Biscalix[4]arene Derivative As a Very Efficient Phase Selective Gelator for Oil Spill Recovery
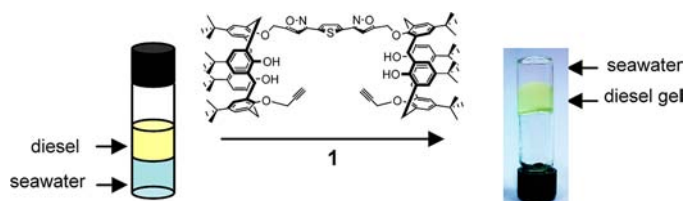
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ABSTRACT

A biscalixarene framework, without long alkyl chains, has been readily synthesized in three steps starting from the parent calix[4]arene. The biscalix[4]arene 1 was able to form organogels in various alcoholic solvents; furthermore, it exhibited an excellent phase selective gelation property that is potentially useful in oil spill recovery.

Recently, low molecular weight supramolecular organogels[1] have attracted considerable attention due to their unique self-assembly and phase separation properties. The molecular gelation processes from a bottom-up approach allows us to create various nanoscale classes of smart materials that can be used in molecular sensing,[2] drug delivery,[3] light harvesting,[4] and oil spill recovery.[5] An oil spill is a release of liquid petroleum or oil into the environment, which causes severe or irrecoverable damage to the environment and the ecosystem. Therefore, there is a great need to develop materials and methods that can treat oil spills speedily and efficiently.

Current methods to clean up oil spills include bioremediation, dispersants, solidifiers, and sorbents; however, each of these methods has its own advantages and disadvantages. In general, the methods of dispersants, solidifiers, and sorbents have difficulty in recovering the oil and sometimes these materials are toxic to marine life. Although the bioremediation is considered to be a environmentally friendly method to treat oil spills, it was reported to take more than 28 days to convert 98% of the spilled hydrocarbons to carbon dioxide and water.[5d] In an emergency and massive oil spills, one needs a more efficient method so that the recovery process can be sped up. In this context, a smart material for the easy and efficient treatment of oil spills is needed and it was first reported by Bhattacharya in 2001 that an amino acid amphiphile can form a phase selective gelation (PSG) of the oil from oil/water mixtures.[5a] The PSG achieved an easy separation of the oil spills from an oil/water mixture.[5]

Scrutinizing recent literature reports on low molecular weight organogelators (LMOGs), we found that they usually contain the following three common features: (1) functional groups that enable multiple hydrogen bonding interactions, (2) long alkyl chains that facilitate the van der

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Scheme 1
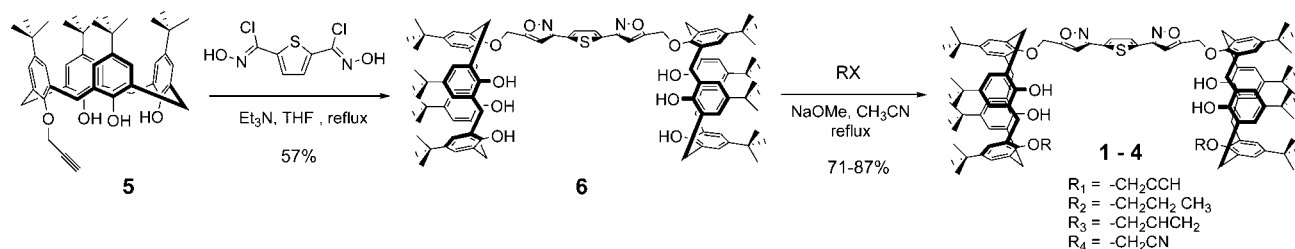
Waals force interactions, and (3) large planar aromatic surfaces (usually π-conjugated) that promote the π−π stacking interactions.[6] However, predicting whether a molecular structure or a functionalized supramolecule is an efficient gelator or not remains to be difficult. Moreover, there are relatively few examples of so-called 3-D macrocycle-based gelators in the research field of supramolecular organogels. In the past decade, we have been interested in the design and synthesis of various calixarene and biscalixarene derivatives using the protocol of 1,3-dipolar cycloaddition reactions and "click" reactions followed by ring-opening reactions.[7] Here we report the synthesis of biscalixarene **1−4** (Scheme 1) and a serendipitous observation of compound **1** forming phase-selective gelation in oil/water mixtures. Our results represent the first example of biscalixarene derivatives that can be used in oil spill recovery.

