



Switchable luminescence and morphology through acid-base vapor annealing in organic materials



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ABSTRACT

Through simple and green strategy, we unprecedentedly synthesized a novel organic compound through methyl-directed aromatic electrophilic substitution reactions. This work indicates that only introduction of methyl group at molecular framework can construct novel seven-membered ring organic materials. Interestingly, this organic material not only reveals the enhanced luminescence, but also the reversible luminescent color (red↔green) switching in the response to acid-base vapor stimuli, which is accompanied by the reversible morphological transformation (3D microbrick↔2D hexangular microflake). The present work provides a promising approach for synthesizing organic materials and a new access to develop dynamic functional materials which can be reversibly switched between different luminescence and morphology based on external acid-base vapor stimuli.

1. Introduction

In the last few decades, the development of luminescent organic compounds has exerted a large influence on the modern materials science. Luminescent organic compounds that molecular structures can be tuned have attracted much attention due to their potential applications in fluorescent sensors, probes, imaging agents in biological systems [1], the OLEDs for lighting and display systems [2], and other organic electronic devices [3]. The organic molecules with extending π system are generally used to prepare tuneable luminescent materials [4]. However, fabrication of such luminescent materials often involves difficult and tedious organic syntheses such as multiple step and/or higher cost. Therefore, the designing and preparing novel luminescent organic compounds by simple and green organic synthesis strategy remain an important challenge. On the other hand, supramolecular assembly has recently been proven to be an efficient method for fabricating photofunctional materials. In general, the supramolecular interactions such as hydrogen bond, short interatomic contact and ion- π interaction, etc., conduce to mediate molecular stacking. Through the supramolecular assembling strategy, well-ordered architectures or unique morphologies bearing interesting photophysical properties are spontaneously assembled from individual chromophore components [5]. Although to date, few assemblies with optically tuneable features are reported [6], the luminescent materials based on supramolecular assemblies are especially attractive because of their prospects for use in advanced light-emitting materials [7].

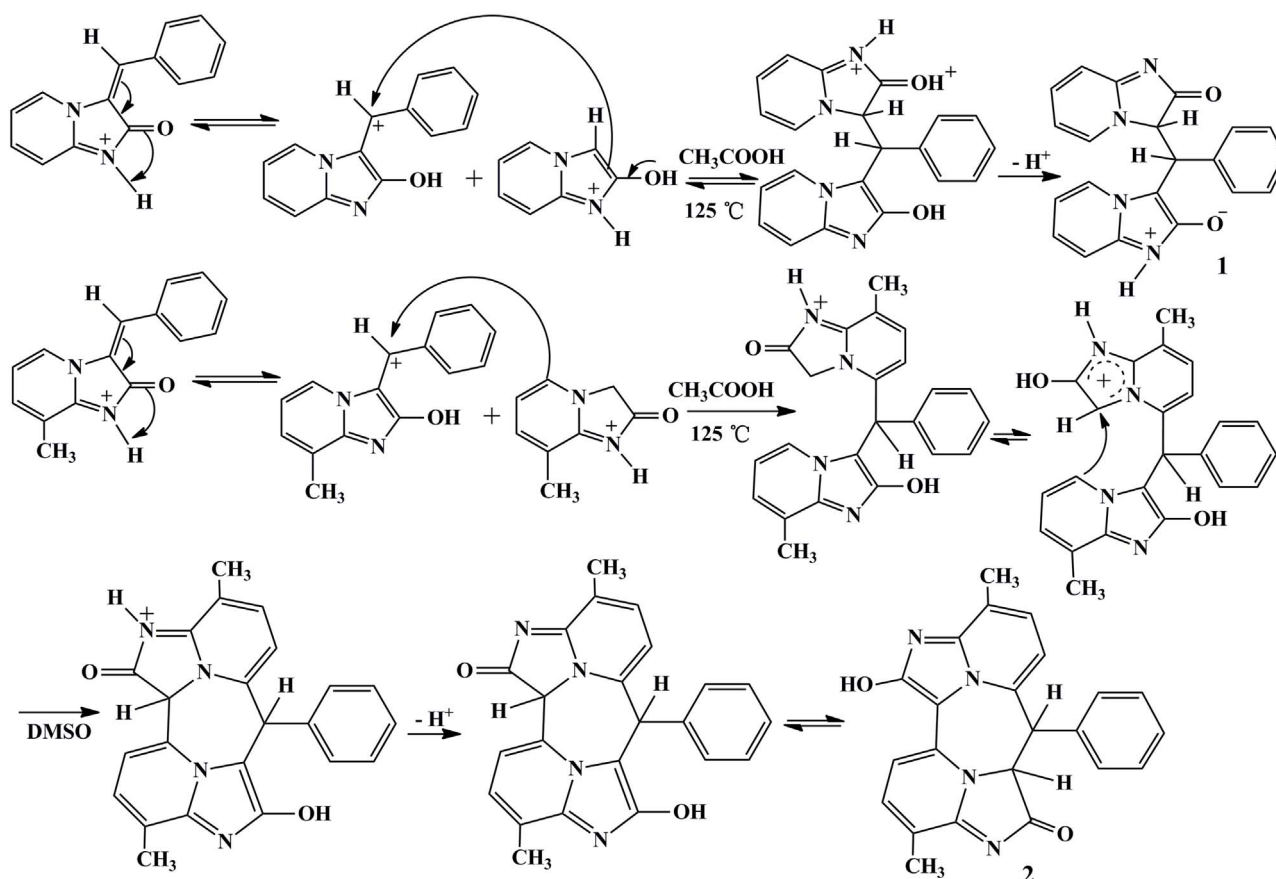
It is well known that many organic materials can reveal interesting

switching behaviors owing to stimuli-responsive structural and/or morphological conversion. Such stimuli-responsive condensed-state emitters are also numerous applications, e.g. in biological evaluations, security markings, sensor and memory applications [8]. However, development of stimuli-responsive solid-state organic materials is still a challenging topic [9]. Because the proton might affect many chemical and biological processes, protonation-deprotonation can not only endow molecule with various structures, but also cause diverse aggregates or morphologies based on the supramolecular interactions [10]. As stronger external promptive factor, the protonation-deprotonation reaction could also induce unique switching behaviors [11]. Several interesting examples that exhibit luminescent transformation in response to acid-base vapor stimuli have been reported [12].

