



Two multi-Functional aggregation-Induced emission probes: Reversible mechanochromism and bio-imaging

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ABSTRACT

Herein, we designed and synthesized two novel probes 4-(2-Hydroxy-phenylimino)-4'-(1, 4, 7, 10-tetraoxa-13-azacyclopentadecyl)-1- cyanostilbene (**L1**) and 4-(2-Hydroxy-phenylimino)-4'-(1, 4, 7, 10-tetraoxa-13-aza cyclopentadecyl) stilbene (**L2**) with aggregation induced emission behavior. **L1** can directly recognize Cu²⁺ with high selectivity and specificity in water, **L2** can distinguish Cu²⁺ with naked-eye in acetonitrile. Moreover, **L1** and **L2** with aggregation-induced emission could be applied to bio-imaging, and **L1** showed a switchable color change feature based on mechanical grinding. The mechanism of the mechanochromic behavior was fully investigated by powder X-ray diffraction, single-crystal structures and differential scanning calorimetry measurements.

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1. Introduction

Organic π -conjugated molecules are gaining considerable attention due to their various functional applications, such as in field-effect transition, organic light-emitting diodes, and organic film solar cells [1]. However, a formidable challenge in the area is the notorious photophysical effect of the aggregation-caused quenching (ACQ): [2] the emission of a conventional luminophore is often weakened or even totally annihilated when its molecules are aggregated due to π - π stacking and the formation of excimers and exciplexes [3]. Hence, aggregation-induced emission (AIE) or aggregation-induced enhanced emission (AIEE) were proposed by Tang and coworkers to overcome the disadvantages of ACQ [4,5], which has attracted the interest of researchers [6–8]. For example, Tian's group reported a series of heterocycle replaced 1,4-bisstyrylbenzenes functionalized with a cyan group in the styrene double bond to produce steric hindrance which then activated AIE performance [9]. These compounds possessed enhanced emission *in vivo* as the intracellular environment was water, which made them potential materials for biophotonic applications. So the

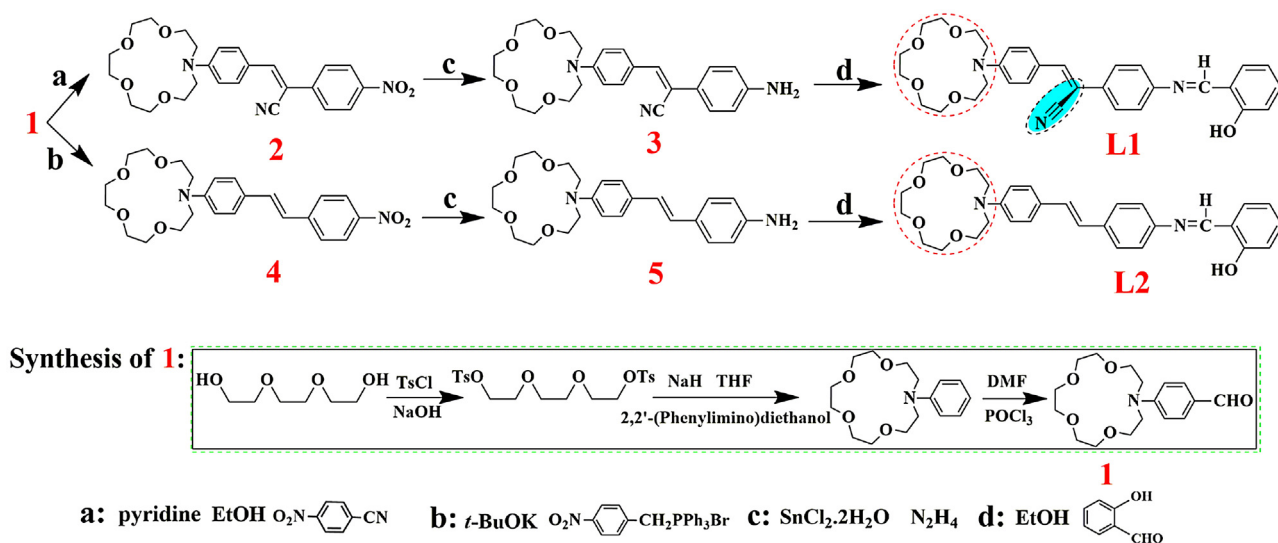
design and synthesis of an organic π -conjugated molecule possessing AIE or AIEE property is a key in biology and further research.

It is well known that Schiff base compounds usually display superior AIE property due to the isomerization/rotation of —C=N group, and the intramolecular hydrogen bond which restricted the intermolecular rotation process. It is also a moderate electron accepting group (A). Moreover, the crown ether group has become a rising star of donors (D) in the fluorescent chemosensor community due to their remarkable properties such as good solubility and environmental stability [10]. More importantly, they bind alkali, alkaline earth metal ions and other cations by the macrocycle and the association constant of the complex depends on factors such as the diameter of the ions relative to the size of the cavity formed by the macrocycle, the number of binding sites on the crown, the type of donor atoms (e.g., oxygen, nitrogen, or sulfur), and the solvent [11,12]. The cyan group is also an outstanding electron withdrawing group, which could adjust the molecular dipole moment and intramolecular charge transfer (ICT) [13].

