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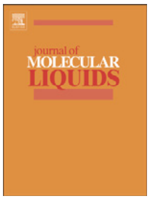

C_2-symmetric benzene-based organogels: A rationally designed LMOG and its application in marine oil spill

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ABSTRACT

With the efforts to exploit the marine and marine transport development, marine oil spill often happens in the process of marine transportation, which has a great negative effect on the environment. 1,4-Bi(phenylalanine-ethylene glycol monohexyl ether)-benzene (PEB) may be useful to solve this problem, which shows selective gelation of oil from aromatic solvents in the presence of water. A set of techniques including Fourier transform infrared (FT-IR) spectroscopy, ^{1}H nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and circular dichroism (CD) have been employed to confirm a β-turn arrangement and a fibrous structure of PEB gelators, which is formed through hydrogen bonding, π–π stacking, and van der Waals interactions.

1. Introduction

In the past decades, the synthesis and preparation of low molecular weight organic gels (LMOGs) have attracted great interest because of their potential applications in sensors, templated materials, drug delivery agents, enzyme-immobilization matrices, cosmetics, water purification, as well as in phase selective gelation [1–8]. These organogelators are a family of small molecules (typically with a molecular weight - 1000 Da) that can immobilize organic solvents and self-assemble into fibrous, tubular, or helical structures through various non-covalent interactions, including hydrogen bonding, π–π stacking, and van der Waals interactions [9–13]. Although the gelation mechanism [14,15] of LMOGs has been extensively studied, it is still difficult to predict the formation of gels from low molecular compound. Thus, a major challenge in this field is the rational design and synthesis of gelator molecules [16–19].

So far, most of LMOGs have been derived from the amphiphilic [20–22] species, with good gelation abilities. However, these amphiphilic gelators exist as highly hydrophobic derivatives that can probably lead to the formation of kinetically trapped aggregates before their self-assembly, which directly influences the following assembly efficiency and controllability in turn. Recently, our group reported a new family of effective low-molecular-weight hydrogelators with a modular architecture based on a C_2-1,4-diamide benzene core. The highly symmetrical chemical structures of the gelators render their initial distribution in water and no trapped aggregates are formed before the assembly is triggered [23]. The subsequent self-assembly process, which results in the formation of versatile hydrogels, is highly efficient and can be performed in a controlled manner [24]. Although a series of C_2 benzene based hydrogelators have been developed, gelators that can gel in organic solvent in preference to water from a given mixture have been not reported.

Herein, we found that incorporation of an alkyl chain at the C terminus of the C_2-gelator precursor leads to the development of efficient gelator for organic solvents. Typically, this C_2 based organic gelator showed selective gelation of organic solvents in the presence of water, which has tremendous implications for resolving problems such as marine oil spill. The details of the findings are presented in this report.

2. Experimental

2.1. Materials and synthesis

1-Ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride was purchased from Darui. All other chemicals were obtained from Aldrich and used without further purification. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures of unknown compounds were confirmed using ^{1}H nuclear magnetic resonance (^{1}H NMR) and high resolution ESI mass spectrometry.

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The organogelator (PEB) (Scheme 1) was synthesized according to the procedure described as follows:1,4-benzenedicarbonyl dichloride (2.3 g, 11.1 mmol) in 30 mL dry dichloromethane (DCM) was added dropwise into a solution of L-phenylalanine methyl ester hydrochloride (5.0 g, 20.0 mmol) and Et_3N (8.3 mL, 59.3 mmol) in 80 mL dry DCM at 0 °C. The mixture was stirred at room temperature for 12 h. Water (80 mL) was added, then extracted with CH_2Cl_2 (50 × 3 mL). The organic layer was washed with brine (100 × 3 mL), dried over Na_2SO_4 and evaporated in vacuo to give compound **1** (5.1 g, 93.0%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta = 7.75$(s, 4H), 6.62–7.30(m, 10H), 5.04–5.09(m, 2H), 3.77(s, 6H), 3.19–3.31(m, 4H). For the hydrolysis, aqueous NaOH (20.0 mL, 2.0 M) was added to a suspension of compound **1** (5.0 g, 10.2 mmol) in MeOH (50.0 mL). The mixture was stirred at room temperature for 5 h and a clear solution was obtained. The solution was then acidified with concentrated HCl to pH < 3, and a gel-like precipitate formed. The gel phase was filtered, washed with ultrapure water 3 times, and finally dried in the vacuum oven to give pure compound **2** (4.6 g, 98%). ^1H NMR (DMSO-d6, 400 MHz, 298 K): $\delta = 12.77$(s, 2H), 8.80(d, J = 8 Hz, 2H), 7.81(s, 4H),7.14–7.30(m, 10H), 4.60(m, 2H), 3.07(d, J = 3.07, 4H). A mixture of compound **2**(1 g, 2.2 mmol), ethylene glycol monohexyl ether(1.6 g, 10.9 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (1.7 g, 8.7 mmol), and 4-dimethylamiopryidine (DMAP) (0.5 g, 4.3 mmol) in CH_2Cl_2(10.0 mL) was stirred at room temperature overnight under nitrogen atmosphere. The solution was diluted with 20.0 mL CH_2Cl_2, and washed by water (50 × 2 mL), dried over Na_2SO_4, and evaporated under reduced pressure to get the crude product, which was purified by column chromatography (SiO_2, CH_2Cl_2: MeOH = 100:1) to afford the compound **3** (1.0 g, 62.0%) as a oily solid. ^1H NMR (DMSO-d_6, 400 MHz, 298 K): $\delta = 8.97$(d, J = 8 Hz, 2H), 7.83(s, 4H), 7.15–7.30(m, 10 H), 4.60–4.70(m, 2H), 4.16(t, J = 12.32Hz, 4H), 3.50(t, J = 14.12Hz, 4H), 3.32(t, J = 64Hz, 4H), 3.12(d, J = 192Hz, 4H), 1.36–1.43(m, 4H), 1.12–1.20(m, 12H), 0.789(t, J = 68Hz, 6H). HRMS (ESI) (m/z): calcd for $C_{42}H_{56}N_20_8$, 716.4; found 715.4 [M].

