SUPRAMOLECULAR ORGANOGEL WITH AGGREGATION-INDUCED EMISSION AND LIQUID CRYSTAL PROPERTIES FROM 1,3,5-TRIAZINE-2,4,6-TRICARBOXAMIDE FOR SENSING METAL IONS AND COLOUR TUNABLE MATERIALS

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DEDICATION

This thesis is dedicated to my parents and family

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ABSTRACT

The purpose of this research is to develop supramolecular organogel with liquid crystal (LC) mesophase and fluorescent properties for optical application as chemosensor of metal ions and colour tunable materials. The organogel was synthesised utilizing 1,3,5-triazine-2,4,6-tricarboxamide (TZTC12NH) as the self-assembly organic motif. In the first part of the research, TZTC12NH was synthesized in three steps to give a white powder solid in 52% yield. The compound was found to form columnar LC properties with mesophase range of 73.0 to 185.0^{o}C and gave fluorescent emission maxima at 417 and 468 nm upon excitation at 254 nm. The compound was then utilized for the formation of an organogel at 10 wt. % of benzene which gave blue emission upon exposure to a wavelength excitation of 365 nm under a hand-held UV lamp. This organogel showed two emission bands centered at 417 and 468 nm with enhanced intensity when excited at 254 nm. Besides, the organogel shifted the columnar LC mesophase of TZTC12NH to 61.3 - 178.2^{o}C. Polarized optical microscope imaging indicated that the organogel displayed a focal conic fan-like texture for typical arrangements of discotic hexagonal columnar LC. The organogel was utilized as chemosensor of metal ions *via* fluorescent quenching which showed selective response toward Cu^{2+} and Ag^{+} ions over other metal ions under consideration. The sensitivity based on linear Stern-Volmer plot K_{sv} value is 1.183×10^{5} M with LOD 1.104×10^{-6} M for Cu^{2+} ions and K_{sv} 1.135×10^{5} M with LOD 1.057×10^{-6} M for Ag^{+} ions, respectively. Upon doping the gel with Eu^{3+} ions at 0.01 M, the blue emission of the gel turned red under hand-held UV lamp and gave a new sharp emission band centered at 617 nm when excited at 250 nm due to the formation of metallogel. In addition, when few drops of methanoic acid were added to the gel, the red emission of the gel turned back to blue with disappearance of the emission band at 617 nm. Hence, this research showed the successful synthesis of new TZTC12NH as simple supramolecular self-assembly organic scaffold for development of organogel, chemosensor and colour tunable material.

ABSTRAK

Tujuan penyelidikan ini ialah untuk membangunkan organogel supramolekul yang memiliki sifat mesofasa hablur cecair (LC) dan pendarfluor untuk aplikasi optik sebagai penderia kimia bagi ion logam dan bahan tala warna. Organogel itu telah disintesis menggunakan 1,3,5-triazina-2,4,6-trikarboksimida (TZTC12NH) sebagai motif organik swahimpunan. Dalam bahagian pertama penyelidikan ini, TZTC12NH telah disintesis dalam tiga langkah untuk menghasilkan pepejal serbuk putih dengan hasil 52%. Sebatian itu didapati membentuk sifat LC berturus dengan mesofasa dalam julat 73.0 hingga 185.0^{o}C dan menghasilkan pancaran pendarfluor maksima pada 417 and 468 nm apabila diuja pada 254 nm. Seterusnya, sebatian tersebut telah digunakan untuk membentuk organogel dengan menggunakan benzena 10 wt. % yang menghasilkan pancaran biru apabila terdedah kepada pengujaan pada panjang gelombang 365 nm di bawah lampu UV mudah alih. Organogel ini menunjukkan dua jalur pancaran yang berpusat pada 417 dan 468 nm dengan peningkatan keamatan apabila diuja pada 254 nm. Selain itu, organogel tersebut telah menganjak mesofasa LC berturus TZTC12NH kepada 61.3 - 178.2^{o}C. Pengimejan mikroskop optik terpolarisasi menunjukkan bahawa organogel tersebut memaparkan tekstur kon tertumpu seperti kipas yang merupakan susunan tipikal LC berturus heksagon diskotik. Organogel tersebut telah digunakan sebagai penderia kimia ion logam melalui pelindapan pendafluor yang menunjukkan tindak balas selektif terhadap ion Cu^{2+} dan Ag^{+} melebihi ion logam yang lain di bawah pertimbangan. Kepekaan masing-masing berdasarkan nilai K_{sv} plot Stern-Volmer ialah 1.183×10^{5} M dengan LOD 1.014×10^{-6} M bagi ion Cu^{2+} dan K_{sv} 1.135×10^{5} M dengan LOD 1.233×10^{-6} M bagi ion Ag^{+}. Apabila didopkan dengan ion Eu^{3+} 0.01 M, pancaran biru gel itu bertukar menjadi merah di bawah lampu UV mudah alih dan memberikan jalur pemancaran baharu yang tajam berpusat pada 617 nm apabila diuja pada 250 nm disebabkan oleh pembentukan metalogel. Tambahan lagi, apabila beberapa titis asid metanoik ditambah kepada gel tersebut, pancaran merah gel tersebut kembali semula menjadi biru dengan kehilangan jalur pemancaran pada 617 nm. Oleh itu, penyelidikan ini telah menunjukkan TZTC12NH telah berjaya disintesis sebagai perancah organik penswapasangan supramolekul ringkas bagi pembangunan organogel, penderia kimia dan bahan tala warna.

