



World Scientific News

An International Scientific Journal

WSN 144 (2020) 103-113

EISSN 2392-2192

A new cyclotrimeratrylene derivative as turn-off fluorescent probe with quinoline appended arm for the selective and sensitive determination of Cu^{2+} ions

Patrick F. Fernandes, Divya R. Mishra*

¹Department of Chemistry, School of Sciences, Gujarat University,
Ahmedabad – 380009, Gujarat, India

*E-mail address: pfer3115@gmail.com

*Tel.: +91 79 26302363

*Fax: +91 79 26302363

ABSTRACT

A novel supramolecular fluorescent molecular probe constructed on cyclotrimeratrylene based derivative allied to 8-quinolinesulfonyl chloride (8QSC) was synthesized and used for the detection of copper ions among the various cations. Using ¹H-NMR, ¹³C-NMR, and ESI-MS techniques the compound was successfully characterised. Furthermore the complexation behaviour of 8QSC-CTV with different cations were studied. A shift in the absorption spectra showed the detection of copper ion with the ligand 8QSC-CTV which concludes the strong binding interaction between the ligand and the cation. Furthermore the metal ion showed quenching in the emission spectra. The quantum yield of the metal complex was also studied. The stern volmer analysis concluded that the mechanism of fluorescence quenching is either purely dynamic or purely static.

Keywords: cyclotrimeratrylene, 8-quinolinesulfonyl chloride, copper ions, Fluorescence studies, Sensors

1. INTRODUCTION

Sensing of transition metals using organic and fluorescent chemosensor have been of great interest for chemists in the recent times [1-4]. Also there is a need for the detection of metal ions and transition elements owing to its acute toxicity to environment after a certain level [5]. Owing to this, different types of sensors have been developed for the detection of transition elements in recent years [6-8].

Copper one of the transition elements is the third most abundant element which is widely used by humans in industries and also it is an important element in the human body responsible for many enzymatic mechanisms [7, 9-10]. However excess of copper levels in the body is considered harmful and results in gastrointestinal, cataract, Wilson disease, hypoglycaemia and dyslexia, neurodegenerative Diseases (such as Alzheimer's disease) [11-12].

Fluorescence is the one most attractive method used due to its high sensitivity, selectivity, rapidity, ease of measurement from among the various techniques that is available, and sensors based on fluorescence techniques for sensing and estimating toxic metal ions are currently in high demand for the detection of compounds in various classes of chemistry, biology and environmental science. Fluorescent chemosensor (fluoroionophores) are usually made up of three components: a receptor (ionophore); a fluorophore (signalling moiety); and, a spacer to link them together [13].

Cyclotrimeratrylene (CTV) is a cyclic molecular host. Its crown conformation gives it a bowl-shape with a molecular cavity in which guest molecules can be non-covalently bound [14]. Recent studies based on Quinoline based fluorophore have shown that these sensors exhibit good selectivity and a low limit of detection [15-18].

With a view to develop a cyclotrimeratrylene based sensor, herein we report the synthesis and characterization of a new molecule 8QSC-CTV and its complexation behaviour with different cations. Also the binding constants and quantum yield studies are also shown. We have also tried to explain the shift in absorbance and emission spectra and the quenching of emission intensity of 8QSC-CTV in presence of copper ions.

2. EXPERIMENTAL SECTION

2. 1. Synthesis of 8QSC-CTV

Cyclotriguaiacyclene (CTG) was prepared by the reaction of cyclotrimeratrylene and AlCl_3 in MDC according to a previously reported procedure [19]. CTG (0.4 g, 0.9 mmol) and K_2CO_3 (0.5 g, 0.31 mmol) were added to 10 mL of dry DMF. 8-quinoline sulfonyl chloride (8QSC) (0.6 g, 0.29 mmol) was added, and the mixture was conducted at 150 °C for appropriate reaction time with TLC monitoring. The reaction mixture was cooled at room temperature, followed by filtration and washing with water (3×10 mL) and dried to yield a pure light brown solid material. ^1H NMR (500 MHz, DMSO): ^1H NMR (500 MHz, Chloroform-*d*), δ 8.93 (t, 3H), 8.25 – 8.18 (m, 2H), 8.18 (t, 1H), 8.15 (d, 1H), 8.00 (d, 1H), 7.89 (d, 2H), 7.62 (d, 1H), 7.61 – 7.55 (m, 4H), 7.52 (d, 1H), 7.47 (t, 2H), 6.92 (d, 2H), 6.87 (t, 1H), 6.74 (t, 1H), 6.69 (t, 1H), 6.60 (d, 1H), 4.67 (s, 4H), 3.92 (d, 4H), 3.83 (d, 8H), 3.70 (d, 2H). ^{13}C NMR (500 MHz, DMSO): 35.7, 55.6, 113.4, 125.4, 125.9, 128, 131.9, 132.04, 147, 162.2; ESI-Mass: 982 M.P.: 106 °C.

