



Protonation-induced change in the conformation, crystal structure and property of triarylmethyl carbocation radical[☆]



Cong Zhang, Ya Feng, Chen Shen, Guoping Yong^{*}

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

ARTICLE INFO

Article history:

Received 8 December 2015

In final form 16 February 2016

Available online 22 February 2016

ABSTRACT

We report a new triarylmethyl carbocation radical which was easily synthesized via “one-pot” approach. Interestingly, this “*cis*” triarylmethyl carbocation radical converted to the “*trans*” one upon protonation. Such an obviously conformational change is triggered by the intermolecular hydrogen bond interaction involving one exocyclic “keto” oxygen atom and the protonated pyridinium nitrogen atom. Two triarylmethyl carbocation radical crystals were characterized by the elemental analysis and single crystal X-ray diffraction. A change in conformation also brings about change in crystal structure, phosphorescence and magnetic susceptibility properties.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The supramolecular assembling process using noncovalent interactions such as hydrogen bond, π – π stacking, C–H– π , ion– π , electrostatic and hydrophobic interaction [1], has been recognized as a high-potential technique to construct functional molecular materials. Many novel organic solids have been assembled through noncovalent interactions, which reveal potential applications in pharmaceutical [2], electronic [3], optical [4,5], luminescent [6], catalytic [7], ferroelectric [8], or magnetic [9,10] fields. Of these noncovalent interactions, the hydrogen bond is an important tool for creation of desired organic molecular arrangements and interesting properties [11]. Moreover, the noncovalent interactions provide frameworks within which or between which controllable dynamic structural changes of large amplitude (molecular motions) can be envisaged such as rotations and translations or combinations thereof [12]. Molecular motions can be triggered by various means such as protonation, ion binding, electron transfer, and light excitation. The protonation even can induce large conformational changes of the molecular frameworks [13–18].

Although stable triarylmethyl radical derivatives as molecular materials have been extensively investigated [19], in order to probe new triarylmethyl radicals, we recently reported three novel triarylmethyl carbocation radicals. It is found that these

three triarylmethyl carbocation radical salts are positional isomers and exhibit different magnetic susceptibility values at 300 K [20]. Herein, we unveil the syntheses, crystal structures and properties of a triarylmethyl carbocation radical (denoted as **TAM⁺·Cl⁻**) and its a conformational changing product. It is interesting to note that protonation at pyridine nitrogen of **TAM⁺·Cl⁻** induces obviously conformational change, giving rise to the formation of “*trans*” **HTAM²⁺·2ClO₄⁻·H₂O** triarylmethyl carbocation radical (Scheme 1). A change in conformation triggered by protonation also brings about the change in crystal structure and properties. Compared to the protonated “*trans*” **HTAM²⁺·2ClO₄⁻·H₂O**, the “*cis*” **TAM⁺·Cl⁻** possesses highly hydrophobic one-dimensional (1D) channels, attributable to its change in crystal structure. Moreover, both also exhibit different phosphorescent characters and magnetic susceptibility data owing to the conformational change.