The synthesis of biscalix[4]arenes **1−4** started with the double 1,3-dipolar cycloaddition reactions of 25-monopropargyloxycalix[4]arene **5** with thiophene 2,5-dinitrile oxide.[7a] The thienyl-2,5-bisisoxazolylmethylbiscalix[4]arene **6** was obtained in 57% yield which then underwent an SN2 reaction with 2 equiv of propargyl bromide, propyl iodide, allyl bromide, and bromoacetonitrile to give biscalix[4]arenes **1−4** in 71−87% yields, respectively (Schemes 1 and S1, Supporting Information). The structures of all products (**1−4**) were fully characterized by spectral data, including ^{1}H and ^{13}C NMR (Figures S8−S15, SI), mass, and high resolution mass spectrometry (Experimental Section, SI).

The gel forming abilities of biscalixarenes **1−4** in various solvents were tested, and the results are summarized in
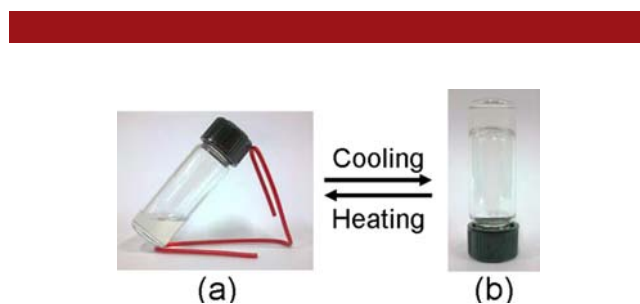

Figure 1. Temperature dependent gel properties of **1** in *n*-hexane/ethyl acetate (v/v = 1:0.06): (a) at 323 K and (b) at 293 K.

Table S1 (SI). Among the solvents and biscalix[4]arene derivatives examined, only the biscalixarene **1** formed organogels in alcoholic solvents, and the minimum gelation concentration (MGC) of **1** in different alcoholic solvents ranged from 0.05 to 0.13 (w/v %). We were also pleased to find that if compound **1** was predissolved in organic solvents (such as ethyl acetate or chloroform) and then added to a hexane solution, they formed organogels (Figure 1). None of the biscalixarenes **2−4** form organogels in any of the solvents tested. Neither would **2−4** form organogels when they were predissolved in other organic solvents followed by treating with hexanes or long chain alkanes. Based on these findings, we prepared a solution of biscalixarene **1** (10.0 mM) in ethyl acetate and then added it to several commercially available gasoline fuels. To our delight, the solution of **1** in ethyl acetate could form organogels with almost all commercially available gasoline fuels (such as diesel, pump oil, and silicone oil) except petrol (95) (see Tables 1 and S2). It is worth noting that the MGC of **1** in ethyl acetate, ranging from 0.097 to 0.37 w/v %, represents one of the best PSGs ever reported.[5] The very low MGC of **1** may be because its 3D structures were preorganized; therefore, they readily immobilized the oils forming phase selective gels.

Selective gelation of oil from an oil/water mixture is considered to be a very important method in treating an oil spill problem. We thus investigated the gelation property of **1** (10 mM in ethyl acetate) at room temperature by adding it to a two-phase system of a 1:1 (v/v) mixture of seawater and hexane (or various oils). The oil/seawater mixture was allowed to equilibrate for a few minutes, and the oil layer was completely gelled and separated from the seawater phase (Figure S1, SI).

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		BMGC	
solvent	MGC	pure water	seawater[c]
hexane	0.097	0.129	0.178
diesel	0.081	0.097	0.129
petrol (95)[d]	–	–	–
pump oil	0.210	0.226	0.226
silicone oil	0.307	0.371	0.371

[a] The values in parentheses are minimum gelation concentrations (MGC) and biphasic minimum gelation concentrations (BMGC) of the gelator **1** (wt/v %, g/100 mL). [b] The biphasic system is water (or seawater) and oil as 1:1 mixture. [c] The seawater comes from Taiwan Strait. [d] Solution.
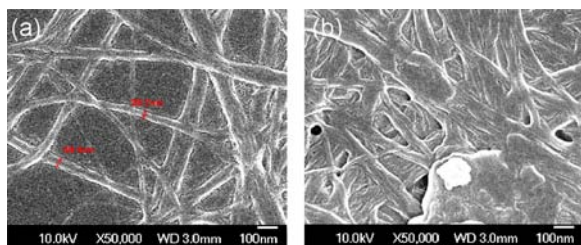

Figure 2. FE-SEM images of **1** (a) 10^{-4} M, and (b) 10^{-3} M in *n*-propanol.