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LIST OF ABBREVIATIONS

^{1}H-NMR	-	Proton nuclear magnetic resonance
FTIR	-	Fourier transform infrared spectroscopy
MALDI-TOF-MS	-	Time–of–flight mass spectrometer with laser
DR UV-Vis	-	Diffuse reflectance ultraviolet-visible
XRD	-	X-ray diffraction
TGA	-	Thermogravimetric analysis
DSC -	-	Differential scanning calorimetry
POM	-	Polarized optical microscope
SEM	-	Scanning electron microscope
THF	-	Tetrahydrofuran
DMF	-	Dimethylformamide
$CHCl_3$	-	Chloroform
$(COCl_2)$	-	Oxalic chloride
D_2O	-	Deuterated water
Et_3N	-	Triethylamine
NaOH	-	Sodium Hydroxide
TZTC12NH	-	1,3,5-triazine-2,4,6-tricarboxamide
TZTCOCl	-	1,3,5-triazine-2,4,6-trichloride
TZTCOOEt	-	1,3,5-triazine-2,4,6-tricarboxylate
TZTCOOH	-	1,3,5-triazine-2,4,6-tricarboxylic acid
BTA	-	Benzene-1,3,5-tricarboxamide
CTA	-	1,3,5-cyclohexanetricarboxamide
LC	-	Liquid crystal
Col_h	-	Columnar hexagonal
Col_r	-	Columnar rectangular

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Supramolecular organic soft materials have received much attention because of their potential applications in diverse field such as sensors, organic light-emitting devices, luminescent materials, self-healing materials and gels. These materials are fabricated through rational design and synthesis of organic molecules as supramolecular building moieties. A proper design of molecular building moieties to tune the strength and direction of interactions between the molecules play a crucial role in developing functional supramolecular materials. These materials are expected to give intriguing properties via self-assembly by non-covalent interactions [1,2]. The molecules self-assemble to form different shapes, sizes and structure, depending on the molecular structure and the functional groups present [3]. Although a large number of supramolecular building moieties are available, however, many of them require multi-step synthesis or exhibit limited aggregation. In the past decades a little number of simple organic molecules were known for the construction of supramolecular architectures, such as benzene-1,3,5-tricarboxamide (BTA) [4], and 1,3,5-cyclohexane-tricarboxamide (CTA) [5]. Therefore, it is crucial to rationally design and develop new system as supramolecular building scaffold for the construction of novel functional materials. Hence, due to the excellent electronic and optical properties of 1,3,5-triazine, the development of new supramolecular organic motif from 1,3,5-triazine would contribute immensely to the construction of diverse structures with tunable properties and functionalities for versatile applications.

