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Invited paper

Novel fluorescent vanadylmoxifloxacinato complexes as sensors for Cu²⁺



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ABSTRACT

Three novel mixed ligands complexes of VO²⁺, (**C1–C3**) with the ligands moxifloxacin and dipeptides have been synthesised and characterised by Infrared and Ultraviolet-visible spectroscopy, Mass spectrometry, Electron spin resonance spectroscopy and elemental analysis. The fluorescent spectral measurements revealed that complexes **C1–C3** are selective fluorescent sensors for Cu²⁺ but not for metal ions such as Na⁺, K⁺, Al³⁺, Fe³⁺, Co²⁺, Ni²⁺, Zn²⁺ and Cd²⁺. The detection limit for the determination of the Cu²⁺ ion was estimated as low as 2.0 μM. Furthermore, EDTA cannot turn on the quenched fluorescence of complexes **C1–C3** induced by Cu²⁺ (“off” type sensor).

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1. Introduction

Luminescent metal complexes have attracted increasing attention in the literature over the last few decades. Spearheaded by pioneering developments in ligand field theory and in the understanding of electronic transitions and spectroscopy of transition metal complexes, these compounds have enjoyed widespread application in photochemistry [1,2], organic optoelectronics [3,4] and luminescent sensors [5,6]. In contrast to conventional organic fluorophores, which are singlet emitters, transition metal complexes display triplet emission due to spin-orbit coupling imparted by the heavy atom effect, which leads to efficient singlet–triplet state mixing and enhancement of phosphorescence quantum efficiency. The phosphorescence behaviour of metal complexes has found potential use in the construction of organic light-emitting diodes (OLEDs) for display or lighting applications [7–10].

In the context of luminescent sensing, transition metal complexes have unique advantages that make them suitable for chemosensing or biosensing applications. These include their (i) high luminescence quantum yield, (ii) long phosphorescence lifetime that allows their emission to be distinguished from a fluorescent background, (iii) large Stokes shift for effective discrimination of excitation and emission wavelengths, (iv) sensitivity of their emissive properties to subtle changes in the

local environment, and (v) modular synthesis that allows facile synthesis of analogues for fine-tuning of their chemical and/or photophysical properties [11]. In light of these advantages, transition metal compounds have been widely studied for luminescent sensing applications, particularly the d⁶, d⁸ or d¹⁰ electron complexes based on ruthenium(II), platinum(II), iridium(III), osmium(II), gold(I), zinc(II) and rhenium(I) [11]. Compared with organic fluorophores, the excited state properties of transition metal complexes are complicated and can include metal-to-ligand charge-transfer (MLCT), ligand-to-ligand charge transfer (LLCT), intraligand charge-transfer (ILCT), ligand-to-metal charge transfer (LMCT), metal–metal-to-ligand charge-transfer (MMLCT), ligand-to-metal–metal charge-transfer (LMMCT) and metal-to-ligand–ligand charge-transfer (MLLCT) states [12,13]. The properties of the excited states are highly sensitive to the metal centre, the type of ligands, and the nature of the local environments, allowing the photo physical properties (such as emission wavelength, lifetime, and intensity) of metal complexes to be tailored for specific applications.

Copper is an essential trace element for growth and development in all forms of life. It is the second most important trace metal in the human body and tends to be an integral part of a number of metalloenzymes covering the whole range of functionality [14]. However excessive amount of copper can cause toxicity and do great harm to the body. Cu²⁺ metabolism disorders have been reported to cause Wilson's disease which leads to excessive Cu accumulation in vital organs like kidneys, liver, lungs and brain causing malfunctioning of these organs [15]. This potential hazard makes it indispensable to monitor the amount of copper in

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environmental water. Toward alleviating this issue, the selective detection of Cu^{2+} ions in aqueous solutions with high sensitivity is of great importance. To ensure safety, a detection limit as low as $20 \mu\text{M}$ (1.3 ppm) is recommended by the Environmental Protection Agency (EPA) [16]. Recently, ZnO@ZnS core-shell nanoparticles [17] and fluorescent gold nanoclusters [18] have been introduced to achieve efficient and selective detection of Cu^{2+} ions. Functionalized gold nanoparticles (AuNPs) [19] were also used for the detection of metal ions including Cu^{2+} . SERS (Surface-enhanced Raman spectroscopy) has also been used to discriminate Cu^{2+} ions in aqueous solutions with an interference of Hg^{2+} and Co^{2+} [20,21]. Nguyễn Hoàng Ly et al. have reported detection of copper (II) ions using glycine on hydrazine-adsorbed gold nanoparticles using Raman spectroscopy [22]. Another report has been published by J. Hwang et al. on sensitive detection of copper ions via ion-responsive fluorescence quenching of engineered porous silicon nanoparticles [23]. The standard method of measuring Cu^{2+} ions, however, employs ion-selective electrodes, which presents difficulties when considering the presence of various non-specific biomolecules (i.e. proteins, enzymes, other ions). From this perspective, a simple and convenient method to detect Cu^{2+} ions with high specificity and sensitivity is desirable.

