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Aggregation-induced blue shift of fluorescence emission due to suppression of TICT in a phenothiazine-based organogel

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ABSTRACT

A new D–π–A type gelator based on a phenothiazine derivative, which can gel cyclohexane, hexane, and ethanol/water under ultrasound treatment, has been synthesized. Because such gelators can act as twisted intermolecular charge transfer (TICT) probes, their emission in solution can be tuned by varying the polarity of the solvents. It is notable that an unusual aggregation-induced blue shift of the emission has been detected on account of the suppression of TICT in the gel phase.

1. Introduction

Low-molecular-weight gelators (LMWGs) have recently excited enormous interest from colloid chemists due to their unique supramolecular architectures and potential applications in optoelectronic devices, sensors, template synthesis, drug delivery, and biomimetics systems [1–5]. In general, the gels are colloidal matter in which the solvents are trapped in the network structures formed by a small quantity of gelators. LMWGs can self-assemble into fibrous superstructures driven by multiple, weak noncovalent interactions such as dipole–dipole, π-stacking, hydrogen bonding, and ionic interactions [6–9]. Such physical gels are sensitive to external stimulation, including temperature, light, pH, ultrasound, etc. [10–15]. Notably, the microenvironment around the gelator molecules in the gel phase is very different from that in the solution, so the aggregation-induced novel optical and electrical properties in the gel states based on π-conjugated systems can be expected, such as enhanced charge transfer [16,17], excitation energy transfer [18], and enhanced fluorescence emission [19]. It is well-known that the twisted intramolecular charge transfer (TICT) probe molecules may give color-tunable fluorescence emission depending on the polarity of solvents [20–22]. In other words, the TICT is not only affected by the conformational relaxation of the excited molecule itself [23,24], but also quite sensitive to the external environment. Therefore, it seems evident that the alignment of the organogelators with TICT emission in the gel phase will have an effect on the conformational changes between the ground and the excited states, resulting in unusual photophysical properties. To the best of our knowledge, the gel system based on TICT probe molecules is rarely reported [25]. Herein, a phenothiazine unit, which is a recognized pharmaceutical compound with a butterfly conformation in the ground state, was introduced into a gelator for the first time, and it was found that gelator **1c** (Scheme 1) could gel cyclohexane, ethanol/water, and hexane under ultrasound. As expected, such a D–π–A type molecule **1c** showed a color-tunable photoluminescence in the solvents with different polarity on account of the occurrence of the conformational twist of the excited state from the ground state. Remarkably, aggregation-induced blue shift of the emission could be detected during the sol–gel transition process. It is opposite to the fact that the emission of the phenothiazine-based films would red-shift compared with the solution due to the increase of complanation of the phenothiazine units in the solid state [26,27]. In addition, the comparison of the fluorescence spectra at 298 and 77 K suggested that suppression of TICT played a key role in the blue shift of the fluorescence emission of gelator **1c** in the gel phase compared with the solution.

2. Materials and methods

^{1}H NMR spectra were recorded on a Mercury plus 500 MHz using $CDCl_3$ as solvent. Mass spectra were performed on an Agilent 1100 MS series and AXIMA CFR MALDI/TOF (matrix-assisted laser desorption ionization/time-of-flight) MS (COMPACT). UV–vis absorption spectra were determined on a Shimadzu UV-1601 PC spectrophotometer. Fluorescence spectra were carried out on a Shimadzu RF-5301 luminescence spectrometer. Temperature-dependent fluorescence spectra were measured with LABRAM-UV

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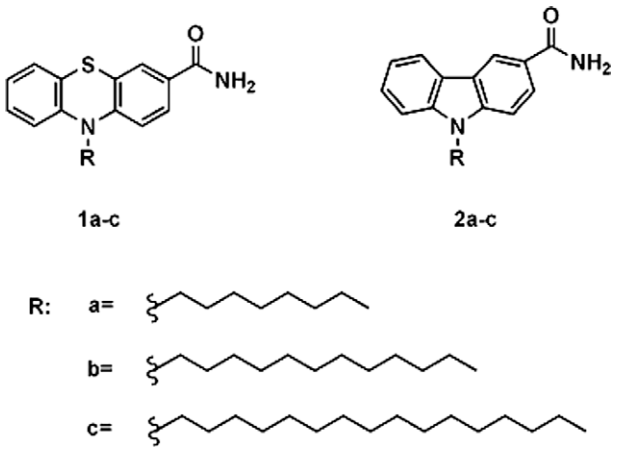


Scheme 1. Molecular structures of phenothiazine and carbazole derivatives.