2.2. ^1H nuclear magnetic resonance (^1H NMR) experiments

^1H NMR studies were carried out on a Brüker Advance III 400 Instrument operating at 400 MHz. All spectra were recorded in DMSO or $CDCl_3$.

2.3. Mass experiments

Mass spectra were recorded on a Waters Q-Tof Mass Instrument by positive mode electrospray ionization. Methanol was used as the solvent.

2.4. Scanning electron microscopic (SEM) study

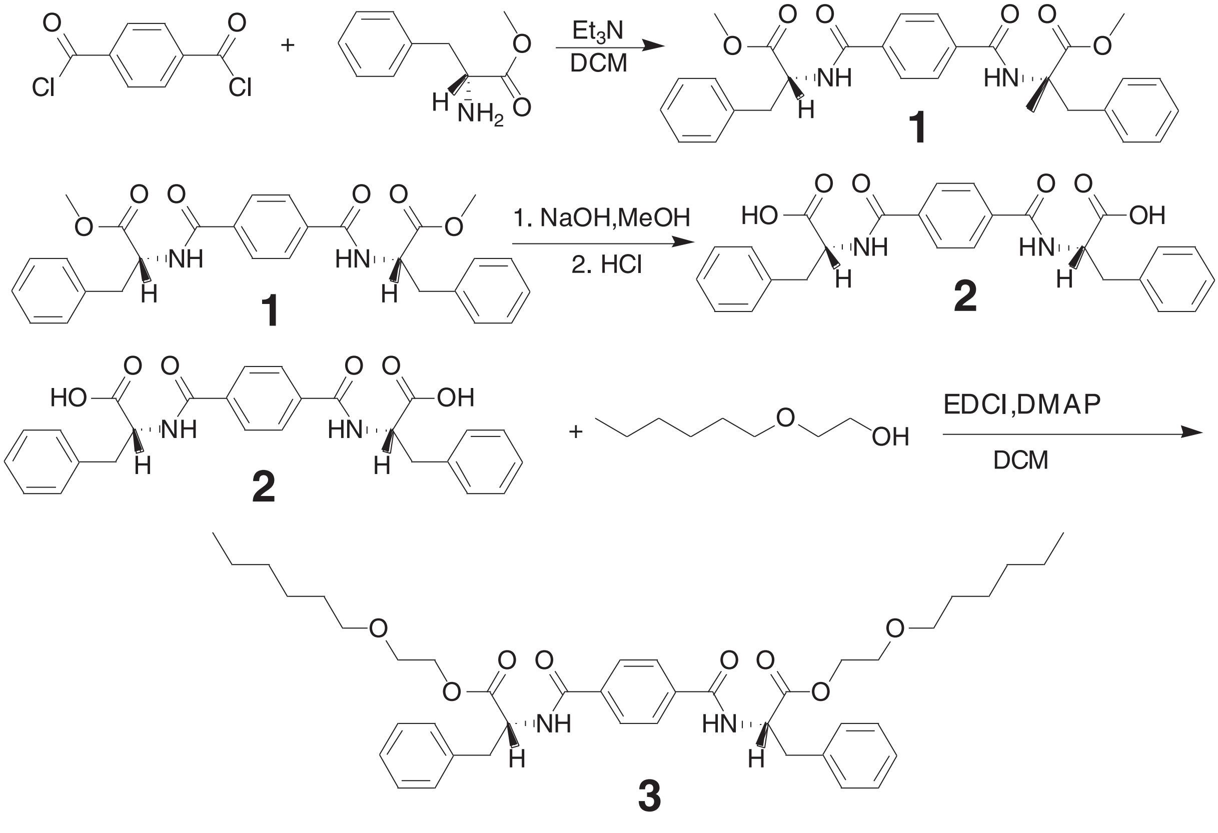
Images were obtained using a FEI QUANTA 250 Microscope. Samples were prepared by depositing dilute solutions of gel materials on silicon slices and drying under vacuum, and coated with gold on a sputtering coater.

2.5. Atomic force microscopy (AFM)

Images were obtained using a Vecco NanoScope IIIa Atomic force microscope and Mikro Masch NSC11 cantilevers/tips (radius of curvature less than 10 nm). Fiber diameters were measured by Nanoscope 5.30r3sr3 software. Samples were prepared by depositing dilute solutions of gel materials on mica plate and drying under vacuum.

2.6. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra of compound **3** xerogels were taken using Bruck EQUINOX55 Instrument. The KBr disk technique was used for the



Scheme 1. The synthesis of compound **3**.