In the present work, novel VO^{2+} mixed ligand complexes **C1–C3** based on an antibiotic drug moxifloxacin and the dipeptides glycylleucine (**C1**), glycyglycine (**C2**) and glycyalanine (**C3**) were synthesized and characterized by infrared (IR) and ultraviolet-visible (UV-vis) spectroscopy, mass spectrometry (MS), electron spin resonance (ESR) spectroscopy and elemental analysis, and their potential to detect Cu^{2+} ions through UV-vis absorption and fluorescence spectroscopy is reported. The complexes emitted strong fluorescence at $\sim 450 \text{ nm}$ and with the incremental addition of Cu^{2+} , the fluorescence of the complexes were quenched gradually. The response showed high selectivity for Cu^{2+} compared with other metal ions and could be used to detect Cu^{2+} .

2. Experimental

2.1. Reagents and instrumentation

All the chemicals and solvents used for synthesis and characterization of the complexes were of analytical reagent

grade and were used as purchased. MFL (Moxifloxacin) was kindly donated by Alembic Research Centre (Gujarat, India). The metal salts and solvents were purchased from Merck. Dipeptides were purchased from SRL (Sisco research laboratory, Mumbai, India.). Infrared (IR) spectra ($400\text{--}4000 \text{ cm}^{-1}$) were recorded on Perkin Elmer RX-1 FTIR with samples prepared as KBr disks. ESI Mass spectra of the ligands were recorded on ThermoScientific DSQ – II Mass spectrometer and those of the complexes were recorded on Applied Biosystem API 2000 Mass spectrometer. C, H and N elemental analysis were performed on a Perkin-Elmer 240B elemental analyzer. UV-vis absorption spectra were recorded in DMSO solution on Perkin Elmer Lambda-35 dual beam UV-vis spectrophotometer. EPR spectra at liquid nitrogen temperature were recorded on JES – FA200 ESR Spectrometer. Fluorescence spectra were recorded in solution on JASCO FP-6300 fluorescence spectrophotometer. The metal content in each of the complexes was determined by gravimetric/complexometric titration method after decomposition of the complexes.

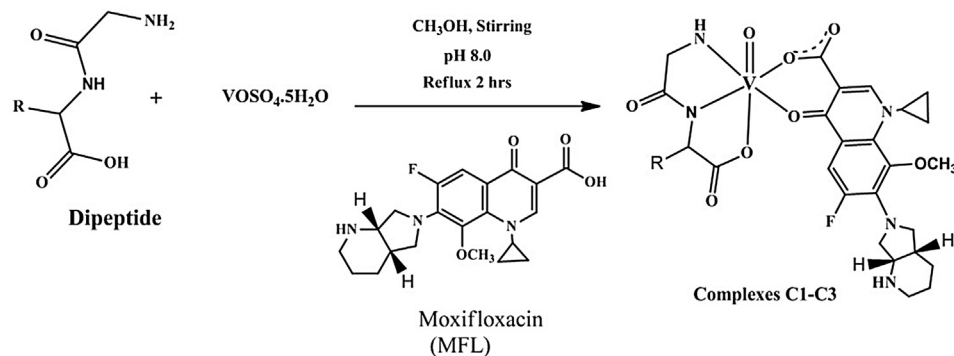
2.2. Synthesis of complexes

To a stirred methanolic solution (10 mL) of oxovanadium(IV) sulfate (0.25 g, 1.0 mmol) was added an aqueous solution of the dipeptide (1.0 mmol) followed by addition of KOH (0.056 g, 1.0 mmol). The reaction mixture was stirred for 2 h at room temperature to obtain a clear green color solution. A methanolic solution (20 mL) of moxifloxacin (MFL) (0.401 g, 1.0 mmol) was added to the above reaction mixture and refluxed for another 2 h. The green colored solid was filtered, thoroughly washed with ice cold methanol and dried in vacuum over anhydrous CaCl_2 (Scheme 1). The complexes were characterized by IR, ESR, Mass spectral and elemental analysis techniques.

2.3. Physicochemical properties of the complexes

2.3.1. $[\text{VO}(\text{glyleu})(\text{MFL})](\text{C1})$

Yield: 75%, Molecular weight: 655.59 g/mol, Molecular formula: $\text{C}_{29}\text{H}_{38}\text{FN}_5\text{O}_8\text{V}$, Calc. (%): C, 53.21; H, 5.85; N, 10.70.; V, 7.78., Found (%): C, 54.21; H, 5.85; N, 10.60.; V, 7.8, λ_{max} : 224, 288 ($\epsilon = 16305 \text{ L mol}^{-1} \text{ cm}^{-1}$), 333 nm, ESI-MS [Me OH, m/z]: 655.8 [M+].



-R	dipeptide	Complex
$-\text{CH}_2\text{CH}_2(\text{CH}_3)_2$	glycylleucine	C1
-H	glycyglycine	C2
$-\text{CH}_3$	glycyl alanine	C3

Scheme 1. Synthetic scheme of complexes **C1–C3**.

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