Dyes and Pigments 152 (2018) 67–74

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Colorimetric detection of Cu^{2+} and UO_2^{2+} by mixed solvent effect

Jun Wen[a,*], Shuo Li[b,**], Zeng Huang[a], Weiyi Li[c,***], Xiaolin Wang[a]

[a] *Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, Sichuan Province, China*
[b] *School of Chemical Engineering, Chongqing University of Technology, Chongqing 400054, China*
[c] *School of Science, Xihua University, Chengdu, Sichuan 610065, China*

ARTICLE INFO

Keywords:
Solvent effect
Selectivity
Colorimetric recognition
Coordination control
DFT calculation

ABSTRACT

We herein report the synthesis of a novel 2-(2-pyridylazo)-5-(diethylamino) phenol (PADAP)-containing tetraphenylethene (TPE) derivative, T-PADAP, to examine the solvent effect in the selective colorimetric detection of Cu^{2+} and UO_2^{2+}. We found that the coordination of metal ions was influenced by adjusting the H_2O:DMSO ratio, which ultimately led to differently colored solutions in the presence of the two metal ions. More specifically, T-PADAP exhibited a purple color in the presence of Cu^{2+} in a DMSO/H_2O mixture containing 60% water, and a blue color in the presence of UO_2^{2+} in a DMSO/H_2O mixture containing 40% water. T-PADAP was therefore considered a suitable colorimetric sensor for both Cu^{2+} and UO_2^{2+}. Importantly, this compound exhibited a high selectivity, a wide effective pH range, and good anti-interference qualities. As such, this system constitutes a simple method for the detection of both Cu^{2+} and UO_2^{2+} using a single colorimetric sensor and through facile variation in the solvent ratio. In addition, it illustrates the use of solvent effects to regulate the coordination abilities of sensors. We expect that this study will promote the development of novel recognition methods for metal ions in environmental samples.

1. Introduction

Chemosensors constitute a convenient method for optical detection due to their low cost, high selectivities, and fast responses. In general, two types of chemosensors exist that produce optical responses, namely colorimetric and fluorescent sensors. Indeed, colorimetric sensors have received considerable attention because of their simplicity and their ability to distinguish between target ions without the use of advanced equipment [1–6].

Recently, numerous reports on the use of colorimetric sensors for metal ion analysis have been published, with Cu^{2+} detection receiving significant attention [7–22]. The Cu^{2+} ion is of particular importance as it acts as an oxygen carrier and a redox catalyst in the active sites of various enzymes; however, abnormal Cu^{2+} levels can lead to Alzheimer's, Parkinson's, and Wilson's diseases, in addition to amyotrophic lateral sclerosis [23–26]. Uranium has also received significant attention in the field of colorimetric recognition [27–29]. This metal has a number of important applications, including in nuclear energy generation and nuclear weapons. However, uranium is both radioactive and toxic, with human exposure to uranium causing lung cancer, urinary system ailments, and genetic diseases [30,31]. Considering the widespread use of these two metals and their significant toxicities, the development of analytical methods for their determination is essential. Although colorimetric sensors exhibit good recognition abilities toward copper and uranyl ions, no sensor currently exists that is capable of detecting both of these ions. As such, the development of a simple, rapid, highly selective, and low-cost colorimetric sensor for their detection remains a challenge.

It was therefore proposed that changes in ultraviolet-visible (UV/Vis) spectra could provide a facile optical method for the colorimetric determination of target species. Such spectral changes can often be attributed to coordination effects between ligands and metal ions or by ligand-mediated reactions resulting in the formation of new molecules [32,33]. It is generally understood that selective recognition is facilitated by selective coordination between certain groups within a ligand. As such, ligand design is considered the most important factor in determining the selectivity of colorimetric sensors. Although the solvent is also an important component in ion recognition, it is often overlooked when considering selectivity. Typically, solvents are only considered as reaction media, despite their known effects in metal ion coordination [34,35]. Indeed, very few reports into the effects of solvents in metal ion analysis exist, except for aggregation-induced

---

[*] Corresponding author.
[**] Corresponding author.
[***] Corresponding author.

E-mail addresses: junwen@caep.cn (J. Wen), lishuo@cqut.edu.cn (S. Li), weiyili@mail.xhu.edu.cn (W. Li).

https://doi.org/10.1016/j.dyepig.2018.01.038
Received 6 December 2017; Received in revised form 24 January 2018; Accepted 24 January 2018

emission (AIE) sensors, which require specific solvent mixtures to induce ligand aggregation and promote AIE [36–42]. In addition, Jeon et al. reported an azobenzene-based dye containing a dithiaazadioxo ring for Hg^{2+} detection in diverse solvents [43]; this sensor exhibited high selectivity toward Hg^{2+} and yielded different colors in acetonitrile and chloroform solvent systems. However, the control of sensor selectivity through adjusting the solvent ratio has yet to be reported, and so it would be desirable to gain an improved understanding of the effects of solvents on colorimetric sensors for metal ion recognition.

Thus, we herein present a novel 2-(2-pyridylazo)-5-(diethylamino) phenol (PADAP)-containing tetraphenylethene (TPE)-based colorimetric sensor, T-PADAP, for the highly selective detection of Cu^{2+} and $UO_2{}^{2+}$ at low detection limits. This simple detection process based on solvent effects is expected to allow Cu^{2+} and $UO_2{}^{2+}$ ions to be clearly distinguished visually from other transition and alkali metals by varying the solvent ratio.