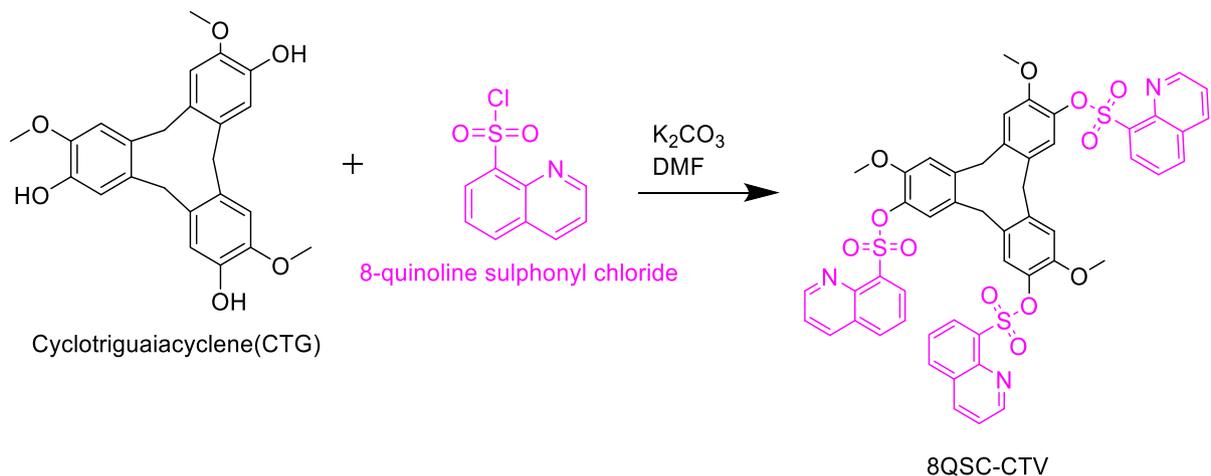


Figure 1. Synthetic scheme for the preparation of 8QSC-CTV.

2. 2. General procedure for performing the spectrophotometry and spectrofluorimetric analysis for the detection of cations

The same concentration (4×10^{-5} M) of 8QSC-CTV stock solution and various cations were prepared in acetonitrile. An equal volume (2.5 ml) of the stock solution of the 8QSC-CTV and that of each cation were added to 5 ml volumetric flasks, so that the effective concentration of 8QSC-CTV and the cations was 2×10^{-5} M.

The absorption spectra in the presence of other cation solutions and that of 8QSC-CTV were compared. An emission titration study was performed using the same stock solution of fluoroionophore (8QSC-CTV) with different cations. To prepare the reaction mixtures, 2.5 ml of each cation solution was added to a 5 ml volumetric flask. Comparison of the fluorescence spectra of the prepared solutions and that of the 8QSC-CTV was then performed.

3. RESULTS AND DISCUSSION

3. 1. Absorption and emission studies

The signalling ability of 8QSC-CTV was investigated by conducting UV–visible and fluorescence studies of 8QSC-CTV with various metal ions such as Fe^{3+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Cr^{3+} , Ca^{2+} , Co^{2+} , Mg^{2+} , Ag^+ , Pb^{2+} , Sr^{2+} , Hg^{2+} , Ba^{2+} , K^+ , Na^+ , and Bi^{3+} in Acetonitrile as the solvent.

The absorption studies revealed an observable change in the wavelength for Cu^{2+} ions compared to other metal ions (Fig. 2). In the presence of Cu^{2+} ions, the absorption band of 8QSC-CTV at 287 nm shifts to 270 nm. The observed shift indicates that the Cu^{2+} ions interact with 8QSC-CTV. Furthermore, comparative interference absorption studies were conducted with other cations with Cu^{2+} ions (Fig. S1).

The ion-induced shifts in the absorption mostly reflect the electrostatic interaction between the lone pair of electron(s) from the donor hetero-atoms in or conjugated to the ligand's Π system and the cation [20]. An increase in the conjugation of the ligand in a tightly bound complex commonly leads to a shift.

