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# Photoluminescence Emission Enhancement and Coordination-driven Isomer-locking Effects of Cr(III) on Azobenzene-bearing Tweezer Anchored to Binaphthdiazacrown Macrocycles

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## Abstract

In this report, the synthesis of a new bi-macrocycle tweezer linked through an azobenzene moiety, **L** was undertaken. The characterization of the tweezer was accomplished by employing IR, <sup>1</sup>H and <sup>13</sup>C NMR, UV-vis, fluorescence spectroscopy and CHN microanalysis while the UV-visible spectroscopy illustrated a *trans* ⇌ *cis* photo-isomerization for **L**. According to our preliminary fluorescence observations, a metal-ion chemosensing behavior was established for *trans*-**L** isomer towards Cr(III) ion among the library metal ions. The quenching of the respective *trans* ⇌ *cis* isomerization in the presence of Cr(III) ion suggested the preference of a strong interaction between Cr(III) ion with **L**, leading to isomer-locking of the *trans*-**L** isomer. Since the Job plots for **L** in the presence of Cr(III) metal ion suggested a 1:2 ratios for the interaction of Cr(III) with **L**, an electronic effect of Cr(III) ion with the phenolic groups on **L** was suggested as the main factor for the observed isomer-locking process in *trans*-**L**. The binding constant and the detection limit for Cr(III) ion by **L** were also assessed as  $1.55 \times 10^8 \text{ M}^{-1}$  and  $10^{-8} \text{ M}$ , respectively, suggesting **L** as a new chemosensor for Cr(III) metal ion.

**Keywords:** tweezer, azobenzene, isomer-locking macrocycle, fluorescence, naphthdiazacrown

## 1. Introduction

Nowadays, constructing of photoresponsive materials by applying the azobenzene chromophores is one of well-known research areas in chemistry [1]. Principally, azobenzene moiety can reversibly experience a *trans* ⇌ *cis* conformational transformation upon irradiation with light as well as thermal conditions. Thus, the abovementioned light-triggered switching capability has been employed in an assortment of molecular machines, proteins, chelates, polymers, and modified materials [2-4]. Due to potential application of the *trans*-*cis* isomerization phenomena in optical-based phase transformations, numerous devices such as artificial muscles, optical switches and memory storages enjoy from this phenomena [5,6].

From the practical point of view, ON/OFF mode in photo-responsive key-lock systems is applicable to control the molecular motions, whereby the information could be store in molecular scale. Recently, the developing of new photo-responsive key-lock systems with metal coordination locking feature have been considered as ON/OFF switches, owing to their potential applications as the cores of molecular machines [7,8]. Typically, these chemical sensors have benefit from key-lock systems, wherein a specific analyte is selectively detectible by a specific receptor through a strong binding protocol. For instance, Bandara *et al* synthesized 2,2'-bis[N-(2-pyridyl)methyl]diaminoazobenzene as a chemosensor with isomer-locking feature in the presence of metal ion [9]. The persistence of two robust intramolecular hydrogen bonds within the chemosensor were introduced as the main reason to impose a barrier to proceed the photo-isomerization due to the adaptation of the molecule to a rigid planar structure [9]. In another review, a self-assembled macrocyclization was

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