1.1.1 Organogels

Interestingly, among the supramolecular soft materials, organogels have gained immense attention among the researchers, due to their outstanding properties and broad applications such as in template materials, opto-electronic materials, sensing, drug and gene delivery, and cosmetics [6,7]. Generally, organogels are formed by self-assembly of organic molecules leading to the formation of fibrous network immobilising organic solvents. The non-covalent interactions among the fibres create the 3D network [8,9]. In most cases, hydrogen bonding, π-π stacking, van der Waals interactions are chiefly utilized in the construction of a suitable structure for gelation [10]. Despite the enormous benefit of organogels in the fabrication of functional materials, it has been found to have their limitations. They can be easily thermally deformed which limits their functions in applications at extreme conditions such as aerospace, marine, military technology and metrology research. Therefore, in order to develop high-performance organogel, it should be able to have thermal resistivity over extreme heat environment. Besides, organogels with fluorescent and liquid crystal properties are required for their sensitive response to multiple external stimuli as functional soft materials.

Recently, the physical gelation of functional fluids such as liquid crystals is a new approach to the development of functional supramolecular organogel, which leads to the formation of a new class of anisotropic gels that have great potentials for electrical, and functional materials [11]. For these kinds of gels, the anisotropic transitions due to liquid crystals introduce new order and mobility into the gels which could enhance their physical properties [12]. Thus, considering these properties, it is important to rationally design and develop supramolecular organogel with liquid crystal properties over a wide temperature range and fluorescent properties as well as thermally stable in their functions. However, many reports have been focused only on the development of supramolecular organogel from luminescent organic chromophores with complicated molecular design and synthesis, without liquid crystal properties or with the disappearance of liquid crystal properties at a small mesophase range. [13,14]. Therefore, it is vital to develop supramolecular luminescent organogel from a simple organic molecule having both liquid crystal mesophase over a wide temperature range and fluorescence properties for wider applications.

1.1.2 Metal ions Sensing

Environmental pollution is one of the major concerns of the scientific community especially transition metal ions can have adverse effects on animals and the environment. For example, copper is an essential mineral, however, excess copper can constitute a health risk. Such as gastrointestinal health problems, and in the long term, kidney damage. Silver also plays a significant role in different industrial fields such as photography imaging, soldering production, electrical and electronics, automobiles and as a catalyst in oxidation reactions. However, the Ag^+ ions are highly toxic to aquatic organisms and may accumulate in the human body through the food chain. The high concentration of Ag^+ ion can lead to a variety of adverse health effects, brain damage, nerve damage and immune systems [15–17]. Therefore, it is crucial to detect transition metals to assess health risks and for environmental monitoring [18–20]. Transition metals accumulate in the environment gradually due to mining, smelting and processing of minerals, combustion of coal and oil, incineration of waste, production and recycling of electronics, electroplating [21,22].

The conventional methods to determine transition metals involve Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Emission Spectroscopy (ICP-ES), Inductively coupled plasma atomic emission spectrometry (ICP-AES), Inductively coupled plasma mass spectrometry (ICP-MS). While these techniques are capable of accurately detecting low levels of transition metals, they often require extensive sample preparation and expensive instrumentation and thus are low throughput [23]. Therefore, the development of other techniques which are inexpensive and fast is of great practical importance. Optical sensing of metal ions, especially using organic fluorescent materials is of immense importance to many areas of science, technology and ecology. This technique has certain advantages; because it does not require extensive sample preparation, instrumentation and it is relatively fast and sensitive [24]. Moreover, during the last decade, optical sensing of metal ions based on conjugated aromatic macrocyclic compounds has received significant attention Figure 1.1 [25–27]. However, this strategy has experienced some limitations. Thus, it requires synthetic efforts for covalent immobilisation of the chromophore to the metal receptor, and due to their extended conjugation they tend to form strong π-interactions and experiences self-quenching of fluorescence with increase in concentration. Furthermore, their properties are not easily tunable [28]. Interestingly, supramolecular self-assembly utilising non-covalent interactions represent a promising strategy for the development of well-controlled materials with dynamic and tunable properties, especially supramolecular organogel which possess rapid response to external stimuli, inherent reversibility owing to the non-covalent nature of the aggregation process. Therefore, it is essential to develop chemosensor from simple 1,3,5-triazine derivative as organogel with fluorescent and liquid crystal properties for sensing metal ions utilising its alkyl amide NH units as the metal ions binding sites.

