DOI: 10.1002/chem.201003603

Oligo(*p*-phenylene-ethynylene)s with Backbone Conformation Controlled by Competitive Intramolecular Hydrogen Bonds

Wei Hu, Qifan Yan, and Dahui Zhao*[a]

Abstract: A series of conjugated oligo(*p*-phenylene-ethynylene) (OPE) molecules with backbone conformations (that is, the relative orientations of the contained phenylene units) controlled by competitive intramolecular hydrogen bonds to be either co-planar or random were synthesised and studied. In these oligomers, carboxylate and amido substituents were attached to alternate phenylene units in the OPE backbone. These functional groups were able to form intramolecular hydrogen bonds between neighbouring phenylene units. Thereby, all phenylene units in the backbone were confined in a co-planar conformation. This planarised structure featured a more extended effective conjugation length than that of regular OPEs with phenylene units adopting random orientation due to a low rotational-energy barrier. However, if a tri(ethylene glycol) (Tg) side chain was appended to the amido group, it enabled another type of intramolecular hydrogen bond, formed by the Tg chain folding back and the contained ether oxygen atom competing with the ester carbonyl group as the hydrogen-bond acceptor. The outcome of this competition was proven to depend on the length of the alkylene linker joining the ether oxygen atom to the amido group. Specifically, if the Tg chain folded back to form a five-membered cyclic structure, this hydrogen-bonding motif was sufficiently robust to overrule the hydrogen bonds between adjacent phenylene units. Consequently, the oligomers assumed non-planar conformations. However, if the side chain formed a six-membered ring by hydrogen bonding with the amido NH group, such a motif was much less stable and yielded in the competition with the ester carbonyl group from the adjacent phenylene unit. Thus, the hydrogen bonds between the phenylene units remained, and the co-planar conformation was manifested. In our system, the hydrogen bonds formed by the back-folded Tg chain and amido NH group relied on a single oxygen atom as the hydrogen-bond acceptor. The additional oxygen atoms in the Tg chain made a negligible contribution. A bifurcated hydrogen-bond motif was unimportant. From our results, in combination with the results from an independent study by Meijer et al.,[13] it is evident that intramolecular hydrogen bonds involving back-folded oligo(ethylene glycol) moieties may differ in their structural details. Absorption spectroscopy served as a convenient yet sensitive technique for analysing hydrogen-bonding motifs in our study.

Keywords: hydrogen bonds · ethylene glycols · oligo(phenylene-ethynylene)s · planar conformation · supramolecular chemistry

Introduction

In addition to being a ubiquitous force participating in the construction of well-defined three-dimensional structures of biomacromolecules, hydrogen bonding serves as one of the most useful and versatile non-covalent interactions in the "toolbox" of chemists, helping to realise self-assemblies of diverse artificial supramolecular organisations.[1] Numerous elegantly designed intermolecular and intramolecular hydrogen-bonding motifs have been applied for such purposes.[2] Due to its ready availability and biocompatibility, oligo(ethylene glycol) (OEG) has emerged as a popular side chain for attaining optimal solubility of supramolecular assemblies and their modules in polar organic and aqueous solutions. Hence, hydrogen bonds and OEG side chains have frequently been implemented simultaneously in supramolecular architectures.[3–10] However, caution ought to be used in designing such systems because the oxygen atoms in OEGs are potential hydrogen-bond acceptors and may interfere with the designed hydrogen-bonding motifs. Recently, "back-folding" of OEG side chains driven by intramolecular hydrogen-bond formation with hydrogen-bond donors in the core structure was observed and investigated in a number of systems.[7–13] Due to the importance of both hydrogen bonds and OEG side chains, the circumvention or harnessing of such interactions to achieve the desired hydrogen-bond designs has become a research topic of growing importance.

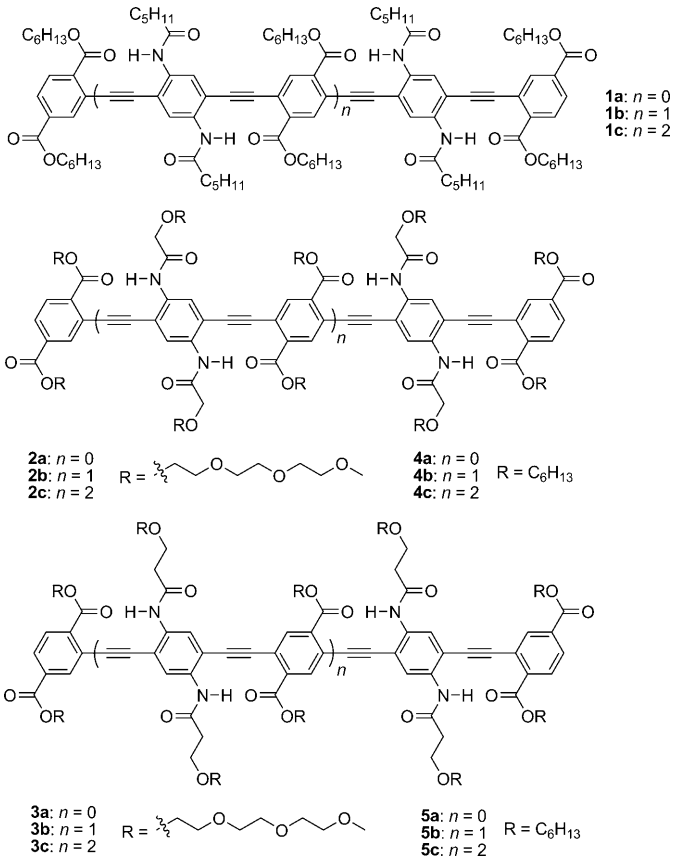
Phenylene-ethynylene polymers and oligomers are a family of conjugated systems with highly diversified structures and wide applications as (opto-)electronic materials.[14]

