



# Control of supramolecular nanoassemblies by tuning the polarities of linkages and solvents

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## ABSTRACT

Novel polycatenars bearing a central bisphenyl sulfonyl moiety connected to the triazole dendrons at both ends through amide or ester linkages were synthesized via click chemistry. In their bulk states, only one ester compound with the longest alkyl chains can self-assemble into p6mm columnar phase, all the other compounds are nonmesogens. These polycatenars can form organogels with much more ordered morphologies in polar solvents than in apolar or less polar solvents. In DMF solvent, gels with spherical flower-like morphologies are formed by ester compounds, while gels with nanosheet morphologies are formed by amide compounds. The amide polycatenars can also act as chemosensors for detecting metal ions with high selectivity. The results showed that both the polarities of the linkages and the polarities of the solvents dramatically influenced the creation of supramolecular nanostructures.

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## 1. Introduction

Design of small molecules which can self-assemble into well-defined nanostructures have arisen large interest because of their numerous technological applications [1–8]. Liquid crystals and organogels are two kinds of promising self-assembly materials and have achieved fantastic nano/microstructures by controlling the noncovalent interactions including  $\pi$ - $\pi$  stacking, dipole-dipole interactions, van der Waals interaction and hydrogen bonding etc. [9–13].

Biphenylsulfone derivatives have found wide applications in OLEDs, blue emitting, nonlinear optical materials, and membranes for water purifications and proton conductors etc. [14–18]. However the diphenylsulfone is nonlinear and considered usually as a nonmesogenic unit. Only until 2013, Kato etc. [19] reported the first examples of bisphenylsulfone-based polycatenar mesogens, in which the terminal alkoxy substituted phenyl groups are connected to the central biphenylsulfone core via ether or carboxylate linkages. Such compounds can self-assemble into polar columnar phases, and one ether compound can additionally form fibrous gel aggregates in solution. However only four compounds were reported, the influence of the terminal chains and the type of the linkages between the central core and terminal groups on the aggregation behavior was not studied in detail.

In order to study the self-assembly behavior in more detail, we decided to elongation of the rigid core by CuAAC (copper-catalyzed azide-alkyne cycloaddition) click reaction [20–23]. In such way the  $\pi$

interaction between the rigid cores, and the incompatibility between the rigid core and flexible terminal chains would be enhanced, both factors would facilitate the molecular self-organization.

According to this designing idea, in our recent work, the central diphenylsulfone core has been connected to the triazole dendrons via ether linkages at both ends [24,25]. Indeed all these ether compounds are LCs with columnar or cubic structures, and the effects of the type of the terminal flexible chains (alkyl chains or PEO chains) and the volume of triazole dendrons (1st generation or 2nd generation) on the self-assembly behavior were studied. Most interesting various morphologies such as twist nanobelt and microsphere were observed in the organogels formed by such compounds in solvents.

The self-assembly behaviors of such bisphenylsulfone-based polycatenars are worth to be studied further, thus herein series of novel compounds **IC<sup>m</sup>/n**, **IA<sup>m</sup>/n** and **IIA<sup>m</sup>/n** with different polar linking groups (carboxylate or amide) were synthesized (Scheme 1). Large triazole dendrons were attached to both sides of bisphenylsulfone unit via CuAAC click reaction to promote the formation of the ordered assembled structures. Moreover, we focused on the effect of polarity of the linkages (carboxylate or amide) on the self-assembly behaviors of these compounds.

## 2. Results and discussion

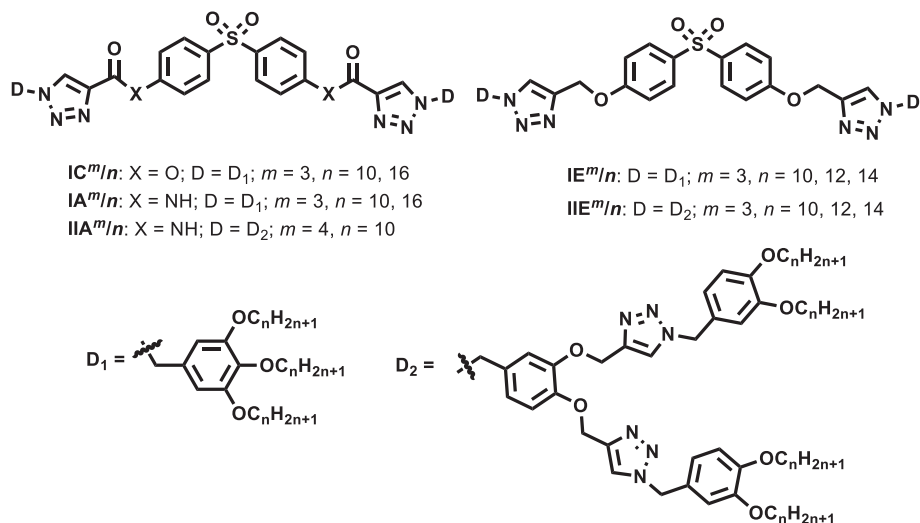
### 2.1. Synthesis

The synthesis way for the target compounds **IC<sup>m</sup>/n**, **IA<sup>m</sup>/n** and **IIA<sup>m</sup>/n** is shown in Scheme 2. The ethyl 3,4(5) di(tri)hydroxybenzoate **1** or **2** was alkylated with appropriate alkyl bromides, the ester groups of the

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**Scheme 1.** Structure of compounds  $\text{IC}^m/n$ ,  $\text{IA}^m/n$  and  $\text{IIA}^m/n$  under investigation and our previously reported ether polycatenar analogues  $\text{IE}^m/n$  and  $\text{IIE}^m/n$  [24].

