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Folding a Conjugated Chain: Oligo(*o*-phenyleneethynylene-*alt*-*p*-phenyleneethynylene)

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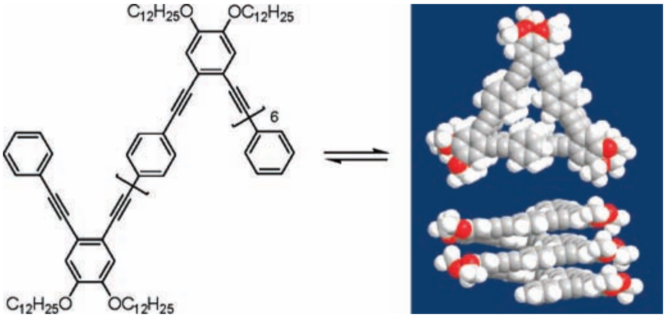
ABSTRACT



An oligo(*o*-phenyleneethynylene-*alt*-*p*-phenyleneethynylene) was synthesized to create a conjugated molecule capable of adopting a helical secondary structure. A special feature of such a folded molecule is that the effective directions of energy/charge transport via covalent conjugation and through $\pi-\pi$ stacking are converged to be along the helix axis. The transition from random conformations to the helix, driven by solvophobic and aromatic stacking interactions, was controlled by solvent properties. UV−vis and fluorescence spectroscopies gave supportive evidence for the folding process.

Due to a superior combination of (semi)conducting, illuminating, optoelectronic, mechanical properties, and solution processability, conjugated polymers[1] have found a wide range of applications, such as field-effect transistors,[2] light-emitting diodes,[3] solar cells,[4] chemo- and biosensors,[5] lasing devices,[6] etc. In spite of the vast merits of solution processing, the device performance is sometimes limited by the amorphous nature of the resulting materials. Self-assembly of conjugated (macro)molecules into ordered nano- or microstructures is envisioned to help improve certain properties while maintaining the solution processability.[7] Also, self-assembly of conjugated systems offers a potent bottom-up approach to fabricating (supra)molecular devices.

Currently, studies on conjugated-molecule self-assembly are mainly focused on intermolecular organization behaviors and architectures. Manipulations of single molecules with optical or electronic functions into well-defined, higher-order structures are less common,[8,9] although natural and artificial systems of nonconjugated structures exhibiting single-molecule supramolecular architectures are ubiquitous and

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widely investigated for their structure-enabled functions. For example, foldamers of varied structures and functions have been widely explored,[10,11] among which *m*-phenyleneethynylene (PE) oligomers are intensively studied.[12] Analogous to *m*-PE helices with six repeating units per turn, oligo(*o*-PE) chains may fold into helices of 3 PE units per turn. Among a few other studies,[13] Tew and co-workers demonstrated with NMR spectroscopy that *o*-PE oligomers folded into helices.[14]

Here, we introduce a design that folds a conjugated chain into a helical conformation. Such a helical structure imparts a novel characteristic to the system. In the folded state, $\pi-\pi$ stacking takes place intramolecularly. The effective directions of energy/charge transport via covalent conjugation and through $\pi-\pi$ stacking are thus converged to be along the helix axis in a single molecule. The two electronic coupling mechanisms may thus work jointly and cooperatively. This unique feature may bring about new properties and functions inaccessible with traditional, linear conjugated polymers.

The idea of folding a conjugated molecule is first tested with a PE oligomer. Besides capable of folding, the molecular structure was specifically devised to maintain conjugation along the backbone, such that the molecule preserves desirable optical and electronic properties. *ortho*-Phenylene was selected as the repeating unit to confer nonlinear bond angle and constitute "turns" within helices. This choice was also made because the linkage displays a certain degree of conjugation.[15] As depicted in Figure 1, the oligomer backbone is constructed with alternating *o*-PE and *p*-PE units.[16] The reasons for incorporating *p*-PE units are as follows. In order to accommodate a helical pitch corresponding to the typical distance between stacked aromatic rings, a folded oligomer comprising exclusively *o*-PE units has to assume a significant dihedral angle at the *o*-phenylene linkage.[13,14] With a *p*-PE segment inserted between every other *o*-PE units, the torsional strain at the *o*-phenylene linkage can be greatly relieved in the folded state, and the coplanarity of adjacent phenyl rings is also improved. This would favor π-electron delocalization and thus energy/charge transport along the covalent chain. The *p*-PE units also help extend the effective conjugation length, making the molecule more suitable for photonic or opto-electronic applications. As a modular design, either or both of the *p*- and *o*-PE units can be substituted with alternative aromatic moieties of proper bond angles. Thereby, functionalization and fine-tuning of the optical or electronic properties of the system can be realized.

