different supramolecular arrangements. For ligands, with zero-crossing at $\lambda = 206$ nm, a negative band was observed at 204 nm and a positive one at 208 nm. A positive band was seen at 211 nm by Complex [14].

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