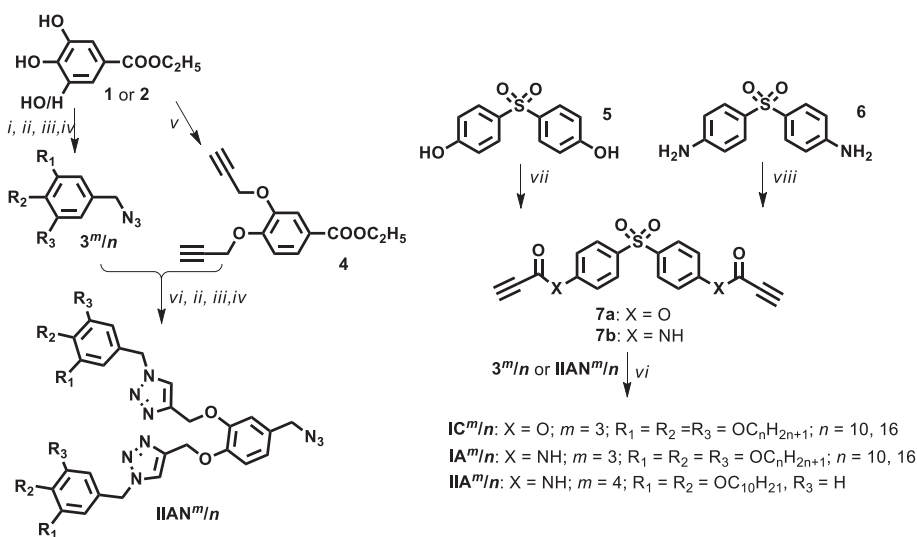
yielding intermediates were reduced with  $\text{LiAlH}_4$ , followed by substitution of the benzylalcohols with  $\text{SOCl}_2$  yielding benzylchlorides. Benzylchlorides were substituted with sodium azide affording the aryl azides  $\mathbf{3}^m/n$ . 3,4 Dihydroxybenzoate  $\mathbf{2}$  was etherified with propargyl bromide to give compound  $\mathbf{4}$  [26]. CuAAC reaction between the aryl azides  $\mathbf{3}^m/n$  and the compound  $\mathbf{4}$  afforded the aromatic azides  $\text{IIAN}^m/n$ . Propiolic acid reacted with 4,4' sulfonyldiphenol  $\mathbf{5}$  or 4,4' sulfonyldianiline  $\mathbf{6}$  affording  $\mathbf{7a}$  and  $\mathbf{7b}$  respectively [27,28]. CuAAC reaction between the bisacetylene  $\mathbf{7a}$  or  $\mathbf{7b}$  and the appropriate substituted benzyl azide  $\mathbf{3}^m/n$  or  $\text{IIAN}^m/n$  yielded the target compounds  $\text{IC}^m/n$ ,  $\text{IA}^m/n$  and  $\text{IIA}^m/n$  [29–31]. Purification of the compounds was done by column chromatography; all target compounds were identified by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and elemental analysis (see Supporting Information).

## 2.2. Mesomorphic properties

The thermotropic properties of compounds  $\text{IC}^m/n$ ,  $\text{IA}^m/n$  and  $\text{IIA}^m/n$  are collected in Table 1. Only hexacatenar ester compound  $\text{IC}^3/16$  with the longest chain exhibited an enantiotropic columnar mesophase, all

the other compounds were crystals. Under POM, the fan-like texture characteristic for columnar phase was observed for compound  $\text{IC}^3/16$ . The investigation with an additional  $\lambda$ -plate indicated optically negative of the columnar phase (Fig. 1a) in which the major intramolecular  $\pi$ -conjugation pathway was perpendicular to the column long axis. In the SAXS profile of this columnar phase, there were three small angle reflexes in a ratio of 1:1/3<sup>1/2</sup>:1/2 indexing to the (10), (11), (20), supporting the arrangement of hexagonal columnar phase with p6mm symmetry (Fig. 1b and Table S1). It could be calculated that there were two molecules assembled in the cross section of one column with a height of 0.45 nm. Therefore two molecules were organized into a disk, and piled up to be supramolecular columns, and such columns further organized to a 2D columnar lattice (Fig. 1c) [32]. The results were also supported by the molecular dynamics (MD) annealed model (Fig. 1d) [33,34].

By comparison with our previously reported ether polycatenar analogues  $\text{IE}^m/n$  and  $\text{IIE}^m/n$  (Scheme 1) [24], which displayed broader range of mesophases (Fig. S2). It indicated that replacement of less polar ether linkage with polar carboxylate or amide group hindered the formation of the mesophase. The much higher melting



**Scheme 2.** Synthesis of compounds  $\text{IC}^m/n$ ,  $\text{IA}^m/n$  and  $\text{IIA}^m/n$ : Reagents and conditions: i) C<sub>n</sub>H<sub>2n+1</sub>Br, DMF, K<sub>2</sub>CO<sub>3</sub>, 90 °C, 12 h; ii) LiAlH<sub>4</sub>, THF, RT, 2 h; iii) SOCl<sub>2</sub>, THF, RT, 1 h; iv) KI, NaN<sub>3</sub>, DMF, 45 °C, 12 h; v) K<sub>2</sub>CO<sub>3</sub>, propargyl bromide, acetone, 50 °C, 10 h; vi) tert-butanol, THF, H<sub>2</sub>O, sodium ascorbate, CuSO<sub>4</sub>·5H<sub>2</sub>O, RT, 20 h; vii) propiolic acid, DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, RT, 72 h; viii) propiolic acid, DCC, CH<sub>2</sub>Cl<sub>2</sub>, RT, 12 h.

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