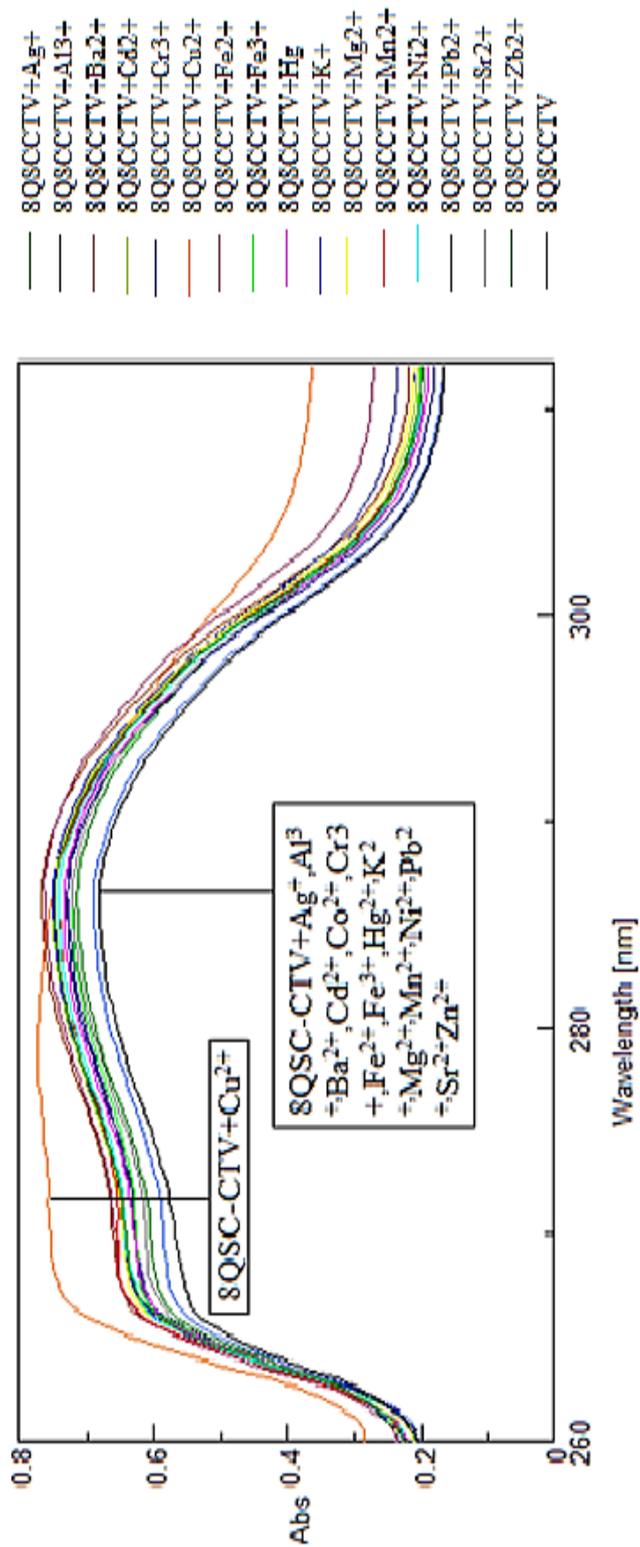


Figure 2. Absorption spectra upon addition of different cations

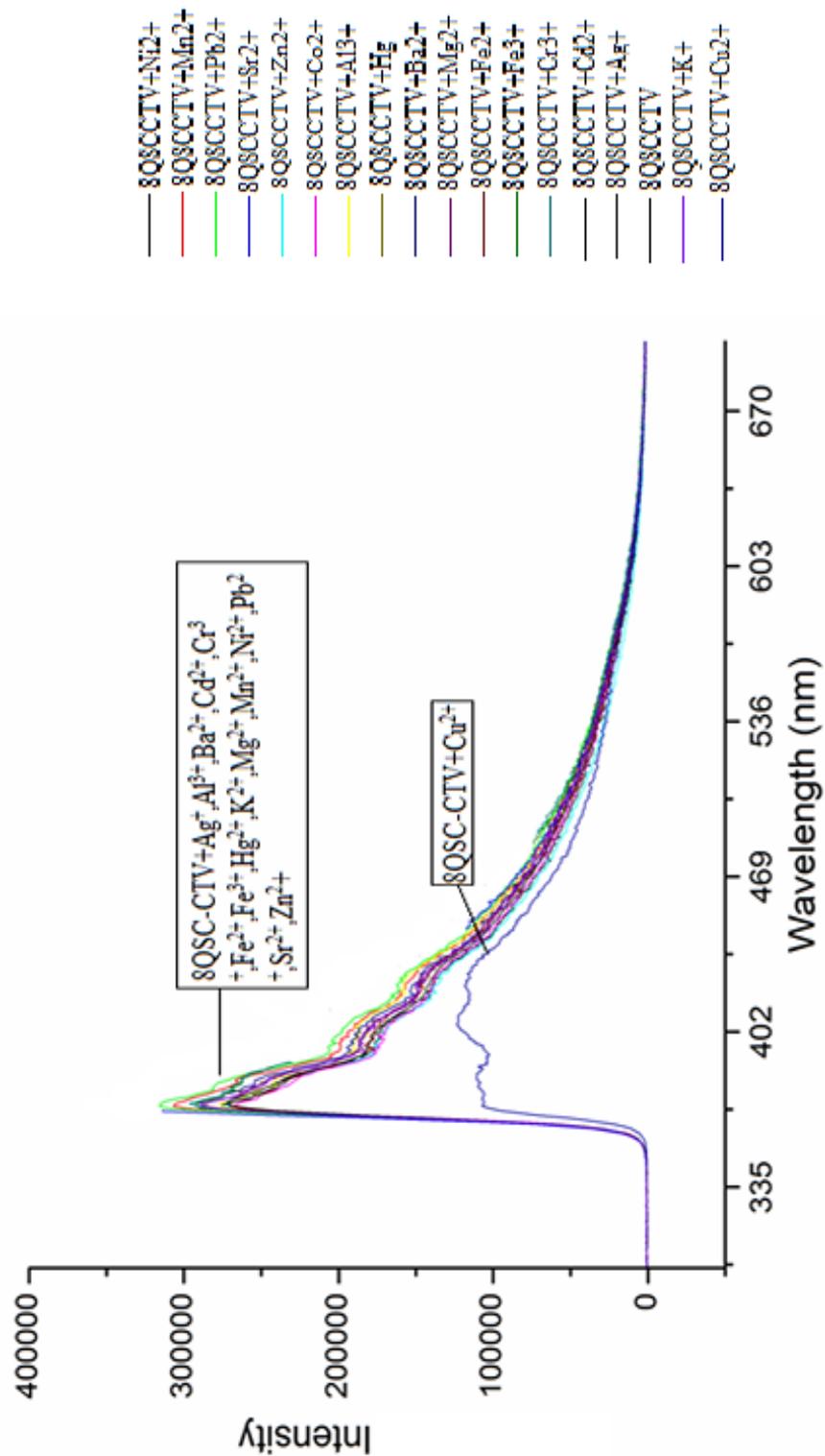


Figure 3. Fluorescence spectra of 8QSC-CTV with various Cations

Therefore, it can be said that the coordination of the Cu^{2+} ions with the ligand induces photo physical changes, which can be described in terms of a change in the dipole interaction.

During excitation, the more the dipole moment changes, the more the absorption band shifts [21]. Thus, a shift in the absorption spectra is caused due to the Cu^{2+} ion interaction with 8QSC-CTV, and the excited state is more stabilized than the ground state [22].

A strong quenching in the emission intensity of 8QSC-CTV was observed in the presence of Cu^{2+} ions in comparison to other metal ions (Fig. 3). The maximum emission intensity of 8QSC-CTV was found to be 272538 cps. The addition of Cu^{2+} ions to the 8QSC-CTV solution resulted in a strong and regular fluorescence quenching (Fig. 3). Further, no interference effect based on interference emission studies of other cations with Cu^{2+} ions was observed (Fig. 3).

As only Cu^{2+} ions showed quenching in its fluorescence, its emission titration was used to evaluate the binding constant of the 8QSC-CTV- Cu^{2+} complex, which was calculated as 10.67 M^{-1} (Fig. 5).

Based on the literature, the quantum yield [23] was also determined to determine the photochemical effects on the formation of the 8QSC-CTV Cu^{2+} complex. The quantum yield of 8QSC was nearly 0.55, as described in the literature, and the quantum yield of 8QSC-CTV was 0.435.

As the number of emitted photons decreased with an increase in the concentration of Cu^{2+} ions, it is confirmed that quenching has occurred.

A strong fluorescence quenching for Cu^{2+} ions is as shown in (Fig. 3). The quenching mechanism is well understood by plotting Stern-Volmer graph [24, 25] as shown in Fig. 6.

