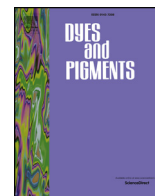




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Gelation properties of terpyridine gluconic acid derivatives and their reversible stimuli-responsive white light emitting solution

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ABSTRACT

Two gluconic acid derivatives **C3** and **C6** bearing a terpyridyl moiety were designed and synthesized. Thanks to the hydrophilic interaction from glucosyl moiety, **C3** and **C6** can dissolve in polar solvents and gel aromatic solvents with a critical gel concentration of weight 1.5%. The solution consisting of organic ligand **C3** as sensitizer and Ln^(III) ions as emitters can realize white light emission with thermo- and chemical stimuli-response properties in luminescence spectra. Further, the self-assemblies of **C3** and **C6** were examined by the combination of the theoretical calculations via hybrid density functional theory (DFT) with ¹H nuclear magnetic resonance (¹HNMR) and powder X-ray diffraction (PXRD) analysis. The study actually provides a reliable method for the formation of potential functional smart materials.

1. Introduction

Smart materials have attracted much attention because of their capabilities to carry on reversible changes in response to physical and chemical stimuli from the surrounding environment [1,2]. The reversible stimuli-responsive property relying on the stimuli-induced reversible breaking and reformation of dynamic molecular non-covalent interaction has opened new pathways to potential applications in sensors, drug delivery, and energy storage and conversion [3–8]. Thanks to the presence of dynamic molecular non-covalent interaction such as dispersion forces, hydrogen bonding, π - π and electrostatic interactions, the supramolecular self-assembly of small molecules represents a powerful strategy for the construction of smart materials in solution or gel state [9–11]. In recent years, much effort has been focused on the molecular design to introduce numerous functional groups to combine the molecular self-assembly properties with material functions [12,13]. As a functional group, terpyridine not only builds unique assembly patterns in different orientations and angles by π - π stacking interaction, but also coordinates with Ln^(III) ions offering particularly attractive dynamic properties for smart materials design since they form ‘ionic’ complexes which nature provides unique environmental triggers and intermediate bond strength for expanded control of bond cleavage and

ligation [14–17]. Due to the metal-centered photoluminescent properties, in the system involving metal-coordination bonds of terpyridine and Ln^(III), UV-light-absorbing functional group terpyridine as an organic sensitizer transfers energy to Ln^(III) ions to realize stronger light emission [18–24]. This mechanism is called “antenna effect”, which has realized application in optical sensor in medicine and electroluminescent devices in electronics [25,26]. Here we designed two molecules *N*-(3-([2,2':6',2''-terpyridin]-4'-yloxy)propyl)-2,3,4,5,6-pentahydroxy-hexanamide (**C3**) and *N*-(6-([2,2':6',2''-terpyridin]-4'-yloxy)hexyl)-2,3,4,5,6-pentahydroxy-hexanamide (**C6**) by introducing terpyridyl moiety into gluconic acid. Due to the presence of the hydrophilic glucosyl moiety, **C3** and **C6** can dissolve in polar solvents and gel aromatic solvents with a critical gel concentration (CGC) of weight 1.5%. The solution consisting of **C3** as sensitizer and Ln^(III) ions as emitters can realize white light emission with thermo-chemical stimuli-response properties. Compared with monochromatic light-emitting materials, this multicolor white light-emitting material with more sensitive response is in growing demand to satisfy the expanding tunable optical applications. Thus, in future, the molecular structure can be further tuned to change the self-assembly properties of the molecules in solutions and gel states, which actually provides a reliable method for the formation of potential smart optical materials.

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2. Experimental

2.1. Materials

Gluconolactone, pyridine-2-carboxylic acid ethyl ester, 6-amino-1-hexanol, 3-aminopropanol and 4-dimethylaminopyridine were purchased from Heowns Biochem Technologies. The chemical reagents were commercially available and directly utilized without further purification.

2.2. Synthesis

3-([2,2':6',2''-terpyridin]-4'-yloxy)propan-1-amine (5a) and 6-([2,2':6',2''-terpyridin]-4'-yloxy)hexan-1-amine (5b). The key intermediates **5a** and **5b** were synthesized from the starting material **1**. The condensation reaction led to compound **2**. The subsequent cyclization (**3**) and two substitution reactions afforded **5**. The detailed experiment and characterization can be found in Ref. [29].