Morphological features of these organogels have been investigated using Field Emission Scanning Electron Microscopy (FE-SEM), and the results are shown in Figure 2. The FE-SEM images of the xerogels in Figures 2a and S2a (SI), prepared from the solution of biscalixarene **1** in *n*-propanol and hexane respectively, displayed the presence of a fibrous network of different thicknesses. At a higher concentration of **1** (10^{-3} M, Figure 2b), an interwoven three-dimensional network was obtained from the assembly of these nanofibers, and the fibrous network may be responsible for entrapment of large volumes of organic solvents and oils. These FE-SEM images of **1** showed a profusion of fibers with varying width ranging from 30 to 70 nm. Similar morphological features have been observed using AFM studies (Figure S2b, SI).

In order to understand why molecule **1** forms aggregates in various alcoholic solvents, we took a series of its VT ^{1}H NMR spectra in CDCl$_3$/hexane (Figures 3 and S3, SI). When the solution temperature decreased from 323 to 253 K (sol to gel), the signals of the thiophene protons (Ha) slightly downfield shifted, whereas the isoxazole protons (Hb) were downfield shifted by 0.27 ppm. The latter results suggest that dipole−dipole interactions[6c] between the two isoxazole groups must have played an important role in the gel formation of **1**. The phenolic−OH protons (Hd) of **1** exhibited the most downfield shift from 6.58 to 7.33 ppm (+0.75 ppm), indicating the strong involvement

of hydrogen bonding interactions between the phenols. The protons on the phenolic carbons of calixarene (Hc), the OCH$_2$ bridge protons (He) between calixarene and the two isoxazole groups, and the terminal alkyne protons (Hg) showed only small downfield shifts when the solution temperature of **1** decreased from 323 to 253 K (Figure S3, SI). In contrast, the chemical shifts of the protons on the *tert*-butyl groups of calix[4]arene were slightly upfield shifted. Results from the VT ^{1}H NMR of **1** demonstrated that (1) intermolecular hydrogen bonding interactions between the phenolic-OHs, (2) the dipole−dipole interactions of the isoxazole groups, and (3) van der Waals interactions between the *tert*-butyl groups of the calix[4]arenes are important factors in its formation of organogels.
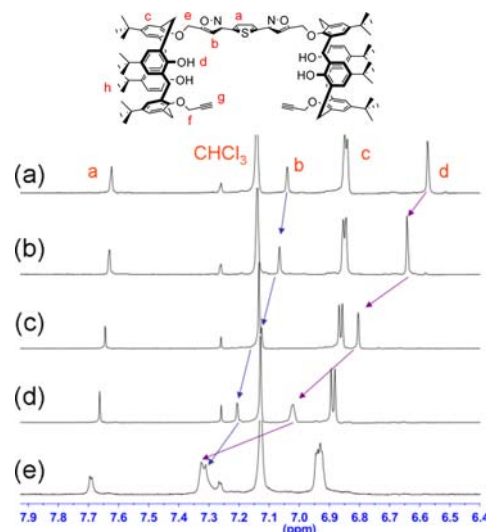

Figure 3. Partial ^{1}H NMR spectra of **1** (8.0 mM) in CDCl$_3$/hexane (v/v = 1/1) at (a) 323 K, (b) 313 K, (c) 293 K, (d) 273 K, and (e) 253 K.

Since the propargyl-substituted **1** exhibited excellent gelation properties, propyl-, allyl-, or aceto-nitrile-substituted biscalix[4]arenes **2**−**4** did not. One expects that significant changes in the chemical shifts of the propargyl protons should be observed; on the contrary, only very small shifts were observed. At first glance, the ^{1}H NMR results seem to be inconsistent with the expectation above; however, the results are rational with the notion that the propargyl groups are inside or near the cavities of the biscalix[4]arenes. Due to the large magnetic anisotropy effect[8] of the propargyl group, it caused larger chemical shift changes on nearby *tert*-butyl protons (Figure S3, SI). On the other hand, the *tert*-butyl protons exert minimal magnetic anisotropy effect on the chemical environment of the propargyl protons, therefore, causing very small change in its chemical shift.