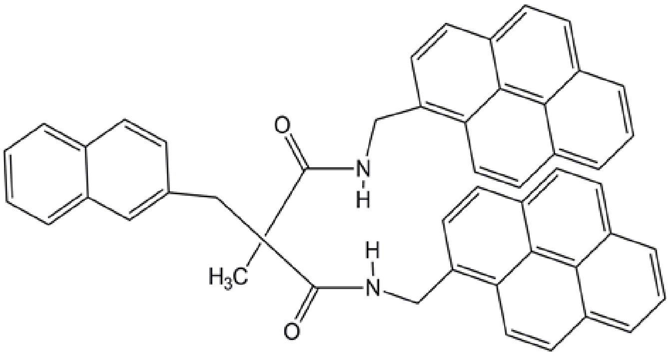

Figure 1.1 Macrocyclic organic motif for sensing metal ions [27]

1.1.3 Colour Tunable Materials

Recently, interest have been focused on the development of colour tunable fluorescent materials for display and organic-light-emitting-diodes (OLED) applications [29]. Supramolecular organogels are also reported to give luminescent colour changes upon metals permeation and metallogel formation [30]. This system demonstrated colour tunable metallogel with phosphorescent properties by silver ion

(Ag^+) permeation. Hence, considering the advantage of trivalent europium ion, with narrow-band luminescence with high colour purity and quantum efficiencies would be suitable for the development of efficient colour tunable material. These properties are observed not only for Eu^{3+} ions doped into crystalline host matrices or glasses but also for europium(III) complexes with organic ligands. These ligands can act as an antenna to absorb the excitation light and to transfer the excitation energy to the higher energy levels of the Eu^{3+} ion, from which the emitting excited levels can be populated [31]. Therefore, it is essential to investigate the colour tunable properties of 1,3,5-triazine supramolecular organogel by europium ion (Eu^{3+}) permeation within the 3D gel structure.

1.2 Problem Statement

A large number of supramolecular building organic motif involving conjugated organic dye systems are available however, many of them require tedious and multistep synthesis or show limited aggregation properties [3]. Hence, there is need to synthesise a simple supramolecular organic motif with access to intermolecular hydrogen bonding to enhance molecular aggregation for the development of supramolecular functional materials. Therefore, in this study a simple supramolecular organic motif 1,3,5-triazine-2,4,6-tricarboxamide (TZTC12NH) was synthesised.

Organogels are soft material that can be easily deformed by thermal stress which limits their functionalities. Many organogel developed base on conventional organic chromophore experience aggregation-caused quenching (ACQ), and reported without LC properties or narrow mesophase range [32]. In order to circumvent this limitations. This research have developed supramolecular organogel base on 1,3,5-triazine-2,4,6-tricarboxamide with aggregation-induced emission and liquid crystal (AIE-LC) properties over wide temperature range.

Although the instrumental technique can detect low levels of transition metals ions, they often require extensive sample preparation, expensive instrumentation and time consuming. In addition, the handling specialized instrument required skilled personnel [23]. Therefore, the optical method is gaining attention due to high sensitivity, selectivity, inexpensive, ease of measurement and quick response time [24]. Optical chemosensor based on organic dye systems has been developed but requires tedious synthesis for covalent immobilization of the chromophore to the metal receptor. In addition the optical properties of the compound are not easily tunable because it involve covalent interactions [28]. Therefore, there is need to develop a simple supramolecular self-assembly organic system utilizing non-covalent interactions with tunable properties. Moreover, the utilization of gel material to sense metal ions is rare and unexplored.

Colour tunable organogel material have been developed from hydrophobic pyrazolate complex by doping with Ag^+ [30]. However, the organogel was reported without liquid crystal properties which limit its functionalities at certain temperature. It is known that luminescence properties associated with the delocalized π-electron system are enhanced due to orientation of molecules induced by liquid crystal ordering [33]. Moreover, emission signals from organic chromophores are normally associated with background signal interference which limits the quality of the images [34]. To overcome this limitations there is need to incorporate liquid crystal properties in colour tunable materials and also by doping with lanthanide ions because lanthanide ions are known to exhibit sharp emission line with brilliant colour purity and high quantum yield [35].

1.3 Research Objectives

The objectives of the research are:

(a) To synthesize and characterize new 1,3,5-triazine tricaboxamide (TZTC12NH) bearing hydrophobic alkyl side chain.

