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Bisphenylsulfone-based polycatenar mesogens via CuAAC click reaction: Self-assembly and their applications in water purification

Hui-Fang Cheng [a, 1], Wei Xing [a, 1], Bei Zhang [a], Juan Yu [b, **], Xiao-Hong Cheng [a, *]

[a] Key Laboratory of Medicinal Chemistry for Natural Resources, Chemistry Department, Yunnan University, Kunming, Yunnan, 650091, PR China
[b] Kunming Institute of Precious Metals, State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum, Kunming, 650106, PR China

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ABSTRACT

Series of novel bent-shaped polycatenar molecules consisting of bisphenylsulfone as the central core and two 1,2,3-triazole dendron as wings were synthesized by copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction. These compounds can self-assemble into liquid crystalline phases in their pure states and organogels in organic solvent. Hexagonal columnar and $Pm\overline{3}n$ cubic phases are displayed by these compounds. Interestingly, the gel shows three dimensional networks of nanofibers. However, with the increasing of aging time, the nanofiber transforms into microspheric morphology, which is constructed by entangled fibers. Moreover, the gel system can be established to remove $\mathbf{I_2}$, $\mathbf{Fe^{3+}}$ and rhodamine B (**RhB**) from wastewater.

1. Introduction

Self-assembly is an important strategy for the preparation of nanomaterials with desirable properties for application in electronics, molecular sensors, bionanomaterials, shape memories and water purification *etc.*[1–6] Great efforts have been devoted to the design of novel functional molecules with well-defined nanostructures via ingenious molecular self-assembly. As a representative of the soft self-assembly materials with significantly technological importance, liquid crystal (LC)[7,8] has opened up a new avenue in increasing the complexity of soft self-assembly.[9] Organogels, defined as soft materials, are constituted of dilute cross-linked systems with mechanical properties ranging from soft to hard.[10,11] Such internal soft network structures should be resulted from physical bonds (physical gels) or chemical bonds (chemical gels).[12] Owing their unique physical properties, organogels have widespread applications in sensors, shape memories,[13,14] drug delivery devices,[15–17] photoresponsive devices,[18,19] molecular sensors[20–23] and oil-spill recoverers[24–28] *etc.* Recently, gels of amide derivatives or amphiphilic molecules have been extensively used to remove the pollutants (organic solvents and dyes) from contaminated water.[29–44]

Biphenylsulfone has been employed as architectural unit for synthesizing functional materials, and its derivatives can be applied as OLEDs, blue emitting, mechanochromic materials,[45,46] water purification membranes, proton conductive membranes,[41,47] and nonlinear optical materials *etc.*[48] Dendrimers with biphenylsulfone as a central unit could be employed as additives in dye-sensitized solar cells.[49] It is highly considered that functional materials with liquid crystalline properties or gel properties would be favorable for molecular packing, and thereby could improve the device performance. Nevertheless, biphenylsulfone-based liquid crystals and gelators are rarely reported. So far, only one literature reported the biphenylsulfone-based mesogens consisting of biphenylsulfone as core with 3,4,5-trialkoxy substituted benzyl ethers or 3,4,5-trialkoxy benzoates at both sides (Fig. 1a).[50] These compounds can aggregate into columnar phases in their pure states and fibrous gels in organic solvents.

The 1,2,3-triazole ring can not only serve as a linker between two molecular fragments, but also contribute to the overall physical and chemical properties of the resulting molecules, such as gelation properties.[51] As far as we know, there is no report on using the

* Corresponding author.
** Corresponding author.
E-mail addresses: juanyu1210@126.com (J. Yu), xhcheng@ynu.edu.cn (X.-H. Cheng).
[1] Both authors contributed equally to this work.

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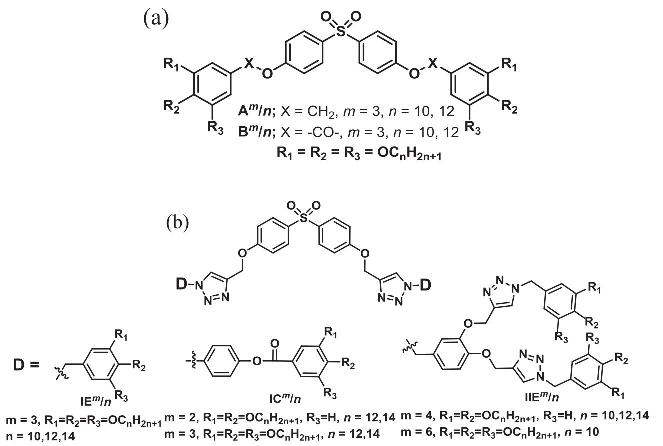

Fig. 1. The molecular structures of (a) the reported biphenylsulfone mesogens **A^m/n** and **B^m/n**;[50] as well as (b) triazole biphenylsulfone mesogens **IE^m/n**, **IC^m/n** and **IIE^m/n** under investigation.

1,2,3-triazole derivatives to remove pollutant from wastewater. In our previous work, we have synthesized series of bent-shaped polycatenars which contain two 1,2,3-triazole dendritic wings and different central cores such as methylene[52] or carbonyl groups.[53] Well defined self-assembly behaviors have been found in such bent-shaped polycatenars. We hoped that novel nano-structures and versatile applications could be realized in such bent-shaped polycatenars by further tailoring the molecular structural parameters.

Herein, novel series of bent-shaped polycatenars with biphenylsulfone as central core and two 1,2,3-triazole dendrons as wings were successfully synthesized by 'click reaction'[54–56] (Fig. 1b). These compounds can self-assemble into both liquid crystalline phases in their pure states and organogels in organic solvents. Not only columnar but also cubic phases have been observed in these compounds. Most interesting, the organogels show extraordinary morphological changes from nanofibers to microspheres. Gel system of these polycatenar molecules was established to remove the pollutants from the contaminated water.