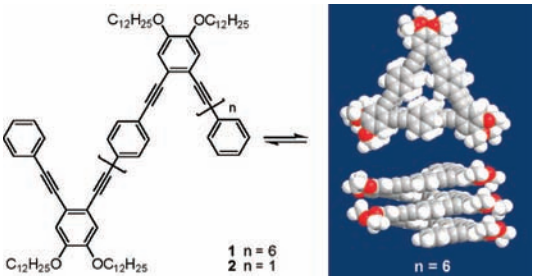

Figure 1. Chemical structures of oligomers **1** and **2**, and top- and side-views of a space-filling model of **1** in a helical conformation (dodecyl side chains were truncated as methyl groups for clarity).

Based on the above considerations, oligomer **1** was synthesized. This molecule contains 15 phenyl(ene) units and has dodecyloxy side chains appended to the *o*-phenylenes. The helical architecture was to be attained by virtue of solvophilicity difference between the aromatic backbone and aliphatic side chains. Specifically, a nonpolar, aliphatic solvent will be used to create a solvophobic environment for the aromatic backbone, while keeping the alkyl side chains soluble.[7] Imaginably, under such conditions a helical conformation will be favored, as it offers a solvophilicity balance by having most backbone units buried and all side chains exposed at the helix periphery.[12] Additionally, the helix can be stabilized by intramolecular $\pi-\pi$ stacking interactions.[12a] Another prerequisite for stabilizing the helical architecture is that the molecule should be long enough to gain sufficient energy from intramolecular $\pi-\pi$ stackings to counteract the entropy loss for adopting an ordered conformation.[12b] Thus, a shorter homologue of **1**, oligomer **2**, consisting of five phenyl rings and therefore incapable of folding, was employed as a reference molecule for comparison studies.

The synthesis of pentadecamer **1** is illustrated in Scheme 1. The final step was accomplished by joining three segments together, a bisfunctional compound **3** with two equivalent **4**, via a Sonogashira−Hagihara reaction. The advantages of such a three-component coupling over linking two longer pieces into one (e.g., a heptamer with an octamer) are not only the less tedious synthetic routes to the shorter precursors but also that the byproduct from oxidative coupling of terminal acetylenes has a distinct chain length from that of the target molecule and may be conveniently separated with column chromatography. As shown in Scheme 1, precursors