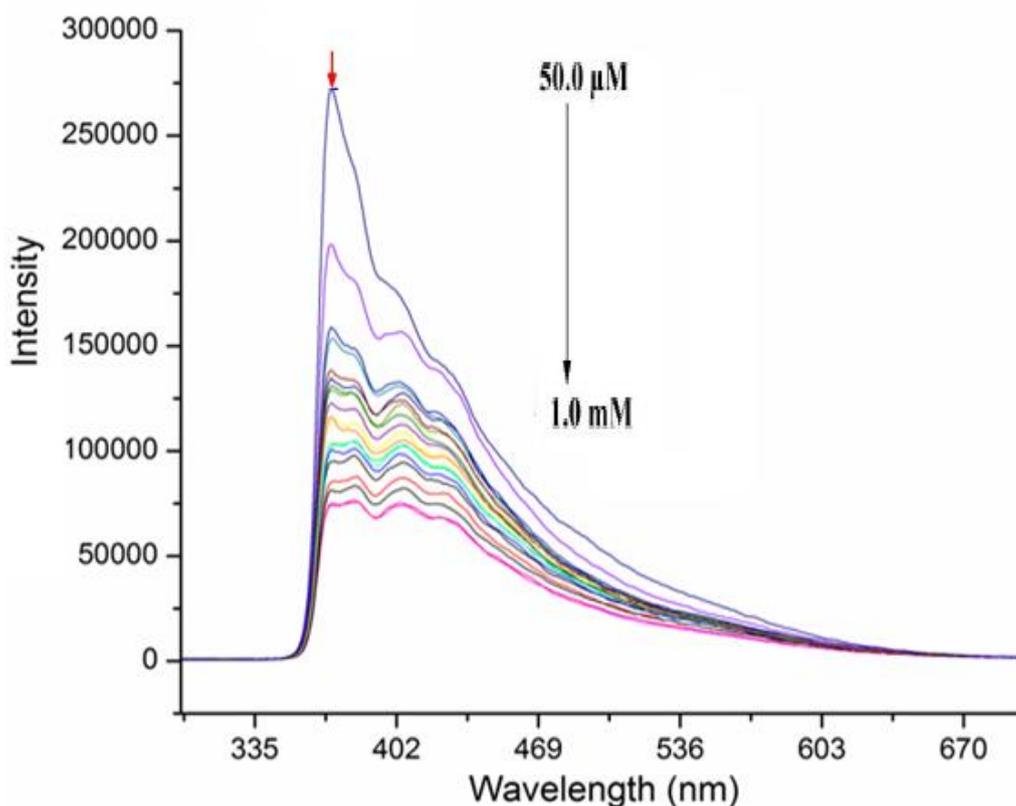


Figure 4. Fluorescence spectral change upon the addition of varying amounts of Cu^{2+}

3. 2. Binding constant and Quantum yield

As shown in Fig 4. The change in the emission intensity of 8QSC-CTV on adding different concentrations of Cu^{2+} ions is displayed. As the concentration of copper ions is increased, it is observed that the fluorescence intensity decreases. These emission titrations are considered for the evaluation of binding constant.

The graphical relation of the fluorescence intensity with the Copper concentration is found by the following equation

$$(F_0 - F)/F - F_1 = ([M]/K_{\text{diss}})^n$$

where F_0 and F_1 represent the relative fluorescence intensities of the complex without the addition of Copper and with the maximum concentration of copper. The binding constant (K_s) is obtained by plotting $\log[(F_0-F)/(F-F_1)]$ versus $\log [M]$. The value of $\log(K_{\text{diss}})$ is obtained by the value of $\log [M]$ at $\log[(F_0-F)/(F-F_1)] = 00$. The reciprocal of the value of (K_{diss}) gives the binding constant (K_s).

The Fig. 5 shows a plot of $\log[(F_0-F)/(F-F_1)]$ versus $\log[M]$. The binding constant of the complex is found to be 10.67 M^{-1} .

