



A new colorimetric chemodosimeter for Hg²⁺ based on charge-transfer compound of N-methylpyrrole with TCNQ

Paramjit Kaur^{a,*}, Sandeep Kaur^{a,b}, Yoganjaneyulu Kasetti^c, Prasad. V. Bharatam^c, Kamaljit Singh^{b,*}

^a Department of Chemistry, Guru Nanak Dev University, Amritsar, India

^b Organic Synthesis Laboratory, Department of Applied Chemical Sciences and Technology, Guru Nanak Dev University, Amritsar, India

^c Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research (NIPER), S.A.S Nagar, India

ARTICLE INFO

Article history:

Received 3 September 2010

Received in revised form 7 October 2010

Accepted 8 October 2010

Available online 15 October 2010

Key words:

Charge-transfer

TCNQ

Colorimetric

Chemodosimeter

Mercury

ABSTRACT

Reaction of N-methylpyrrole and 7,7,8,8-tetracyanoquinodimethane (TCNQ) furnishes an intense blue unsymmetrical charge-transfer compound through regioselective attachment of tricyanoquinodimethane at the 2-position of N-methylpyrrole which was found to be selective chemodosimeter for Hg²⁺ ions in CH₃CN:H₂O mixture (1:1 v/v, pH = 7.0, 0.01 M HEPES, 0.15 M NaCl) as well as in the solid state when supported on silica, over a variety of metal ions. A plausible mechanism for the sensing process has been proposed and supported through the characterization of the resulting Hg²⁺ complex and the density functional theory (DFT) studies.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

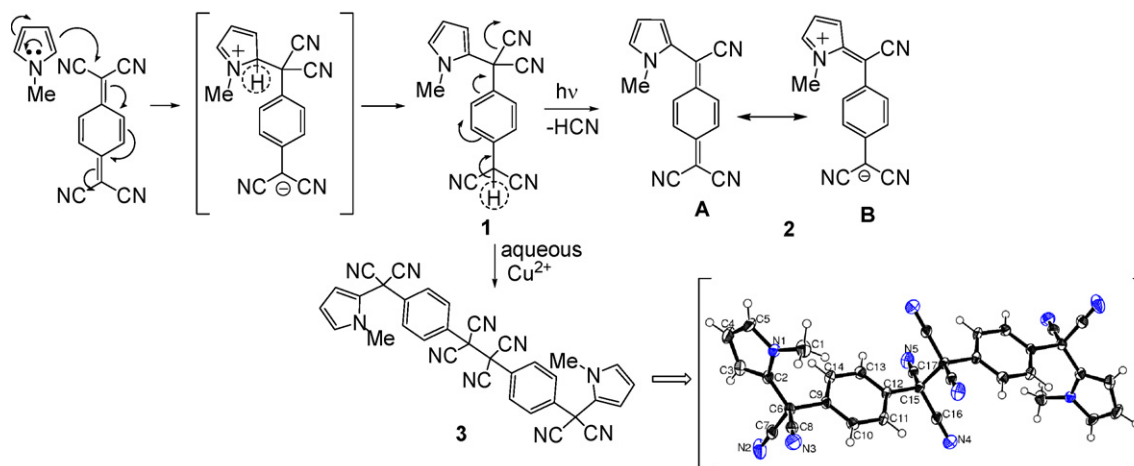
Novel conjugated π -electron chromophores containing a donor and an acceptor have attracted considerable interest owing to their interesting properties and uses in a variety of high-tech applications such as near infrared (NIR) dyes [1] and non-linear optical (NLO) devices [2] owing to the inherent push-pull electronic effects in these molecules. Additionally, depending upon the strength of the covalently linked donor and acceptor components, strong intramolecular charge-transfer (ICT) transitions are facilitated, leading to intense colors of these compounds. The latter property has led to the design of several chemosensors involving charge-transfer [3] for the detection of a variety of ionic analytes and has been the subject of current research interest in our lab [4]. In the present investigation, we are reporting the synthesis of a new charge-transfer compound **2**, (Scheme 1), derived from N-methylpyrrole and 7,7,8,8-tetracyanoquinodimethane (TCNQ), as donor–acceptor combination. Considering the presence of soft electron rich centres in **2**, conducive for binding with soft metal centres, and the consequent perturbation of conjugation, we also report the application of **2** as chemodosimeter for the colorimetric detection

of Hg²⁺ (Scheme 2). The mechanistic rationale, both for the formation of **2** as well as the sensing process is also unambiguously established.