Self-assembly of biscalix[4]arene **1** was also studied using temperature dependent UV−vis and fluorescence

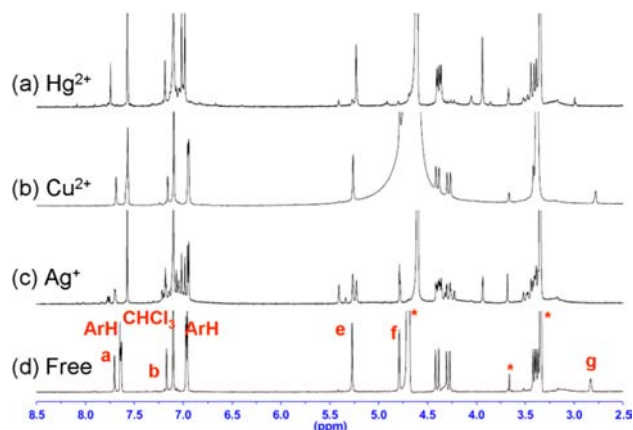(8) Friebolin, H. *Basic one- and two-dimensional NMR spectroscopy*, 5th ed.; Wiley-VCH: Weiheim, 2011; Chapter 2.

Figure 4. Partial ^1H NMR spectra of **1** (2.5 mM) in CDCl$_3$/MeOD-d_4 (v/v = 1/1) in the presence of (a) Hg^{2+} (2 equiv), (b) Cu^{2+} (2 equiv), (c) Ag$^+$ (2 equiv), and (d) free. Where * denotes solvent peaks.

spectroscopies (Figure S4, SI). As the temperature of the solution decreased from 363 to 273 K (sol to gel), all UV–vis absorption bands of **1** showed hyperchromic effects; concurrently, the intensity of the fluorescence band at 352 nm also increased and slightly red-shifted. The red shifts of the fluorescence λ_{max} of biscalix[4]arene **1** at low temperature may originate from its self-assembly into larger aggregates which contains π–π stacking interactions between the 2,5-bisisoxazolyl-thienyl groups.

The responses of the gel solutions of **1** (2.5 mg) in *n*-propanol (2 mL) toward 16 different metal ions (1.6 equiv) were also examined, and the results are shown in Figure S5 (SI). Most of the gel solutions of **1** remained unchanged with added metal ions except those with Ag$^+$, Cu^{2+}, or Hg^{2+}, which caused the collapse of the organogels. To gain insight into the sensing mechanism of the gel, we then took the UV–vis, fluorescence, and ^1H NMR spectra of **1** in the absence and presence of metal ions. The UV–vis and fluorescence spectra of **1** toward 16 different metal perchlorates were screened in CHCl$_3$/MeOH (v/v = 1/1) solution, and the results are shown in

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Figure S6 (SI). In the absence of cations, biscalixarene **1** exhibited an absorption band with λ_{max} = 290 nm and a very weak emission in the region 310–450 nm when excited at 290 nm. Among the 16 metal ions screened, only Ag$^+$, Cu^{2+}, and Hg^{2+} led to some shifts in the UV–vis spectra of **1**. Moreover, Hg^{2+} and Ag$^+$ also caused significant quenching of the fluorescence intensities of **1**.

The ^1H NMR spectra of **1** in the absence and presence of Ag$^+$, Cu^{2+}, and Hg^{2+} were recorded to understand the possible sensing modes of the gel materials with these metal ions (Figure 4). The free phenols of the biscalixarene **1** were readily oxidized by Cu^{2+},[7c,9] thereby affecting the self-assembly behavior of **1** in the gel state by disrupting the hydrogen bonding interactions (Figure 4b). The collapse of the gel structures of **1** in the presence of Ag$^+$ and Hg^{2+} can be explained by their tendency of binding toward the thiophenes or triple bonds. The terminal protons (Hg) of the propargyl groups disappeared in the presence of either Ag$^+$ or Hg^{2+} (2 equiv), implying the critical roles played by the propargyl groups in the gelation processes (Figures 4a and c). Based on all information obtained, we surmise a possible aggregation mode of the biscalix[4]arene **1** to form the fibrilla structure in mixed solvents (see Scheme S2, SI).

In conclusion, our results on the selective gelation of **1** on the oil phase of an oil/water mixture is reminiscent of one of the earliest industrial applications of the calixarenes.[9] The biscalixarene gelator **1**, readily synthesized in three steps from a commercially available carlix[4]arene, is useful not only for oil spill recovery but also for metal ion sensing by the naked eye. Moreover, it represents a new type of LMOGs without long alkyl chains and yet it forms organogels at very low w/v % and is very efficient as a PSG. We hope that such a discovery will stimulate new directions in the future design of PSGs for oil spill treatment.

Supporting Information Available. Experimental procedures, VT fluorescence, UV–vis, and ^1H, and ^{13}C NMR spectra data of compounds **1**–**4**. This material is acailable free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.