HIGHLY SELECTIVE TRIPHENYLETHER DERIVATIVE AS FLUORESCENT SENSOR FOR COPPER AND ARGININE

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Copper is the third most abundant transition metal after Fe(III) and Zn(II) in a human body. It is recommended to take the proper dose of it in food every day. Many of the proteins in the human body use copper ions in electron transport processes, or for normal functioning of the brain and nervous system. Yet, excess of copper ions in living cells can damage lipids, catalyse the production of reactive oxygen species (ROS) and cause several diseases such as Alzheimer's disease, Indian childhood cirrhosis, and Wilson disease. According to the World Health Organisation (WHO), the maximum limit of copper in drinking water should be 1.3 ppm. The toxicity of copper is not only a concern to human species but has a great effect on the ambient environment too. An increased copper level has proven to be detrimental to the growth of stream insects, aquatic biota, and certain vegetation also. Therefore, the practical monitoring of Cu^{2+} is highly required [1, 2].

Arginine is a semi-essential amino acid that exists for tRNA, plays an important role in the synthesis of protein, wound healing, and cell replication. Reduced levels of arginine have been reported in various clinical conditions such as asthma, psoriasis, and reperfusion injury. Therefore, the detection of arginine in biological fluids has become an important goal [3].

For sensing metal cations, gases, and amino acids, selective recognition of a receptor is of prime importance. Variety of receptors such as Schiff base, rhodamine b, benzocoumarin etc. have been reported by research groups for the detection of number of target species. Our research group mainly focus on the synthesis of triphenylether based receptors due to several reasons such as easy solubility, proper arrangement of hetero atoms and electrochemical activity [4, 5]. Apart from importance of receptor, transducer techniques, which are used to collect the signal, have huge importance. Now these days, optical response using UV-VIS and fluorescence techniques have been widely used due their low cost and effective results.

Herein, a triphenylether amine (L1) based derivative has shown selective response towards Cu^{+2} ions without the interference from various cations such as Hg^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ca^{2+}, Pb^{2+}, Mg^{2+}, Cr^{3+}, and Zn^{2+} present in the same solution. UV-VIS response of the L1 and in the presence of various metal ions is shown in fig. 1. From Fig 1(a), it is clearly seen that L1 has selectively responded to Cu^{+2} ions following that all the initial absorption bands of receptor at 277 nm, 288 nm, 304 nm, and 334 nm have merged into a single band attributing to the interaction of Cu^{+2} ion with hetero atoms of the L1 and exhibiting a single band at 308 nm, as one whole molecule (fig. 1(b)). From calibration plot, detection limit of L1 towards Cu^{+2} ions was found to be 40 nM with binding stoichiometry of

1:1. Mechanism of interaction is explained on the basis of host-guest interactions between L1 and Cu^{+2} ions with binding constant of 1.5×10^{4} M^{-1}. Following the UV-VIS response, in fluorescence spectroscopy, L1 is fluorescent at 390 nm but addition of Cu^{+2} ions lead to "*turn off*" the fluorescence signal (fig. 1(c)). Technique based response is complemented by naked eye detection under UV lamp. Interference study confirmed the selective behaviour of L1 towards the Cu^{+2} ions (Fig. 1(d)).