The importance of selective detection of Hg²⁺ lies in the fact that Hg²⁺ pollution poses severe problems for human health and the environment [5]. Consequently, many methods have been developed to detect Hg²⁺ ion in the presence of its competitive cations. The techniques based on atomic absorption/emission spectroscopy and inductively coupled plasma mass spectrometry (ICPMS) for screening Hg²⁺ are limited by the cost factor in addition to the intricate sample preparations [6]. In contrast, simplified and straight forward methods for Hg²⁺ detection involving redox [7], chromogenic [8] and fluorogenic [9] changes invariably employ crown ethers [10], calix[4]arenes [11], cyclams [12], squaraines [13], thioureas [14], 1,3-dithiole-2-thione [15], 8-hydroxyquinolines [16], 1,4-disubstituted azines [7], fluoresceins [17], rhodamine lactam or thiolactam [18] etc. Inherent water solubility of several biomolecules such as proteins [19], oligonucleotides [20], DNAzymes [21] and antibodies [22] has allowed their use for the detection of Hg²⁺. Colorimetric sensing of metal ions has been considered as advantageous in many respects and constitutes a dependable technique alongside fluorescence [7], however, reports on the use of colorimetric chemodosimeters which operate by a specific chemical reaction to generate a detectable chemical signal, for Hg²⁺ detection are scanty [23,24].

* Corresponding author. Tel.: +91 183 2258853; fax: +91 183 2258819 20.

E-mail addresses: paramjit19in@yahoo.co.in (P. Kaur), kamaljit19in@yahoo.co.in (K. Singh).



Scheme 1. Formation of blue charge-transfer compound **2** in the reaction of N-methylpyrrole and TCNQ. Inset: X-ray crystal structure of **3** (CCDC No. 760693).

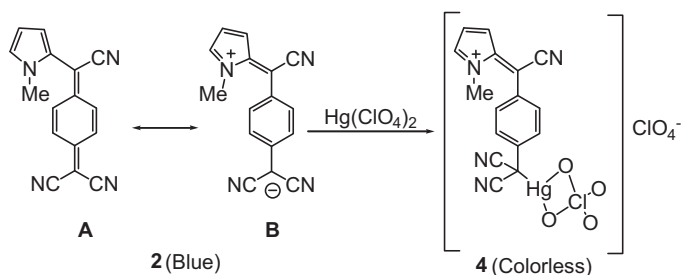
2. Experimental

2.1. Chemicals

All reagents were purchased from Aldrich and were used without further purification. DCM was dried over benzophenone ketyl under inert atmosphere and distilled directly in the reaction flask. DMF was dried over a pinch of calcium hydride and distilled under reduced pressure over 4 Å molecular sieves. Silica gel G (60–120 mesh) was used for column chromatography.