2. Results and discussion

2.1. Synthesis

The synthesis of the target compounds **IE^m/n**, **IC^m/n** and **IIE^m/n** (see explanation on notations later) is shown in Scheme 1. The three hydroxyl groups of methyl gallate **1** were alkylated with appropriate alkyl bromides, resulting in **2^m/n**. Reduction of the ester group with $LiAlH_4$ yielded the 3,4,5-trialkoxybenzylalcohols, which were then converted to the corresponding benzylchlorides **3^m/n** with $SOCl_2$. The aryl azides **IEN^m/n** were synthesized from **3^m/n** by substitution reaction with sodium azide. 3,4,5-Trialkoxybenzoic acids **5^m/n** were obtained by hydrolysis of esters **2^m/n**. 4-Azidophenol **7** was prepared from 4-aminophenol **6** by formation of diazonium salt and subsequent substitution with sodium azide. Compound **8** was esterified with the corresponding intermediates 3,4,5-trialkoxybenzoic acids **5^m/n** to give the 4-azidophenyl 3,4,5-trialkoxybenzoates **ICN^m/n**. 3,4-Dipropargyloxybenzoate **4**[57] was used for the CuAAC reaction with the aryl azides **IEN^m/n**, yielding the dendritic aromatic azides **IIEN^m/n**. The bisacetylene **9** was prepared by etherification of 4,4′-sulfonyldiphenol **8** with propargyl bromide.[58] All of the target compounds **IE^m/n**, **IC^m/n** and **IIE^m/n** were synthesized by CuAAC reaction between the bisacetylene **9** and the appropriate substituted benzyl azides **IEN^m/n**, **ICN^m/n** or **IIEN^m/n**.[52,53,59] The final compounds were purified by column chromatography and all the new compounds were characterized by ^{1}H NMR, the final compounds were additional characterized by ^{13}C NMR and elemental analysis. Detailed synthetic procedures and analytical data are given in the Supporting Information. A representative overlay of ^{1}H NMR of compound **9**, azide **ICN^3/12** and the product **IC^3/12** is shown in SI to prove the completion of the CuAAC recation (Fig. S47). In the notation of the compounds, the letters **I** and **II** indicate the target compounds with the first and the second generation of triazole dendrons, respectively. The letters **C**, **E** and **N** specify the type of linking groups (**C** = carboxylate, **E** = ether and **N** = azide), the following superscript ***m*** defines the number of the terminal alkyl chains at each end, and the number ***n*** after the slash identifies the length of the periphery alkyl chain. Compounds **IE^m/n** and **IC^m/n** with the first generation dendrons are tetracatenar compounds when they possess two alkyl chains at each terminal, or hexacatenar compounds when they have three alkyl chains at each terminal. Compounds **IIE^m/n** with the second generation of 1,2,3-triazole dendrons are octacatenar compounds when they possess four alkyl chains at each terminal ($m = 4$) and are dodecylcatenars having six alkyl chains at each terminal ($m = 6$).

2.2. Mesomorphic properties

The liquid crystalline properties of the synthesized biphenylsulfone based bent-shaped polycatenar compounds **IE^m/n**, **IC^m/n** and **IIE ^{m}/n** were studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and the selected compounds were investigated by small angle X-ray scatting (SAXS). The transition temperatures of these compounds are collected in Table 1.

Columnar phase: Except **IC^2/12** displaying monotropic columnar phase, the other tetracatenar compounds **IC^2/n** and hexacatenar compounds **IE^3/n** and **IC^3/n** as well as octacatenar compounds **IIE^4/n** exhibit enantiotropic columnar phases. All compounds have longer rigid cores and thereby show considerably broader mesophase ranges compared with the reported biphenylsulfone mesogens **A^m/n** and **B^m/n** (Table 1).[50]

The textures of columnar mesophases represent as typical columnar phase with fan-shaped textures and spherulitic domains, as shown in Fig. 2a and Figs. S1a–i. There exists a possible transition to polar columnar phase as observed under POM that the striations of the spherulitic domains along with a significant reduction of the birefringence at defined temperature (Fig. 2b).[60,61]

The columnar phases of these compounds were further investigated by SAXS. For compounds **IE^3/12**, **IE^3/14**, **IC^3/12**, **IC^3/14**, **IIE^4/10** and **IIE^4/12**, there are three small angle reflections with a ratio of their reciprocal spacing 1: $3^{1/2}$: 2, which can be indexed to the 10, 11, 20 reflections of a typical hexagonal lattice with *p*6mm symmetry (Fig. 2c, Figs. S4–5 and Tables S2, S3, S5-8). For compounds **IE^3/10**, **IC^2/14** and **IIE^4/14**, there are only two small angle reflections with a ratio of their reciprocal spacing 1: $3^{1/2}$, which can be indexed to the 10, 11 reflections of a typical hexagonal lattice with *p*6mm symmetry (Figs. S5a, S5d, S5h and Tables S1, S4, S9). Based on the lattice parameter, the number of molecules (μ) organized in a slice of the columns with a height of $h = 0.45$ nm is estimated to be about 4 for the tetracatenar compound **IC^2/14**, about 3 for hexacatenar compounds **IC^3/n**, and about 2 for both hexacatenar compounds **IE^3/n** and octacatenar compounds **IIE^4/n** (Table 1). This phenomenon may be due to the different volume ratio between the central rigid core and peripheral flexible alkyl chains. The larger the volume ratio, the more the number of molecules is required to form a slice. The columns are formed by stacking of such supramolecular