(2R,3S,4S,5S)-N-(3-([2,2':6',2''-terpyridin]-4'-yloxy)propyl)-2,3,4,5,6-pentahydroxyhexanamide (C3). The mixture of **5a** (306 g/mol, 7 mmol, 2.14 g), gluconolactone (178 g/mol, 7 mmol, 1.25 g) and DMAP (4-dimethylaminopyridine, 122 g/mol, 0.08 mmol, 0.01 g) was suspended in methanol (50 ml) at room temperature. After vigorous stirring for 6 h, the solid was separated by filtration. Then the product was obtained by washing with deionized water, methanol and CH₂Cl₂ respectively. Yield: 82%. ¹HNMR (400 MHz, DMSO-d₆): δ 8.72 (d, *J* = 4.1 Hz, 2H), 8.61 (d, *J* = 7.9 Hz, 2H), 8.00 (td, *J* = 7.8, 1.5 Hz, 2H), 7.97 (s, 2H), 7.64 (t, *J* = 5.8 Hz, 1H), 7.50 (dd, *J* = 6.9, 5.3 Hz, 2H), 5.36 (d, *J* = 3.9 Hz, 1H), 4.53 (s, 1H), 4.47 (s, 1H), 4.41 (d, *J* = 7.0 Hz, 1H), 4.33 (s, 1H), 4.23 (t, *J* = 6.4 Hz, 2H), 3.99 (s, 1H), 3.91 (s, 1H), 3.58 (d, *J* = 7.8 Hz, 1H), 3.48 (s, 2H), 3.41–3.35 (m, 1H), 3.12 (tq, *J* = 12.6, 6.3 Hz, 2H), 1.79 (dd, *J* = 13.9, 6.8 Hz, 2H). ¹³CNMR (101 MHz, DMSO-d₆): δ 173.14 (s), 167.19 (s), 157.08 (s), 155.37 (s), 149.70 (s), 137.80 (s), 124.92 (s), 121.36 (s), 107.30 (s), 74.19 (s), 72.91 (s), 72.01 (s), 70.67 (s), 66.48 (s), 63.83 (s), 35.67 (s), 29.19 (s). HRMS (ESI-Q-TOF): *m/z* calc. for C₂₄H₂₉N₄O₇ (M+H)⁺: 485.2036, found: 485.2031.

(2R,3S,4S,5S)-N-(6-([2,2':6',2''-terpyridin]-4'-yloxy)hexyl)-2,3,4,5,6-pentahydroxyhexanamide (C6). The mixture of **5b** (348 g/mol, 3.5 mmol, 1.22 g), gluconolactone (178 g/mol, 7 mmol, 1.25 g) and DMAP (4-dimethylaminopyridine, 122 g/mol, 0.08 mmol, 0.01 g) was suspended in methanol (50 ml) at room temperature. After vigorous stirring for 6 h, the solid was separated by filtration. Then the product was obtained by washing with deionized water, methanol and CH₂Cl₂ respectively. Yield: 78%. ¹HNMR (500 MHz, DMSO-d₆): δ 8.70 (dd, *J* = 2.7, 1.9 Hz, 2H), 8.60 (d, *J* = 7.9 Hz, 2H), 7.99 (td, *J* = 7.8, 1.7 Hz, 2H), 7.94 (s, 2H), 7.64 (t, *J* = 5.8 Hz, 1H), 7.48 (ddd, *J* = 7.4, 4.8, 1.0 Hz, 2H), 5.37 (d, *J* = 5.0 Hz, 1H), 4.55 (d, *J* = 4.8 Hz, 1H), 4.48 (d, *J* = 5.2 Hz, 1H), 4.42 (d, *J* = 7.2 Hz, 1H), 4.34 (t, *J* = 5.7 Hz, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 4.01–3.94 (m, 1H), 3.90 (dd, *J* = 5.1, 1.9 Hz, 1H), 3.60–3.51 (m, 1H), 3.46 (d, *J* = 2.4 Hz, 2H), 3.15–3.04 (m, 2H), 1.85–1.70 (m, 2H), 1.50–1.40 (m, 4H), 1.37–1.29 (m, 2H). ¹³CNMR (101 MHz, DMSO): δ 172.75 (s), 167.17 (s), 157.09 (s), 155.36 (s), 149.67 (s), 137.75 (s), 124.89 (s), 121.32 (s), 107.18 (s), 74.15 (s), 72.92 (s), 71.98 (s), 70.64 (s), 68.41 (s), 63.87 (s), 38.67 (s), 29.55 (s), 28.86 (s), 26.56 (s), 25.59 (s). HRMS (ESI-Q-TOF): *m/z* calc. for C₂₇H₃₅N₄O₇ (M+H)⁺: 527.2505, found: 527.2505.