2. Experimental

2.1. Instrumentation and measurements

^1H NMR and ^{13}C NMR spectroscopy was carried out on a Bruker AM400 NMR spectrometer (400 MHz and 100 MHz, respectively). Electrospray ionization mass spectrometry (ESI-MS) data were recorded on a Finnigan LCQDECA mass spectrometer. Absorption spectra were recorded on a PE Lambda 650 instrument (PerkinElmer). Unless otherwise mentioned, all measurements were carried out at room temperature (~293 K).

2.2. Reagents and solutions

Unless otherwise noted, all materials were obtained from commercial suppliers and were used as received without further purification. All solvents used in the optical spectroscopic studies were of either HPLC or spectroscopic grade. All metal ions were obtained as standard solutions from the National Standards Centre (China).

2.3. Preparation of T-PADAP

The synthetic route employed for the preparation of T-PADAP is shown in Scheme 1. Under a nitrogen atmosphere were dissolved Compound **1** (400 mg), Compound **2** (600 mg), K_2CO_3 (480 mg), and Pd $(PPh_3)_4$ (100 mg) in 1,4-dioxane/water (3:1, 10 mL) in a flask equipped with a sidearm and a magnetic stirring bar. The resulting mixture was then heated at 100 °C over 3 h, after which time, water (20 mL) was added to quench the reaction. Following extraction of this mixture with ethyl acetate, the organic phase was washed with water and dried over anhydrous Na_2SO_4. The dried organic phase was then concentrated in vacuo, and the crude product was purified by column chromatography (hexane:ethyl acetate = 5:1) to obtain T-PADAP as a red solid in 67% yield.

2.4. Spectroscopic measurements

For all spectroscopic measurements, a solution of T-PADAP in DMSO (20 μL, 1×10^{-3} M) and a solution of metal ions in deionized water (50 μL, 4×10^{-4} M) were added to a 5.0 mL glass tube and diluted to 2000 μL with THF/water (water volume fraction, f_w = ~40–99%). After mixing and subsequent equilibration at room temperature for 10 min, each solution was subjected to spectroscopic measurements.

2.5. Computational method

All calculations were conducted using the Gaussian 09 program. Geometry optimization of the $Cu(T\text{-}PDAD)^{2+}$ and $Cu(T\text{-}PDAD)_2{}^{2+}$ complexes was performed using the density functional theory (DFT) approach at the B3LYP level of theory in DMSO and H_2O using the continuum solvation model (SMD). The Cu atom was described using the pseudopotential SDD basis set, while the other atoms (C, H, O, and N) were treated with the 6-31G(d) basis set. Vibrational frequency calculations were also carried out at the same level of theory to ensure that this complex is a local minimum (no imaginary frequency).

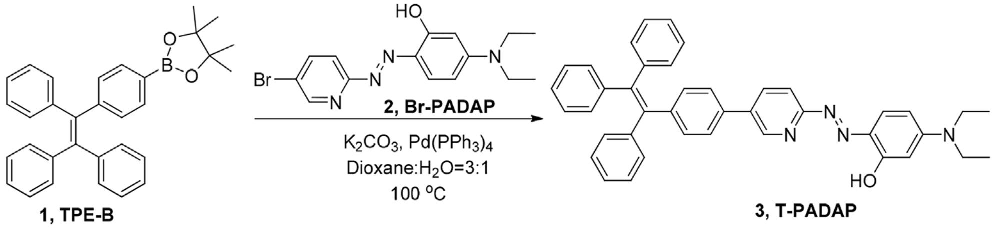
3. Results and discussion

3.1. T-PADAP

The synthetic route toward T-PADAP is shown in Scheme 1. This route produced T-PADAP in a satisfactory yield through a Suzuki-Miyaura cross-coupling reaction. Further synthetic details and characterization data are provided in the Supporting Information. We selected this structure as 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol (Br-PADAP) is a well-known metal chelating unit for transition metals [44–49]. Thus, in addition to bearing this metal chelating moiety, the prepared T-PADAP contains a chromophore that exhibits a red color in the solid form and a yellow color in dilute solutions (i.e., ~10 μM). Thus, upon the addition of transition metal ions to a solution of T-PADAP, coordination effects promote a color change in the T-PADAP solution, thereby permitting their detection, and rendering T-PADAP a potential colorimetric sensor for metal ions.

3.2. Solvent effects in the coordination of metal ions by T-PADAP

We initially investigated the colorimetric response of T-PADAP toward metal ions in water and in a number of common organic solvents that are miscible with water (i.e., DMSO, THF, acetonitrile, methanol, and dioxane). As a result, we found that T-PADAP can coordinate a range of metal ions (i.e., Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}), with color changes being observed upon the dissolution of T-PADAP in organic solvents (see Fig. S1 in Supporting Information). However, no color change occurred when T-PADAP was dissolved in water (water volume fraction: f_w = 99%). This interesting phenomenon may be due to the different solvent effects imparted by water and by the various organic solvents in the coordination of metal ions by T-PADAP. Although T-PADAP coordinates various transition metals, the coordination strengths differ depending on the water-organic solvent mixture employed. As such, the coordination effects can be altered, and the selectivity of the sensor can be modified. Upon considering ligand solubility, water miscibility, volatility, and solvent toxicity, we thus selected DMSO for the dissolution of T-PADAP. The absorption spectra of 10 μM solutions of T-PADAP were obtained in the presence of a range



Scheme 1. Synthesis of T-PADAP.