(Jobin–Yvon) under 325 nm (3.82 eV) excitation (He–Cd laser). Fluorescence lifetimes were measured using the time-correlated single photon counting technique with a FL920-fluorescence lifetime spectrometer. The excitation source was an F900 ns flashlamp. Lifetimes were obtained by deconvolution of the decay curves. FTIR spectra were measured using a Nicolet-360 FTIR spectrometer by incorporating samples in KBr pellets. X-ray diffraction (XRD) patterns were carried out on a Japan Rigaku D/max-γA instrument. XRD was equipped with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å), employing a scanning rate of 0.02 s^{-1} in the 2θ range from 0.7 to 10. Scanning electron microscopy (SEM) observation was carried out on a Japan Hitachi Model X-650 San electron microscope. The samples for these measurements were prepared by casting the organogel on silicon wafers and dried at room temperature, and then coated by gold. Transmission electron microscopy (TEM) was taken with a Hitacdhi Model H600A-2 apparatus by wiping the samples onto a 200-mesh copper grid followed by naturally evaporating the solvent. The fluorescence quantum yields were determined against quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 0.546$) as the standard.

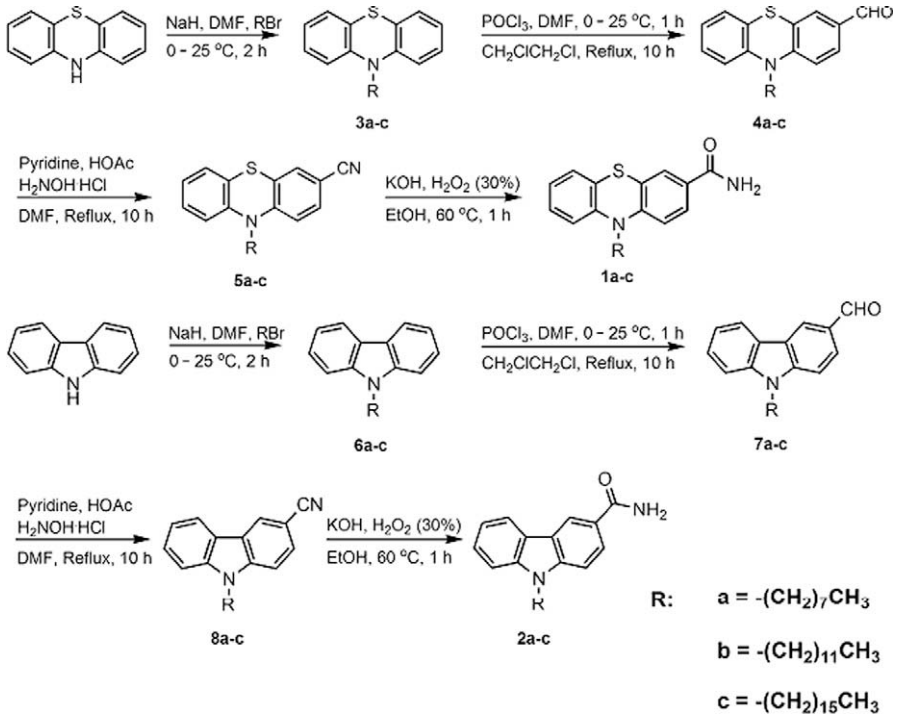
3. Results and discussion

3.1. Synthesis

The synthetic routes for the phenothiazine derivatives **1a–c** with different carbon chains are outlined in Scheme 2. First, the alkylation reactions of phenothiazine afforded compounds **3a–c** [28,29], which could be transformed into compounds **4a–c** via the Vilsmeier reaction. In the mixture of H_2NOH HCl, pyridine, HOAc, and DMF compounds **5a–c** could be obtained from the aldehydes **4a–c** under reflux for 15 h. Compounds **1a–c** were readily synthesized via a hydrolysis reaction of compounds **5a–c** underbasic conditions. In order to investigate the effect of the structure of the aromatic ring on TICT, carbazole derivatives **2a–c** were prepared according to similar synthetic methods of **1a–c**. All the compounds were characterized with FTIR, ^{1}H NMR spectroscopy, and MALDI-TOF mass spectrometry.

3.2. Gelation properties

The gelation properties of **1a–c** and **2a–c** were tested in various solvents by means of the "stable to inversion of a test tube" method [30]. As summarized in Table 1, we found that **1c** showed gelation capability in nonpolar solvents, including hexane and cyclohexane, and in the mixed solvents of ethanol and water (v/v = 5/1 and 4/1) with high polarity via ultrasound treatment indispensably, while it was soluble in ethanol/water (v/v = 6/1) and insoluble in ethanol/water (v/v = 3/1). On the other hand, **1a** and **1b** with similar molecular structures to **1c** except for the length of the alkyl chain could not self-assemble into gels in any tested liquids. It was indicated that the long carbon chain played an important role in the gelation formation, because it could adjust



Scheme 2. Syntheses of compounds **1a–c** and **2a–c**.