(b) To prepare a new supramolecular organogel utilizing 1,3,5-triazine tricaboxamide and study the properties

(c) To investigate chemosensor capability of 1,3,5-triazine tricaboxamide organogel for sensing metal ion.

(d) To investigate fluorescence colour tunable properties of 1,3,5-triazine tricaboxamide organogel by lanthanide metal ion doping.

1.4 Scope of Study

This research focused on the synthesis of 1,3,5-triazine-2,4,6-tricaboxamide (TZTC12NH) bearing hydrophobic alkyl side chains as a new supramolecular building moiety. The fluorescent and liquid crystal properties of the compound was explored. Moreover, the compound was utilized in the preparation of 1,3,5-triazine-2,4,6-tricaboxamide organogel (TZTC12 organogel) and its gelation capability in various organic solvents was tested. In addition, the photophysical and liquid crystal properties of the gel was investigated. The performance of the organogel in sensing relative abundance biologically important transition metal ions such as Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} , and Fe^{2+} was also examined. Furthermore, luminescence colour tunable properties of the organogel was evaluated by doping with lanthanide ions such as Eu^{3+} , Nd^{3+}, Er^{3+} and dedoping with methanoic acid. The samples were characterized by Nuclear magnetic resonance spectroscopy (^{1}H-NMR), Fourier-transform infrared spectroscopy (FTIR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), Diffuse reflectance UV-vis spectroscopy (UV-Visible), Fluorescence spectroscopy (FL) X-ray powder diffraction (XRD), Differential Scanning Calorimetry (DSC), scanning electron microscope (SEM), Polarizing optical microscope (POM) and Thermogravimetric analysis (TGA).

Base on the following observations, in this research compound with C_{12} alkyl chain was chosen. The alkyl chains provide flexibility and van der Waals interactions necessary for LC formation. The shorter alkyl chain length form no LC properties or less ordered LC as compare to longer chain. Although the mesophase temperature increase with increase alkyl chain length [36]. On the other hand, it has been observed that trialkyl cis-1, 3, 5-cyclohexanetricarboxamides with C_{12} alkyl chain was able to form stable organogel, but when the alkyl chain was shortened below C_{12} the gel fail to form due to poor hydrophobic interaction [37]. Moreover, the gel from carbamates with alkyl side chains of different lengths, gelation was possible only up to an alkyl side chain length of 12 carbons. Beyond 12 carbons precipitation occurs, due to the dominant van der Waals interaction between the alkyl chains [38]. The research outline is illustrated in Figure 1.2.