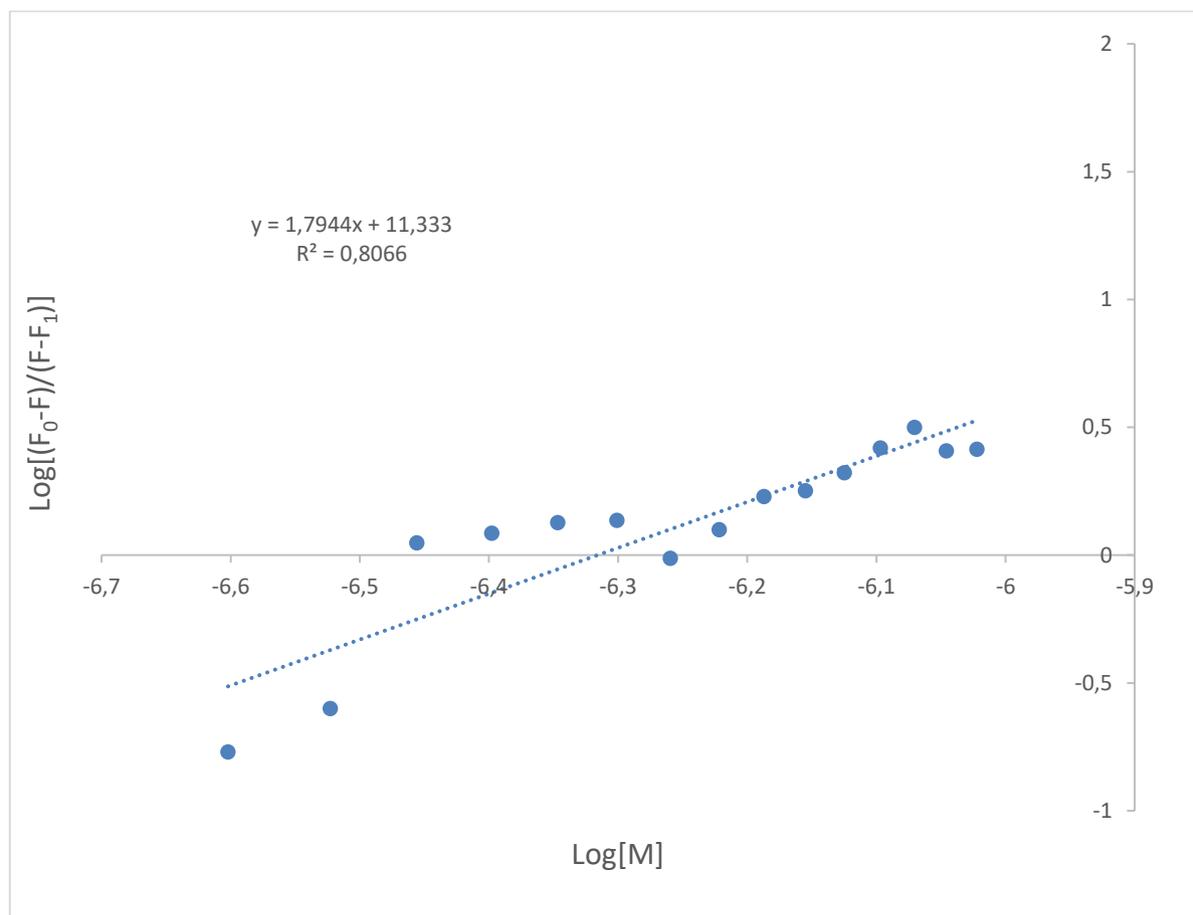


Figure 5. Binding constant

3. 3. Quantum Yield

The efficiency of the fluorescence technique is further confirmed by the determination of the fluorescence quantum yield from the following equation.

$$\Phi = \Phi_{std} \frac{(F \times A_{std} \times \eta)}{F_{std} \times A \times \eta_{std}}$$

where F and F_{std} are the areas under the fluorescence emission curves of the 8QSC-CTV complexes with Cu²⁺ and standard 8QSC-CTV, respectively; η and η_{std} are the refractive indices of the solvent acetonitrile of the sample and the standard, respectively; and A and A_{std} are the relative absorbance intensities of the sample and the standard at the identical wavelength.

The reported quantum yield of 8QSC is approximately 0.55 as described in the literature and that of the complex of 8QSC-CTV with Cu²⁺ is found to be 0.435. This decrease in the value of the quantum yield supports fluorescence quenching, as the number of emitted photons decreases upon increasing the concentration of Cu²⁺.