2. Experimental

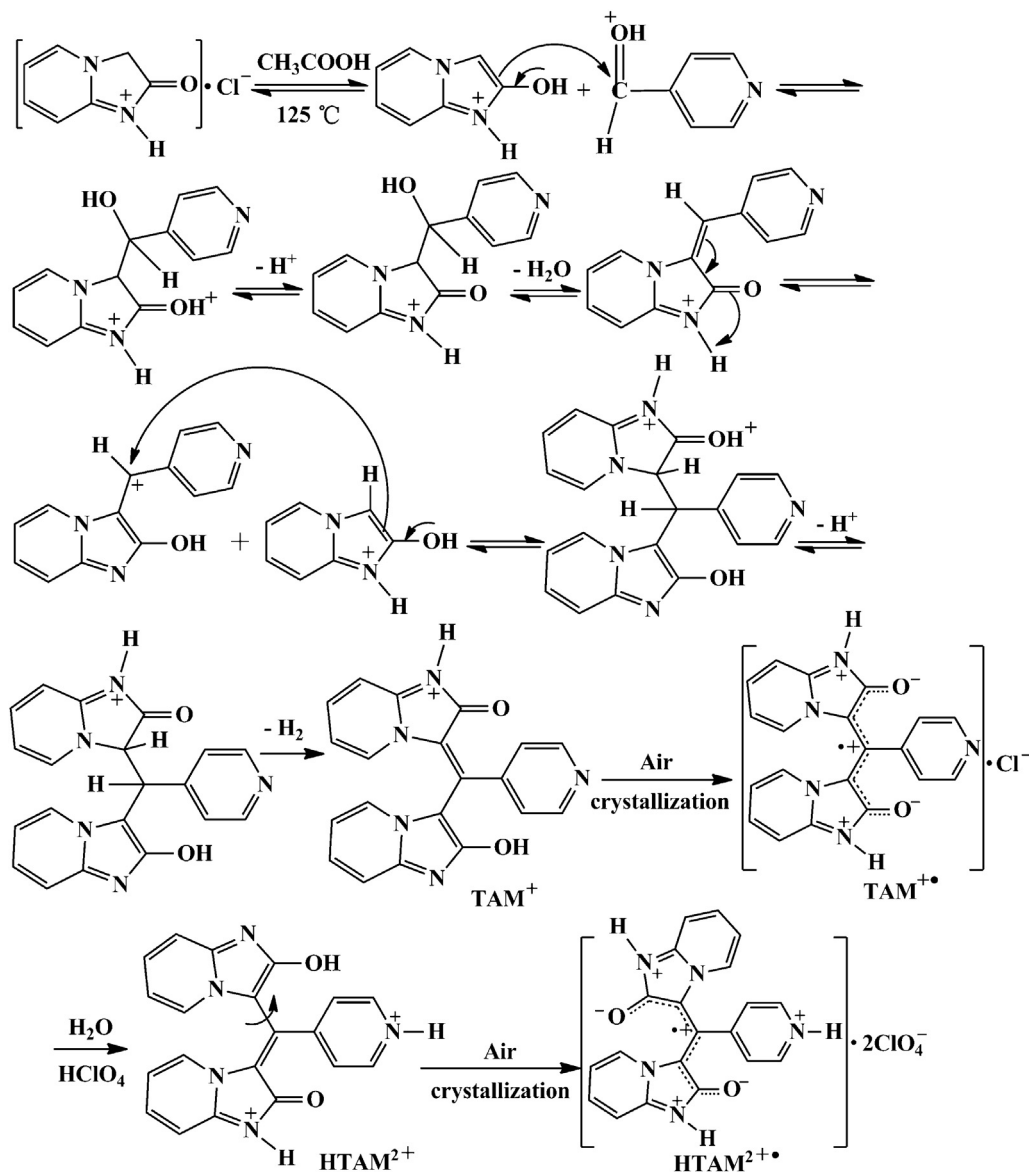
2.1. Materials and methods

All reagents were commercially available and used without further purification. Elemental analyses (C, H, N) were performed on Vario ELIII elemental analyzer. ¹H NMR spectra were obtained on Bruker Avance 400 MHz NMR spectrometer using dms-*d*₆ as solvent and tetramethylsilane (TMS) as the internal standard. The solid-state photoluminescence (PL) spectra and decay lifetimes were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. The quantum yields were measured also on a Fluorolog-3-TAU fluorescence spectrophotometer equipped with a BaSO₄-coated integrating sphere. N₂ adsorption

[☆] Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format for CCDC 976638 (**TAM⁺·Cl⁻**) and 976639 (**HTAM²⁺·2ClO₄⁻·H₂O**).

^{*} Corresponding author.

E-mail address: gpuyong@ustc.edu.cn (G. Yong).



Scheme 1. The proposed reaction mechanism and the protonation-induced conformational change.

and desorption isotherms were obtained at -196°C on an Omnisorp 100 CX instrument. The EPR spectra were recorded on a JES-FA 200 ESR spectrometer at X-band. Temperature dependence of magnetic susceptibilities was measured for microcrystalline samples with a magnetic field of 1000 Oe using a SQUID magnetosusceptometer (Quantum Design MPMS) from 350 K to 4 K.

2.2. Preparation of $\text{TAM}^{\bullet+}\cdot\text{Cl}^-$ crystal

A mixture of imidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride salt (1.72 g, 10 mmol) and 4-pyridine carboxaldehyde (0.54 g, 5 mmol) in acetic acid (30 mL) was heated at 125°C for 4 h. After cooled to room temperature, the resulting solid was collected by filtration and washed with ethanol. Recrystallization of this solid from EtOH/H₂O afforded purple solid. Yield: 1.76 g (4.49 mmol), 89.8% (based on imidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride salt). Purple block crystals of $\text{TAM}^{\bullet+}\cdot\text{Cl}^-$ suitable for X-ray diffraction analysis were obtained by slowly decreasing temperature (from 80°C to room temperature) during recrystallization procedure. Elemental analysis performed on crystals exposed to the atmosphere:

Calc. for $\text{C}_{20}\text{H}_{14}\text{ClN}_5\text{O}_2$ (391.80) (%): C, 61.31; H, 3.60; N, 17.88. Found (%): C, 61.22; H, 3.51; N, 17.95.

2.3. Preparation of $\text{HTAM}^{2+\bullet}\cdot 2\text{ClO}_4^- \cdot \text{H}_2\text{O}$ crystal

$\text{TAM}^{\bullet+}\cdot\text{Cl}^-$ (1.20 g, 3.06 mmol) was added to 8 mL HClO₄ aqueous solution (HClO₄:H₂O = 1:8, v/v), and the resultant mixture was heated at 80°C till solid was completely dissolved. Then, solution was slowly decreasing temperature (from 80°C to room temperature), giving rise to the formation of green X-ray-quality crystals of $\text{HTAM}^{2+\bullet}\cdot 2\text{ClO}_4^- \cdot \text{H}_2\text{O}$. Yield: 1.50 g (2.61 mmol), 85.3%. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{N}_5\text{O}_{11}$ (574.29) (%): C, 41.83; H, 2.98; N, 12.19. Found: C, 41.75; H, 2.85; N, 12.22.

2.4. X-ray crystallography

The X-ray diffraction measurements were performed and the data were collected at 291(2)K and 293(2)K on a Gemini S Ultra CCD diffractometer (Oxford diffraction Ltd.) equipped with Cu-K α ($\lambda = 1.54184 \text{ \AA}$) or Mo-K α ($\lambda = 0.71073 \text{ \AA}$) monochromated

Download English Version:

<https://daneshyari.com/en/article/5379090>

Download Persian Version:

<https://daneshyari.com/article/5379090>

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