

Research Article

Facile Synthesis of Semifluoroalkyl Triazole Derivatives for the Separation of Oil and Water

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Semifluoroalkyl triazole derivatives have been facily synthesized by copper-catalyzed alkyne-azide cycloaddition reaction, which can gelate some organic solvents at weight concentrations of down to 0.5 wt.%. The gelation abilities of triazole derivatives with/without a semifluoroalkyl and an aromatic group were fully characterized. We found that triazole derivatives containing semifluoroalkyl chains and aromatic groups are typically effective in forming supramolecular organogels. Moreover, the gelator in ethyl acetate can solidify oil from an oil-water biphasic mixture for about 1 min.

1. Introduction

The rapid development of industry and economy is associated with many environmental disasters caused by oily wastewater [1]. The oil spill, as an emergency, needs to be expedited handling to decrease the irrecoverable damage to the ecosystem because spilled oil quickly becomes the emulsion caused by wave action to raise the jeopardy [2]. The most common methods for cleaning oil spills such as absorption, bioremediation, dispersion, and solidification have proven to be incapable on different occasions due to their drawbacks [3, 4]. Proper treatments have been developed to meet its requirements in practical application in the oil spill recovery field [5–8].

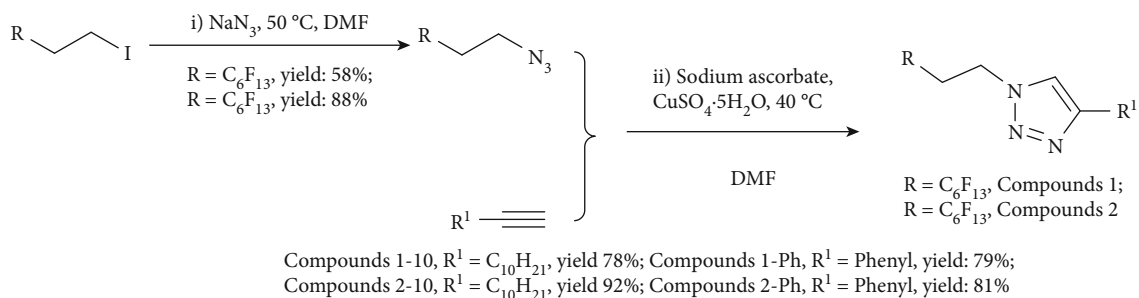
Phase-selective gelators (PSGs), as a type of organic gelator, can selectively solidify oils that is one of the most promising methods for oil spill recovery [9–13]. Although the various types of PSGs have been developed through complex synthetic routes [14, 15], it is necessarily focused on exploiting PSGs in a fast and convenient way that can be fitted with a broad range of applications [16]. As is known, the copper-catalyzed azide-alkyne cycloaddition (CuAAC) is a broadly applicable and easy-to-handle reaction in the arsenal of organic chemistry [17, 18]. Based on our previous experi-

ence, perfluorinated/semifluorinated groups are constantly employed in designing multifunctional materials for enhancing self-assembly, such as bilayer formations in high diluted conditions [19–23]. Herein, we report the semifluoroalkyl triazole derivatives synthesized by CuAAC reaction (Scheme 1) as potential gelators or even PSGs.

To investigate the structure character, 1-semifluoroalkyl-4-substituted-1*H*-1,2,3-triazole (**1**) and the corresponding hydrocarbon derivatives 1-alkyl-4-substituted-1*H*-1,2,3-triazole (**2**) were synthesized.

2. Materials and Methods

2.1. Materials and Chemicals. All commercially available starting materials and reagents were used without any purification. The distinction between dimethyl silicone oil (DMS) and methyl silicone oil (MS) is viscosity 1000 and 500 mPa.s at 25°C, respectively. The reaction mixture was magnetically stirred and monitored by TLC. NMR spectra were recorded on Bruker AV-III 400 MHz NMR spectrometer (400 MHz for ¹H, 101 MHz for ¹³C, and 376 MHz for ¹⁹F). Chemical shifts of these spectra are reported in parts per million (ppm) downfield relative to the internal