Here, we select aza-crown ether as a multi-functional group to construct two A- π -D model structure Schiff base compounds (Scheme 1). The results showed that the prepared **L1** and **L2** both displayed Cu(II)-selective chromogenic behavior in a different way due to the steric hindrance effect of cyan group. Then we applied

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Scheme 1. Synthesis route of L1, L2.

L1 to detect Cu²⁺ in real water samples to demonstrate its practical utility in environmental science.

Furthermore, we systematically researched their biology properties *in vitro*, which showed that **L1** and **L2** both possessed outstanding bio-imaging feature due to the superior AIE performance. And **L1** with the steric hindrance presented a novel mechanochromic (MC) property based on mechanical grinding. MC, is the phenomenon of color change caused by mechanical grinding and reversion to the original color by heating or recrystallization [14]. Generally, it is not chemical structure but the molecular packing model changed under a pressuring stimulus [15].

2. Experimental

2.1. Materials and apparatus

Chemicals were purchased and used as received. Every solvent was purified as conventional methods beforehand. ¹H, ¹³C NMR were recorded on 400 MHz and 100 MHz NMR instruments using DMSO as solvent. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) and coupling constants in Hz. Splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). The powder X-ray diffraction (PXRD) patterns were recorded on an MXP18AHF diffractometer using Cu K_α radiation (λ = 1.54056 Å) in the 2θ range from 2 to 40. The mass spectra were obtained on an LTQ Orbitrap XL. The X-ray diffraction measurements were performed on a CCD area detector using graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 298 (2) K. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with SHELXTL-97 program package. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 1413056 (for **L1**). Dynamic light scattering (DLS) measurements were conducted on a Malvern Zetasizer Nano ZS90 size analyzer. The one-photon absorption (OPA) spectra were recorded on the UV-3600 spectrophotometer. The one-photon emission fluorescence (OPEF) spectra measurements were performed using a Hitachi F-7000 fluorescence spectrophotometer. The quartz cuvettes used were of 1 cm path length. The slit pass width of emission spectra: 5 nm, Voltage: 500 V.

2.2. Synthesis

Synthesis of 1: Phosphorus oxychloride (2.00 mL, 21.45 mmol) was added dropwise to DMF (10.00 mL, 129.20 mmol) at 0 °C under argon condition and the reaction mixture was stirred for 0.5 h. Then (1, 4, 7, 10-tetraoxa-13-azacyclopentadecyl) benzene (1.50 g, 5.10 mmol) was added, and the resulting mixture was stirred at 95 °C for 8 h. After cooling to room temperature, the mixture was poured into ice-water (200 mL), basified with Na₂CO₃ to a weak basicity, then extracted with dichloromethane. The combined organic phase was dried over Na₂SO₄, filtered and concentrated to give red oil. The obtained oil was then purified by silica gel column chromatography using a mixture of petroleum ether–ethyl acetate (2: 1 by volume) to get a yellow solid [16].

Synthesis of 2: Compound **1** (273 mg, 1 mmol) and 4-Nitrophenylacetonitrile (194 mg, 1.2 mmol) were dissolved in 30 mL of ethanol, then piperidine was added in catalytic amount (1 mL) and the reaction mixture was refluxed at 80 °C for 2 h. After the reaction finished, the solvent was removed via vacuum filter and dried to give a red powder. Yield: 60%. ¹H NMR (400 MHz, DMSO-*d*₆, TMS) δ 8.23–8.26 (d, 2H), 7.88–7.90 (d, 2H), 7.76–7.88 (d, 2H), 7.54 (s, 1H), 6.75–6.77 (d, 2H), 6.68–6.70 (d, 2H), 3.62–3.67 (q, 4H), 3.55 (q, 16H). ¹³C NMR (100 MHz, DMSO-*d*₆, TMS) δ 147.65, 147.21, 139.10, 133.43, 120.28, 112.30, 106.60, 112.57, 69.88, 49.56. MS (ESI): *m/z* [(M + H)⁺ 468.2090, found 468.2137].

Synthesis of 3: A ethanol (50 mL) solution of **2** (1.0 g, 2.1 mmol) was added into a flask equipped with a magnetic stirrer, and then SnCl₂·2H₂O (2.4 g, 1.1 mmol) were added and the mixture was refluxed for 0.5 h. The resulting mixture was neutralized with saturated NaHCO₃ to weak basicity, diluted with water (about 30 mL), and extracted with dichloromethane. The combined organic phase was dried over Na₂SO₄, filtered and concentrated to give red oil. The obtained oil was then purified by silica gel column chromatography using a mixture of petroleum ether–ethyl acetate (10: 1 by volume) to get a 0.61 g yellow solid. Yield: 66%. ¹H NMR (400 MHz, DMSO-*d*₆, TMS) δ 8.24–8.26 (d, *J* = 8.0 Hz, 2H), 7.88–7.90 (d, *J* = 8.0 Hz, 2H), 7.76–7.88 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 1H), 6.75–6.77 (d, *J* = 8.0 Hz, 2H), 6.68–6.70 (d, *J* = 8.0 Hz, 2H), 3.62–3.67 (q, 4H), 3.55 (q, 16H). ¹³C NMR (100 MHz, DMSO-*d*₆, TMS) δ 149.74, 149.23, 138.13, 131.11, 126.66, 122.55, 122.11, 120.24, 114.60, 111.89, 104.36, 70.96, 70.17, 69.68, 68.44, 52.58. MS (ESI): *m/z* [(M + H)⁺ 438.2348, found 437.2369].

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