On the basis of (*E*)-3-benzylideneimidazo[1,2-*a*]pyridin-2(3*H*)-ones [13], one novel organic compound (1) was facilely synthesized by the 1,4-conjugation addition reaction [14], as shown in Scheme 1 (top). Surprisingly, another novel organic compound (2) was obtained through methyl-directed aromatic electrophilic substitution reactions (Scheme 1, bottom). Interestingly, through protonation-deprotonation reactions with HCl and NH₃ vapors, compound 2 not only undergoes the reversible morphological transformation, but also discloses reversible luminescent color switching. Such switchable behaviors in response to external stimuli might be of great importance for practical application in optical recording, sensing, organic light-emitting diode, dye-sensitized organic solar cell, or molecular device and switch. This design concept may be of broad general interest for synthesizing novel functional organic materials by simple organic synthesis strategy.

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Scheme 1. The proposed mechanism for compounds 1 and 2.

2. Results and discussion

2.1. Syntheses and crystal structures

The reaction of imidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride and (*E*)-3-benzylideneimidazo[1,2-*a*]pyridin-2(3*H*)-one generated red crystals of compound **1** by simple 1,4-conjugation addition reaction (Scheme 1, top). Interestingly, when imidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride and (*E*)-3-benzylideneimidazo[1,2-*a*]pyridin-2(3*H*)-one were replaced by 8-methylimidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride and (*E*)-3-benzylidene-8-methylimidazo[1,2-*a*]pyridin-2(3*H*)-one, methyl-directed aromatic electrophilic substitution reactions unprecedentedly resulted in the formation of a novel seven-membered ring compound **2** (Scheme 1, bottom). The introduction of methyl group at imidazo[1,2-*a*]pyridine ring enhances electric density of aromatic rings that favors the aromatic electrophilic substitution reactions (Scheme 1, bottom). Whereas, no methyl group at imidazo[1,2-*a*]pyridine ring only performed 1,4-conjugation addition reaction (Scheme 1, top), because of lower electric density of aromatic ring. It is still interesting to note that only introduction of methyl group at imidazo[1,2-*a*]pyridine ring can result in the formation of various organic compound, accompanied by the different structure and property. When dissolved in HClO₄ aqueous solution and made to stand for 1 day, **2** was protonated and converted to yellow crystals of **2a**.

The single crystal X-ray diffraction analysis indicates that **1** crystallizes in the triclinic crystal system and *P*-1 space group. The experimental and calculated powder X-ray diffraction (PXRD) patterns demonstrate the phase purity of **1** (Fig. S1 in the Supporting information). In crystal **1**, one exocyclic oxygen atom reveals higher “enol” character with O2–C10 of 1.272 Å, and another one possesses higher “keto” character with O1–C6 of 1.233 Å (Fig. S2 in the Supporting information). Such structural character is further supported by its ¹³C

NMR spectrum (Fig. S3a in the Supporting information). However, from its ¹H NMR spectrum (Fig. S3b in the Supporting information), one can discover that in solution, two exocyclic oxygen atoms in **1** were converted to symmetric enol structure, because keto form was transferred to enol form (the chemical shift (ppm): 8.71 ~ 6.48 (aryl H), 5.22 (triarylmethyl H), 3.31 (enol-type hydroxyl H); the detailed affiliation of H signals was provided in Fig. S3b (inset)).

In crystal **1**, through double short interatomic contacts (O1...C15 3.370 Å and O1...C21 3.344 Å), two organic molecules form dimer with head-to-tail mode. Then, the dimer is assembled into one-dimensional (1D) chain structure along *b*-axis through hydrogen bonding interactions (O1...O9 2.904 Å, O9...O9' 2.834 Å, O9'...O1' 2.904 Å) between one water dimer and two organic molecules (Fig. 1). Such 1D chain is further assembled into two-dimensional (2D) layer also through hydrogen bonding interactions (O4...O5 2.907 Å, O5...O6 2.754 Å, O6...O5' 2.806 Å, O5...O4' 2.907 Å) between one four-membered ring water cluster and two organic molecules (Fig. 2). It is noteworthy that apart from water dimer (O9) and four-membered ring water cluster (O5 and O6), through hydrogen bonding interactions, other guest water molecules were linked to four-membered ring water cluster (O7...O6 3.000 Å), organic molecule (O8...O4 2.817 Å) and water dimer (O10...O9 2.798 Å), respectively, as shown in Fig. S4 (in the Supporting information). 2D layer is further constructed into three-dimensional (3D) structure (Fig. S5 in the Supporting information) through hydrogen bonds (O8...O2 2.797 Å, O10...O2 2.818 Å, O6...O3 2.757 Å, N3...N2 2.958 Å, N8...N6 2.975 Å).

The single crystal X-ray diffraction analysis indicates that **2a** also crystallizes in the triclinic crystal system and *P*-1 space group. The experimental and calculated PXRD patterns demonstrate the phase purity of **2a** (Fig. S6 in the Supporting information). In crystal **2a**, one exocyclic oxygen atom is enol form with O2–C9 of 1.293 Å, and another one is keto form with O1–C2 of 1.202 Å (Fig. S7 in the Supporting

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