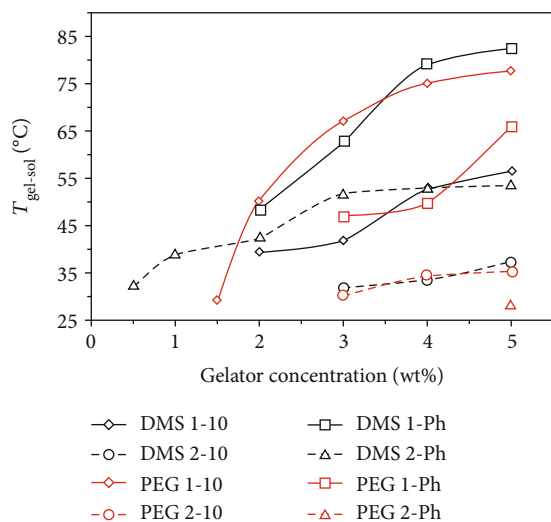


SCHEME 1: Synthetic scheme for compounds 1 and 2.

TABLE 1: Gelation tests and MGCs (wt.%) for 1 and 2.

| Solvents | Compounds (wt.%) | | | |
|-------------------------|------------------|---------|-----------|----------|
| | 1-10 | 1-Ph | 2-10 | 2-Ph |
| Dimethyl silicone oil | G (2.5) | G (1.0) | G (2.5) | G (0.9) |
| Methyl silicone oil | G (4.0) | G (3.0) | S (5.0) | G (4.0) |
| Mineral oil | G (1.0) | G (0.5) | G (4.0) | G (4.0) |
| Paraffin | G (3.0) | G (3.0) | G (3.0) | G (3.0) |
| Polyethylene glycol-400 | G (1.5) | G (3.0) | G (3.0) | G (5.0) |
| DMSO | G (3.0) | G (5.0) | S (5.0) | S (5.0) |
| Deionized water | P (5.0) | P (5.0) | Ins (5.0) | Ins(5.0) |

^aG, S, P, and Ins indicated gel, solution, precipitated, and insoluble. Gelation tests started from a gelator concentration of 5 wt.%.

FIGURE 1: Plots of $T_{\text{gel-sol}}$ vs. concentrations of compounds 1 and 2 in DMS organogels.

standard, tetramethylsilane (TMS). Coupling constants are reported in hertz (Hz). Scanning electron microscope (SEM) images were observed with a JEOL JSM-6510LA.

2.2. Sample Preparations and Tests for Gelation. To avoid evaporating the liquid components, we prepared gels in a sealed 5 mL vial for most studies. Weighed quantities of a gelator (ca. 10-20 mg) and a liquid were heated until a solution was obtained. The vials were then kept at room temperature for a certain period; we deemed them as gels, then the

samples were not visually phase-separated and did not flow perceptibly when the vessels were inverted.

3. Results and Discussion

The gelation behaviors of the compounds were examined in some solvents shown in Table 1. Compounds 1 and 2 dissolved well in DMF, THF, and ethyl acetate at 5 wt.%. Compound 1-10 formed organogels in DMS, MS, mineral oil, paraffin, polyethylene glycol-400 (PEG-400), and DMSO, where minimum gelation concentrations (MGCs) were 2.5, 4.0, 1.0, 3.0, 1.5, and 3.0 wt.%, respectively. On the other hand, compound 2-10 dissolved in MS and DMSO at 5.0 wt.%. At the same time, compound 1-Ph also formed organogels in DMS, MS, mineral oil, paraffin, PEG-400, and DMSO, while compound 2-Ph dissolved in DMSO at 5.0 wt.%, too. The results mean that the semifluoroalkyl chain could enhance gelation ability. Notably, the MGCs of polar aprotic solvents PEG-400 prepared from compounds 1-10 and 2-10 were lower than compounds 1-Ph and 2-Ph. We believe that these tendencies are induced by the difference in self-assembly modes among semifluoroalkyl chain, alkyl chain, and aromatic groups in organogels.