2.3. Measurements

Mass spectrometry. High resolution mass spectra (HRMS) of **C3**, **C6** and their synthetic intermediates were recorded on the ESI-Q-ToF (Bruker Daltonics-microTOF-QII). Mass spectra of **C3**-Eu and **C6**-Eu complexes were recorded on the Maldi-ToF (Bruker Daltonics-Autoflex ToFIII).

NMR measurements. The study was carried out on a Bruker AV

400 M NMR spectrometer with the concentration of 5 mg/0.6 ml for ¹HNMR and 30 mg/0.6 ml for ¹³CNMR in DMSO-d₆.

Luminescence spectra of assembly solution. The luminescence spectra of the luminescent solutions (0.01 M) were measured (The choice of the concentration was based on Ref. [20]) at room temperature by the F-2500 fluorescence spectrophotometer from Hitachi, Japan with the excitation wavelength 365 nm, the excitation slit width 5 nm and the emission slit width 5 nm.

Luminescence spectra of white light emission solution at different temperature. The 0.02 M solution of Cn (n = 3,6) and the 0.02 M solution of Ln (NO₃)₃ (Ln = Eu, Tb) were prepared by using the mixed solvent of DMF/CH₃CN in 1:1 (v/v) ratio, and the white light emitting solution (**C3W**) was prepared by mixing the 0.02 M solution of **C3** and the 0.02 M solutions of Ln (NO₃)₃ (Ln = Eu, Tb) in 1:0.5:0.5 (v/v) ratio. The room temperature solution was examined after 2 h in the water bath at a constant temperature of 25 °C. The high temperature solution was examined after 2 h in the water bath at a constant temperature of 70 °C. The low temperature solution was examined after 2 h in the refrigerator at a constant temperature of –20 °C. The setup of the instrument here is similar to the one used for the measurements of luminescence spectra of the solution.

Luminescence spectra of white light emission solution at different pH. The organic rare earth complex solutions with different pH were prepared by mixing **C3W** (the preparation method is described as above) with hydrochloric acid/aqueous sodium hydroxide solution (10^{–n} M, n = –1, 0, 1, 2, 3, 4, 5) in 9:1 (v/v) ratio. The setup of the instrument here is similar to the one used for the measurements of luminescence spectra of the solution.

Luminescence Decay. The luminescence decay of the luminescent solution was tested by the Fluorolog3 steady state and transient state fluorescence spectrometer from Horiba Jobin Yvon, France with the excitation wavelength of 330 nm, the emission wavelength of 435 nm and the attenuation interval from 0 to 200 ns, and the life-time values were obtained.

Determination of gel properties. Heating and cooling method: 20 mg **C3/C6** and 1 ml solvent were mixed in the test tube (φ = 10 mm) sealed with tin foil. The test tube was heated with an alcohol burner until the gelators were dissolved or could not be dissolved ever. Then the solution was cooled to room temperature, staying overnight. If the system obtains solid-liquid stratification, it is judged as precipitation (P). If the compound is completely dissolved and transparent solution is obtained, it is judged as dissolved (S). If the system has no liquid flowing after inverting, it is judging as gel (G); If the system has little liquid flowing after inverting, it is judging as weak gel (WG).

Critical gelator concentrations (CGCs). The concentration of gel prepared by heating-cooling method was increased 0.1% by adding solvent and repeated heating-cooling. The minimum concentration for the gelator keeping gel performance judged by inverting the test tube is the CGC.

Scanning electron microscopy of xerogel morphology. The xerogel samples obtained by spontaneous evaporation in the air were characterized by scanning electron microscope (SEM, Hitachi s-4800). The accelerating voltage was 5 kV, and the emission current was 10 mA.

Infrared spectroscopy analysis. The xerogel samples of gelator and gelator precipitate were prepared by KBr compression method at room temperature. The samples were tested with Bruker rucker Equinox 55 infrared spectrometer with scanning wavelength of 500–3900 cm^{–1}.

X-ray diffraction. The samples were tested at room temperature using a Bruker D8 Focus X-ray powder diffractometer. The data acquisition conditions are as follows: copper target as radiation source (λ = 1.5418 Å); scanning speed, 4. min^{–1}; 2θ = 3–50°; step size 0.02°.

Calculation method. Using the Gaussian 09 software and method of hybrid density functional theory (DFT) [27], the **C6** and **C3** molecules were optimized and the lowest energy was calculated. ωB97xD function in the DFT-D method is used to calculate the long-range interaction of the molecule. In order to balance the calculation accuracy

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