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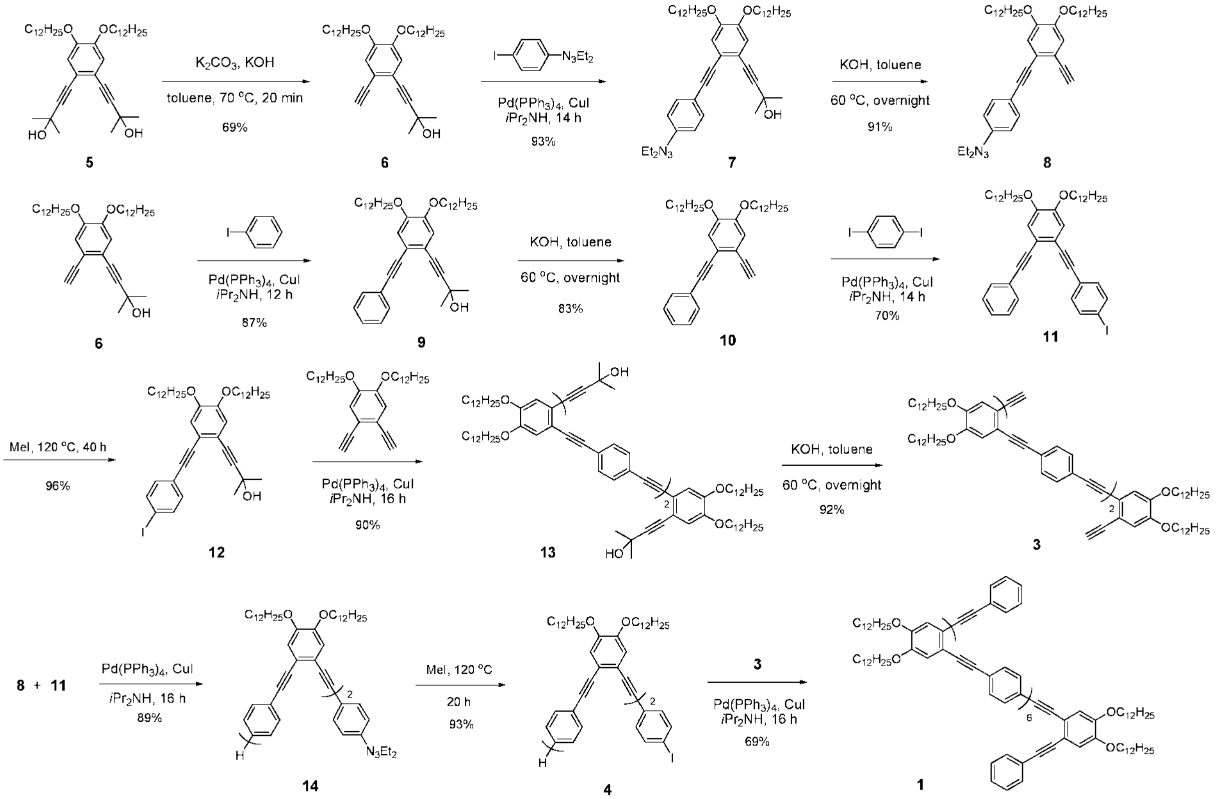
Scheme 1. Synthetic Route of Oligomer **1**



3 and **4** were prepared through multistep Sonogashira cross-couplings, along with orthogonal protecting and masking protocols for the terminal acetylene and aryl halide.

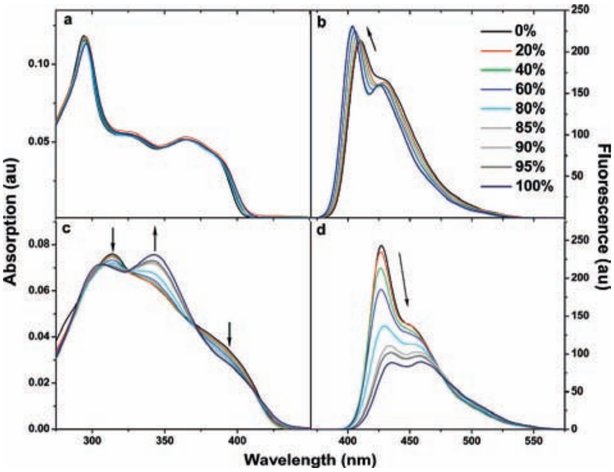


Figure 2. UV−vis absorption and fluorescence emission spectra of **2** (a,b) and **1** (c,d) in chloroform−cyclohexane cosolvent (the legend shows the vol % of cyclohexane; arrows indicate the spectrum shifting trend from chloroform to cyclohexane).

Complementary to the NMR studies conducted by Tew et al.,[14b−d] for the current system UV−vis absorption and fluorescence emission spectra handily provided evidence for folding. In chloroform, which is a good solvent for both the backbone and side chains, the oligomer should adopt random conformations, whereas cyclohexane was selected as the aliphatic solvent that might induce helical folding of the oligomer. Hence, solvent titration experiments were performed with the two solvents to probe the folding transition of **1**. But first, oligomer **2** was examined on how the optical spectra responded to such solvent changes when folding was not involved. It was found that when the volume ratio of cyclohexane to chloroform was increased in the binary solvent, oligomer **2** showed a slight blue-shift and better resolved vibronic structures in the emission band, whereas the absorption spectra exhibited no prominent change (parts a and b of Figure 2). The occurrence of such blue-shifting and fine structures in the emission is fairly common for chromophores experiencing solvent polarity decrease, due to greater solvent relaxations in more polar solvents. In stark contrast, longer oligomer **1** displayed rather distinct responses when subject to the same solvent changes. With an increased cyclohexane content in the mixed solvent, the original absorbance maximum at 315 nm and a side-peak around 400 nm attenuated while a new peak emerged at about 300 nm and the original shoulder peak at ca. 345 nm escalated and