2.2. Instrumentation

UV–vis spectra were recorded on a SHIMADZU 1601 PC spectrophotometer, with a quartz cuvette (path length, 1 cm) and studies were performed in AR grade CH₃CN and double distilled water. The cell holder of the spectrophotometer was thermostatted at 25 °C for consistency in the recordings. ¹H and ¹³C NMR spectra were recorded on a JEOL-FT NMR AL 300 MHz and BRUKER Avance II 400 MHz spectrophotometer using CDCl₃ and DMSO-*d*₆ as solvent and tetramethylsilane (SiMe₄) as internal standard. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, dd = doublet of doublet, m = multiplet), integration, coupling constant *J* (Hz) and assignment. The mass spectra were recorded with Esquire 3000–00037 mass spectrometer and Ultraflex/TOF/TOF mass spectrometer. Elemental analyses were performed with a Thermo Flash EA 1112 analyser and were within $\pm 0.4\%$ of the theoretical values. IR spectrum was recorded on FT IR-SHIMADZU 8400 and Varian 660-IR Fourier-Transform spectrophotometers, in range 400–4000 cm⁻¹. Titration isotherms generated from UV–vis changes were fit in HypSpec [25] software to establish the stoichiometry of the complex and to determine the binding constant. The X-ray structure (CCDC No. 760693) was



Scheme 2. Sensing of Hg²⁺ with **2**.

solved by direct methods using SIR97 [26] and refined by full matrix least-square refinement techniques on F2 using SHELXTL [27].

2.3. Computational Details

Ab initio DFT (density functional theory) studies [28] were carried out using Gaussian 03 software [29]. Initial optimization studies were carried out using semi-empirical PM3 method [30]. Resultant structures were subjected for optimization using B3LYP/LanL2DZ method. Partial atomic charges on the optimized structures were estimated using the NBO (natural bond orbital) method [31]. Electron density analysis has been carried out using the atoms in molecules (AIM) method [32] using the AIM2000 software [33].

2.4. Synthesis and characterization of compounds **1**, **2** and **3**

2.4.1. Synthesis of **1**

To freshly distilled N-methylpyrrole (0.5 g, 6 mmol) in anhydrous DMF (5.0 mL) a dilute solution of TCNQ (1.2 g, 6 mmol) dissolved in anhydrous DMF (150 mL) was added dropwise and the reaction mixture was stirred for 4 h at room temperature. After completion of the reaction, DMF was removed under reduced pressure on a rotary evaporator. The residue was washed with saturated aqueous sodium chloride solution and extracted with ethyl acetate (2 × 100 mL). The combined extract was dried over anhydrous sodium sulfate and the residue was chromatographed using hexane and its mixtures with ethyl acetate as eluent to obtain **1**, which was dissolved in anhydrous DCM (50 mL) and treated with charcoal (2 g). After filtration, the solvent was evaporated and the residue was recrystallized from DCM/hexane mixture to obtain **1** in the pure form (1.23 g, 70%). Mp: 90 °C; (Found: C, 71.20; H, 4.05; N, 24.15 C₁₇H₁₁N₅ requires C, 71.57; H, 3.89; N, 24.55%); $\nu_{\max}/\text{cm}^{-1}$ 2060 (CN); δ_{H} (400 MHz; CDCl₃; Me₄Si) 3.47 (3H, s, NMe), 5.10 (1H, s, CH), 6.06–6.13 (2H, m, 2 × CH), 6.68–6.69 (1H, m, CH), 7.62 (4H, s, ArH); δ_{C} (300 MHz; CDCl₃; Me₄Si) 27.6, 35.1, 45.2, 108.0, 110.9, 112.9, 113.0, 119.5, 127.7, 128.5, 128.7, 134.4; *m/z* (EI): 283.6 (M⁺–1), 256.6 (M⁺–HCN–1).

2.4.2. Conversion of **1** to **2**

To isolate the blue charge-transfer compound **2**, **1** (1.0 g, 3.5 mmol) was dissolved in anhydrous CH₃CN (50 mL) or DMF (10 mL) and kept in direct sunlight or UV-light for 6 h. Solvent was removed under reduced pressure and the residue chromatographed to isolate **2** (0.36 g, 40%) alongwith **3** (an oxidatively coupled product) [34] (0.25 g, 27%).

Download English Version:

<https://daneshyari.com/en/article/1242856>

Download Persian Version:

<https://daneshyari.com/article/1242856>

[Daneshyari.com](https://daneshyari.com)