The $T_{\text{gel-sol}}$ of DMS gels and PEG-400 gels, plotted against the concentration of compounds 1 and 2, is shown in Figure 1. $T_{\text{gel-sol}}$ of organogels formed by compound 1 are higher than those of compound 2. The thermostabilities of DMS organogels formed by compounds 1 and 2 with the phenyl group are higher than those of the decyl chain as a terminal group, while the thermostabilities of PEG-400 organogels formed by compounds 1-Ph and 2-Ph are lower than those of the decyl chain. The results indicated that the thermostability of organogels could be formed by employing a semifluoroalkyl chain, no matter whether polar or nonpolar solvent. At the same time, the role of the terminal group in the thermostability of organogels possibilities depends on the type of solvent. The results also indicated that the semifluoroalkyl chain and the terminal group play an important role in the thermostability of organogels.

The gelation phenomena are also confirmed utilizing a scanning electron microscope (SEM) observation, and the result of a gel formed by compound 1-Ph with mineral oil at 5 wt.% is shown in Figure 2. It is apparent from the figure that three-dimensional (3D) nanofibers are assembled to form the network structures with diameters of less μm order.

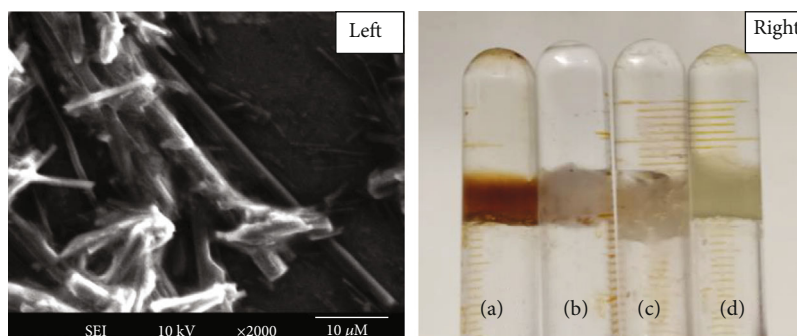


FIGURE 2: (a) SEM image of gel of mineral oil (scale bar: 10 μm); (b) photographs for organogels formed by compound **1-Ph** at 5 wt.% from the oil-water biphasic system; a DMS organogel; b MS organogel; c mineral oil organogel; d paraffin organogel.

To demonstrate compounds **1** and **2** may exhibit phase-selective gelation ability, we took compound **1-Ph** for further study at 5 wt.%. Deionized water (1.5 mL, ca. 4 times organogel's weight) was added to a vial containing organogels formed by compound **1-Ph** in the gelation test. Organogels became an isotropic liquid state (oil solution) and then floated on the water's surface during the heating process. The oil solution was gelatinized again at room temperature. Figure 2 shows a photograph of organogels that can suffer their weight and 4 times their weight of deionized water. Because PEG-400 and DMSO exhibit good solubility in deionized water, compound **1-Ph** could not gelatinize PEG-400 or DMSO again from the aqueous solution. The phase-selective gelation abilities of compounds **1-10**, **2-10**, and **2-Ph** were surveyed and showed similar phase-selective gelation behaviors with compound **1-Ph**.

A cosolvent is a popular approach to deal with the oil-water biphasic system [24]. Herein, ethyl acetate as a suitable cosolvent was selected from DMF, THF, and ethyl acetate. The ethyl acetate solution of compound **1-Ph** at 10 wt.% was added into the DMS-water biphasic system immediately after preparing until the weight percentage of compound **1-Ph** in the organic layer decreased to 5 wt.%. The DMS could form into organogel in just minutes. The gelation process was recorded as a video shown in the attached link at Supplementary Materials. That means compound **1-Ph** can have the phase-selective property in the cosolvent method.

In conclusion, a new type of PSGs that can gelate some organic solvents at weight concentrations of down to 0.5 wt.% has been facilely synthesized based on semifluoroalkyl triazole derivatives. We found that triazole derivatives containing semifluoroalkyl chain and aromatic groups typically form supramolecular organogels. Due to the simple synthesis method and the effective phase-selective performance, semifluoroalkyl triazole derivatives can be probably be used for oil spill recovery from the oil-water biphasic system.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

None of the authors have any conflicts of interest.

Acknowledgments

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Supplementary Materials

Supplementary data to this article can be found online at <http://www.bilibili.com/video/BV1KL4y1W7PN>. (*Supplementary Materials*)

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