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became a major maximum in pure cyclohexane (Figure 2c). During this process multiple isosbestic points were observed, indicating that the molecule was undergoing a gradual transition between two defined states, likely the transoid and cisoid conformational states.[12a] Moreover, the fluorescence intensity of oligomer **1** drastically decreased as the solvent changed from chloroform to cyclohexane, accompanied with a slight red-shift in wavelength (Figure 2d). Since fluorescence quenching is a typical signature of $\pi-\pi$ stacking, it suggested that longer oligomer **1** adopted a more compact conformation in cyclohexane, consistent with the helical structure. This solvent titration experiment was then conducted at a concentration as low as approximately 10^{-8} M of **1**, giving nearly identical spectral changes as shown in parts c and d of Figure 2. This result suggested that the observed spectral changes could originate from a single-molecule behavior, i.e., chain folding, rather than intermolecular interactions. This assumption was further supported by dynamic light scattering (DLS) studies. No particles of measurable sizes were detected by DLS in cyclohexane solutions of **1** from 10^{-8} to 10^{-6} M, the same concentration range for recording the optical spectra.[17]

It can be imagined that under alternative, less optimal conditions, e.g., in poor solvents for both the backbone and side chains, such an ordered helical conformation is unlikely to exist. Rather, the molecules may collapse into compact yet random conformations and/or form ill-defined intermolecular aggregates. Indeed, when adding acetonitrile or methanol into the chloroform solution of **1**, less well-defined changes were recorded with the absorption, although fluorescence quenching took place to a greater extent (Figures S1 and S2, Supporting Information). These results further corroborated the assertion that the spectral changes exhibited in parts c and d of Figure 2 corresponded to a transition to a specific, helical structure.

Additional evidence for the helical conformation came from a macrocyclic analogue, **MC** (Figure 3). This molecule shares the same backbone repeating units with oligomer **1**. The absorption spectra in Figure 3 clearly show that the band shape of **1** in cyclohexane resembles that of **MC**, with two major peaks at ca. 300 and 350 nm, more than that in chloroform. This further supported the helical structure of **1** in cyclohexane, considering the similarity between the macrocycle and a turn in the helix. The particularly large A_{350nm}/A_{300nm} value of **MC** might result from its rigid, cyclic geometry or the unique closed-ring electronic characteristics. Likely due to the more dynamic and crescent backbone conformation, the helix gave a similar yet not identical band shape. Alternatively, this difference might indicate that the helical structure of **1** is not completely stabilized in cyclohexane. Investigations at quantifying the folding stability and possibly further stabilizing the helical structure with other solvent conditions are underway.

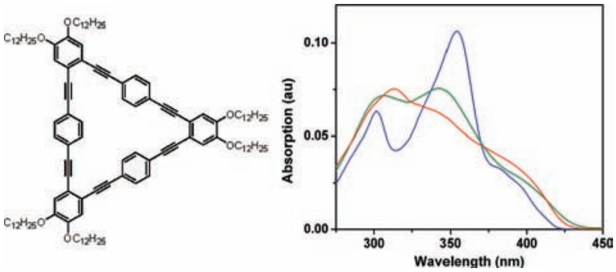

Figure 3. Chemical structure and UV−vis absorption spectrum of **MC** in cyclohexane (blue) in comparison with those of **1** in cyclohexane (green) and chloroform (red).

The current system is a proof-of-principle design, illustrating that higher-order structures such as helices may be realized in conjugated chain molecules. Photophysical characterizations of a monodispersed oligo(*o*-PE-*alt*-*p*-PE) gave supportive evidence for a helical structure under suitable conditions. Alternative aromatic units will be incorporated into the backbone in future studies, making the architecture a versatile folding scaffold to achieve structural and function diversity.

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Supporting Information Available: Synthesis procedures and characterizations of **1**, **2**, and **MC**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] The emission quantum yield of **1** in cyclohexane did not decrease with increasing concentration, which also suggested that no significant intermolecular aggregation occurred.