3. 4. Stern volmer analysis

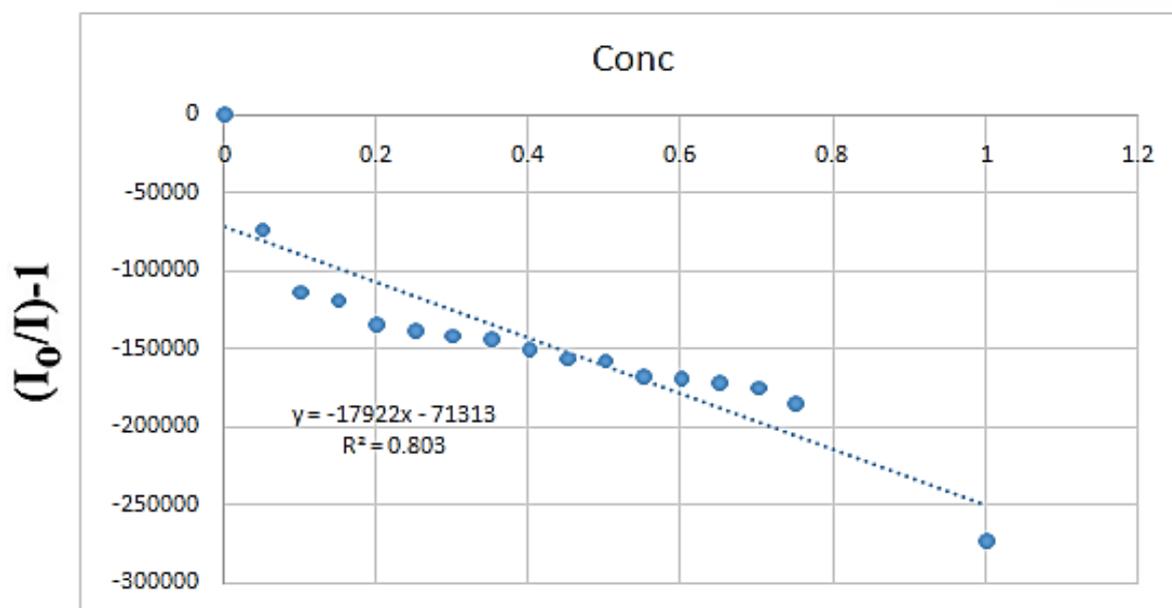


Figure 6. Stern volmer analysis.

To understand the mechanism of fluorescence quenching, stern volmer plots are used based on the following equation:

$$\frac{I_0}{I} = 1 + K_{sv}[Q]$$

where I_0/I and $[Q]$ are the relative emission intensity and quencher concentration respectively. By plotting I_0/I versus $[Q]$, whether the process is static or dynamic can be determined. The static quenching constant K_{sv} can be obtained from the slope of the plotted lines. The fluorescence quenching mechanism can be considered to be either purely dynamic or static if the I_0/I plots are linear for the whole range of quencher concentrations. If the I_0/I plots are non-linear and show an upward curve for higher quencher concentrations then the presence of simultaneous static and dynamic quenching can be deduced.

A quenching displaying a linear plot with a value of 0.859 for the complexation between 8QSC-CTV and Cu^{2+} ion is observed and hence it can be concluded that the fluorescence quenching mechanism is found to occur via a single mechanism, i.e., either purely static or collisional quenching.

4. CONCLUSION

In summary, a novel cyclotrimeratrylene-based chemosensor, 8QSC-CTV is explored for its cation recognition properties towards Cu^{2+} ions. The fluorescence spectral results 8QSC-CTV in the presence of Cu^{2+} ions show a drastic quenching in the intensity with no interference from other metal ions. 8QSC-CTV behaves as a “turn-off” sensor for Cu^{2+} ions among the various cations. Also the mechanism of fluorescence quenching was proposed. Moreover future work can be done in the area of measurement of toxic level and detection of Cu^{2+} ions.

Acknowledgement

The authors gratefully acknowledge Centre of Excellence (NFDD Centre, Rajkot), Oxygen Healthcare-Ahmedabad (O2h) for providing instrumental Facilities, Gujarat University for providing instrumental facilities and Information and Library Network (Ahmedabad) for e-journals.

References

- [1] Wu, Jiasheng, et al. New sensing mechanisms for design of fluorescent chemosensors emerging in recent years. *Chemical Society Reviews* 40.7 (2011) 3483-3495
- [2] Zhang, Xin, Jun Yin, and Juyoung Yoon. Recent advances in development of chiral fluorescent and colorimetric sensors. *Chemical Reviews* 114.9 (2014) 4918-4959
- [3] Gupta, Vinod Kumar, et al. Selective naked-eye detection of magnesium (II) ions using a coumarin-derived fluorescent probe. *Sensors and Actuators B: Chemical* 207 (2015) 216-223
- [4] Gupta, Vinod Kumar, et al. A reversible fluorescence “off–on–off” sensor for sequential detection of aluminum and acetate/fluoride ions. *Talanta* 144 (2015) 80-89
- [5] Gupta, Vinod K., Ajay K. Jain, and Gaurav Maheshwari. Aluminum (III) selective potentiometric sensor based on morin in poly (vinyl chloride) matrix. *Talanta* 72.4 (2007) 1469-1473