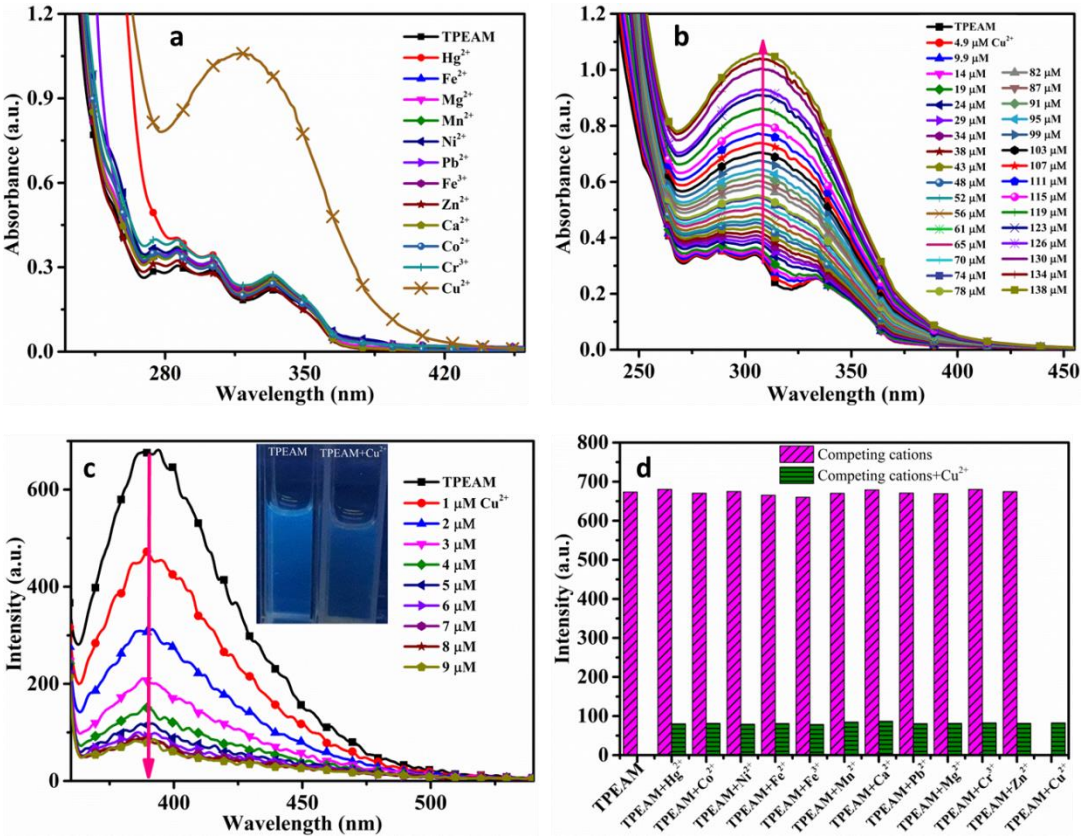

Fig. 1 (a) UV-VIS response of L1 towards Cu^{+2} ions (b) titration of L1 with Cu^{+2} ions (c) fluorescence titration of L1 with increasing amount of Cu^{+2} ions (d) interference study

For practical application, the complex L1-Cu^{+2} was used to see its response towards various amino acids such as asparagine (Asn), lysine (Lys), arginine (Arg), tryptophan (Trp), proline (Pro), glutamine (Gln), histidine (His) and cysteine (Cys). Among all the amino acids, complex showed selective behaviour towards arginine only (fig. 2(a)). Complex L1-Cu^{+2} was non fluorescent at 390 nm but with the addition of arginine, band stared reappearing at 390 nm, showing the selective response of complex towards amino acid. The reason for selective detection of arginine could be due to the conformational flexibility of its long side chain and the presence of large guanidinium moiety which delocalizes its positive charge over many atoms that are involved in the conjugated Y-Π system [6] (fig. 2(b)). The lower detection limit of arginine was found to be 4 μM, based on 3σ method.

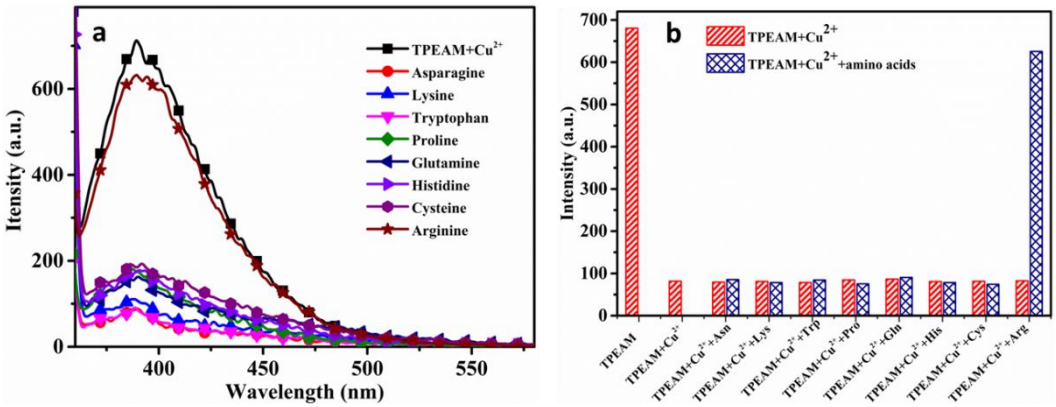

Fig. 2 (a) Fluorescence response of L1-Cu^{+2} complex towards arginine (b) interference study

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