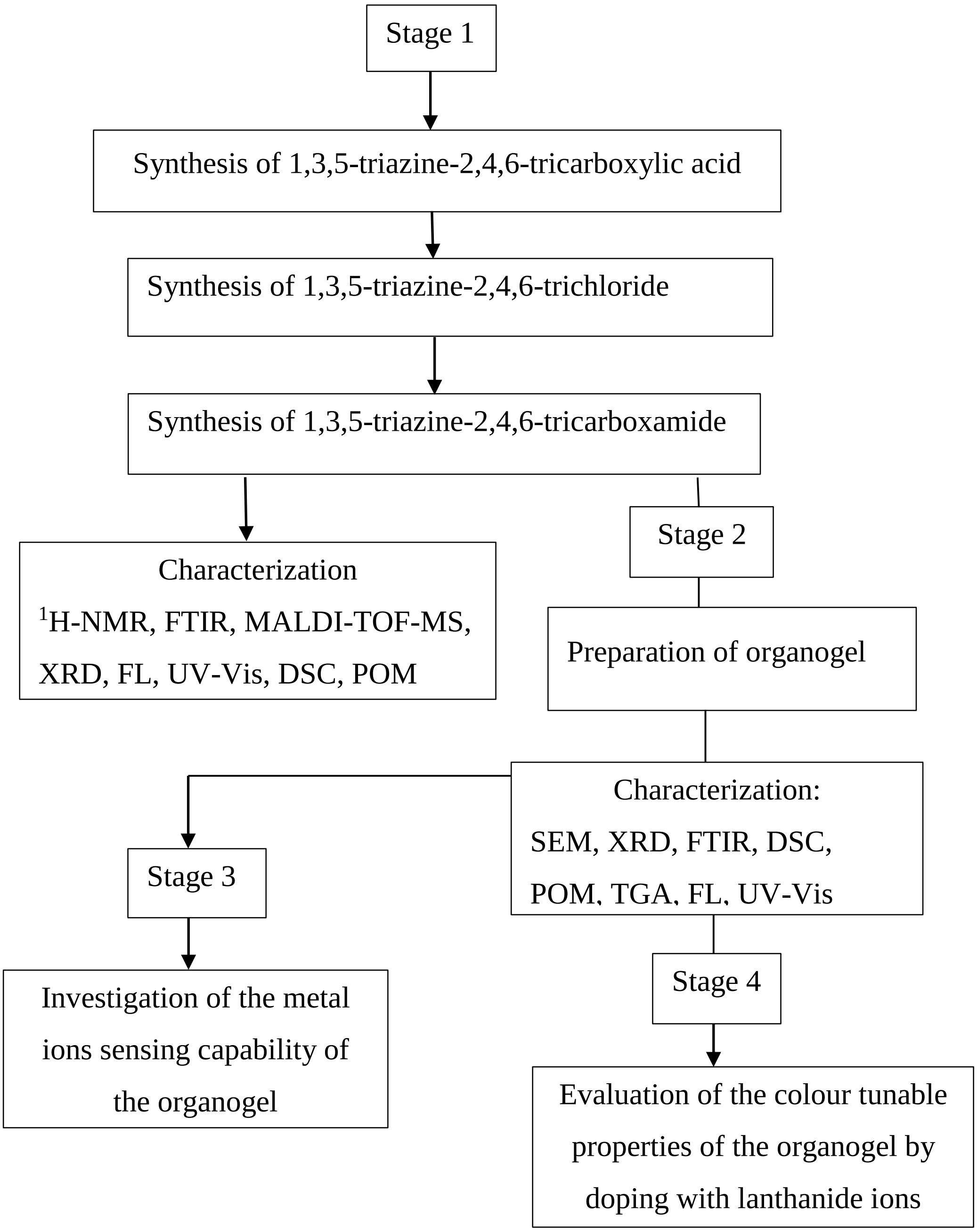

Figure 1.2 Research outline

1.5 Significance of the Study

The research is important as the first example of 1,3,5-triazine tricaboxamide bearing aliphatic alkyl side chain self-assembly soft organic motif. This finding would contribute immensely in the area of supramolecular chemistry. Because of the tendency of three amide groups to form intermolecular H-bonding interactions, aliphatic alkyl chain for van der Waal interactions and aromatic triazine ring for π-π stacking interactions that will lead to a versatile supramolecular building block for many applications. Besides, the formation of the novel supramolecular organogel from 1,3,5-triazine tricaboxamide with AIE-LC properties would lead to the development of diverse functional materials for more extensive applications.

In addition, the use of 1,3,5-triazine tricaboxamide with aggregation-induced emission (AIE) is more effective than without AIE characteristics, because AIE molecules were induced to emit by aggregate formation. Based on their mechanism of restriction of intramolecular rotations, which provides a stable emission for application as luminescent materials [39]. However, the utilization of this material without AIE properties require the incorporation of emissive functional group. This will lead to formation of extended π-conjugation, which promotes loss of excitation energy due to strong π-π stacking interactions. The interaction may results in self-quenching of the emission [40].

Furthermore, the utilization of this new organogel from 1,3,5-triazine tricaboxamide for sensing metal ions would contribute significantly to the area of optical chemosensor of metal ions. Due to the combination of aggregation-induced emission and liquid crystal (AIE-LC) properties the organogel emission will be stable enough to be utilized as chemosensor of metal ions with enhanced sensitivity. In view of the fact that, AIE and LC characteristics gives both restriction of intramolecular rotations and molecular order to promote stable emission which will .lead to enhanced sensitivity. Moreover, the study of the TZTC12 organogel for colour tunable material by doping with europium ion would provide new supramolecular colour tunable material, for display, opto-electronic and imaging applications, considering the advantages of trivalent europium ion having narrow-band luminescence with high colour purity and quantum efficiencies.

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