- [6] Kumar, Rajesh, Vandana Bhalla, and Manoj Kumar. Cu^{2+} and CN^- -selective fluorogenic sensors based on pyrene-appended thiacalix [4] arenes. *Tetrahedron* 64.35 (2008) 8095-8101
- [7] Gupta, Vinod K., et al. Electrochemical analysis of some toxic metals by ion-selective electrodes. *Critical Reviews in Analytical Chemistry* 41.4 (2011) 282-313
- [8] Maher, Niall J., et al. Lower rim isoxazole-calix [4] arene derivatives as fluorescence sensors for copper (II) ions. *Tetrahedron* 71.49 (2015) 9223-9233
- [9] Kaplan, Jack H., and Edward B. Maryon. How mammalian cells acquire copper: an essential but potentially toxic metal. *Biophysical Journal* 110.1 (2016) 7-13
- [10] Gupta, Vinod Kumar, et al. A novel copper (II) selective sensor based on dimethyl 4, 4'(o-phenylene) bis (3-thioallophanate) in PVC matrix. *Journal of Molecular Liquids* 174 (2012) 11-16
- [11] Gupta, V. K., et al. Copper (II)-selective potentiometric sensors based on porphyrins in PVC matrix. *Sensors and Actuators B: Chemical* 117.1 (2006) 99-106
- [12] Su, Yilong, et al. Fluorescent yeast containing intracellularly biosynthesized CdSe QDs as a sensitive probe for simple determination of copper (II) in water and plasma. *RSC Advances* 6.34 (2016) 28187-28193
- [13] Dutta, Mili, and Debasis Das. Recent developments in fluorescent sensors for trace-level determination of toxic-metal ions. *TrAC Trends in Analytical Chemistry* 32 (2012) 113-132
- [14] Hardie, Michael J. Recent advances in the chemistry of cyclotrimeratrylene. *Chemical Society Reviews* 39.2 (2010) 516-527
- [15] Meng, Xiangming, et al. 6-Substituted quinoline-based ratiometric two-photon fluorescent probes for biological Zn^{2+} detection. *Chemical Communications* 48.35 (2012) 4196-4198
- [16] Turel, Matejka, et al. Detection of nanomolar concentrations of copper (II) with a Tb-quinoline-2-one probe using luminescence quenching or luminescence decay time. *Analytica Chimica Acta* 644.1-2 (2009) 53-60
- [17] Zhou, Xiaoyan, et al. A highly selective fluorescent sensor for distinguishing cadmium from zinc ions based on a quinoline platform. *Inorganic Chemistry* 51.17 (2012) 9226-9231
- [18] Zhou, Xiaoyan, et al. Both visual and fluorescent sensor for Zn^{2+} based on quinoline platform. *Inorganic Chemistry* 49.9 (2010) 4002-4007
- [19] Chakrabarti, Ananya, et al. Convenient synthesis of selectively substituted tribenzo [a, d, g] cyclonatrienes. *Tetrahedron* 61.52 (2005) 12323-12329
- [20] Rurack, Knut. Flipping the light switch 'ON' – the design of sensor molecules that show cation-induced fluorescence enhancement with heavy and transition metal ions. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 57.11 (2001) 2161-2195

- [21] Loehr, Hans Gerd, and Fritz Voegtle. Chromo-and fluoroionophores. A new class of dye reagents. *Accounts of Chemical Research* 18.3 (1985) 65-72
- [22] Valeur, Bernard, and Isabelle Leray. Design principles of fluorescent molecular sensors for cation recognition. *Coordination Chemistry Reviews* 205.1 (2000) 3-40
- [23] Darjee, Savan M., et al. A new colorimetric and fluorescent chemosensor based on thiacalix [4] arene for fluoride ions. *Tetrahedron Letters* 55.51 (2014) 7094-7098
- [24] Larsen, Randy W., et al. Ground-and Excited-State Characterization of an Electrostatic Complex between Tetrakis-(4-Sulfonatophenyl) porphyrin and 16-Pyrimidinium Crown-4. *Photochemistry and Photobiology* 69.4 (1999) 429-434
- [25] Sutariya, Pinkesh G., et al. Fluorescence switch on-off-on receptor constructed of quinoline allied calix [4] arene for selective recognition of Cu^{2+} from blood serum and F^- from industrial waste water. *Analyst* 138.9 (2013) 2531-2535