[a] Dr. W. Hu, Q. Yan, Prof. D. Zhao
Beijing National Laboratory for Molecular Sciences
Department of Applied Chemistry and
the Key Laboratory of Polymer Chemistry and Physics
of the Ministry of Education
College of Chemistry, Peking University, Beijing 100871 (P. R. China)
Fax: (+86) 10-62753973
E-mail: dhzhao@pku.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201003603.

With the increasing attention paid to molecular and nanoelectronics, oligo(*p*-phenylene-ethynylene)s (OPEs) have been intensively studied as promising molecular wires due to their very good electric-conducting properties.[15] Herein, we report a study on an OPE system that harnessed competitive intramolecular hydrogen bonds to control the backbone conformation. OPEs of fully planarised backbone structure are of great interest because they are expected to display superior conductivity compared to the analogous oligomers with non-planar conformations.[16] Furthermore, our design allowed a systematic investigation of the structures and properties of hydrogen-bonding motifs involving "back-folded" OEGs.

Due to a low energy barrier, the phenylene units in the OPE backbone undergo rapid rotation around the ethynylene moieties at room temperature.[17] Previously, we synthesised a series of OPEs in which intramolecular hydrogen bonds were implemented between neighbouring phenylene pairs in the backbone (**1a–c**, Scheme 1).[18] The hydrogen-bond donors were the NH protons of the alkanamido groups, and the acceptors were the ester carbonyl oxygen atoms on every other phenyl(ene) unit. Upon formation of the intramolecular hydrogen bonds, all of the phenyl(ene) rings in the backbone were constrained in a co-planar conformation. In comparison with regular OPEs without such intramolecular hydrogen bonds, the planarised backbone exhibited a more extended conjugation length, as evidenced by a bathochromic shift in the absorption spectrum.



Scheme 1. Chemical structures of the studied OPE series.

In our original design of OPE (**1a–c**), the phenylene units in the backbone were appended with linear alkyl side chains. The longer OPE **1c** demonstrated a strong tendency for intermolecular association because of the planarised aromatic skeleton, which resulted in poor solubility in most organic solvents. Chloroform was the best solvent identified, and it afforded only low solubility. To facilitate studies of these planar OPE structures in more diverse solvents, OEG was chosen as an alternative side chain to replace the linear alkyl chains for improved solubility. Furthermore, in order to precisely delineate the effects of the intramolecular hydrogen bonds and planarised backbone on the electronic and conductive properties, a suitable oligomer analogue was desired for a comparison study. Ideally, it would possess a non-planar backbone but would otherwise have nearly identical structural features to those of the planar oligomer. Thus, a molecular design was contemplated in which OEG side chains would be exploited to install competitive hydrogen bonds and achieve control and variation in the backbone conformation.

In the literature, OEG side chains were reported to form intramolecular hydrogen bonds upon back-folding. If such a bonding motif was undesirable, they could be precluded by introducing a long aliphatic spacer between the hydrogen-bond donor and the OEG chain.[9–12] In the current system, we determined that, by adjusting the linker length, the intramolecular hydrogen bonds involving OEG side chains could be formed or disrupted with control. Consequently, the aforementioned hydrogen bonds between adjacent phenylene units were switched "on" or "off", due to competition with the OEG side chains for the same set of hydrogen-bond donors. Thereby, the OPE backbone conformation was varied to be either co-planar or random, and the effective conjugation length was modulated.

In addition to a method for controlling the backbone conformation, important information about the hydrogen-bond motif of back-folded OEGs was revealed by the current study. The stability of the intramolecular hydrogen bond formed by the ether oxygen atom in an OEG associating with the amido NH group was highly sensitive to the size of the ring set up by its formation. Specifically, if a five-membered ring was created, the hydrogen bond was significantly more robust than one formed with a six-membered ring. Furthermore, the results showed that, in the current system, a single oxygen atom played a dominant role in stabilising the intramolecular hydrogen bond formed by a back-folded OEG; that is, bifurcated hydrogen bonds were not important in these oligomers.

In our study, by characterising the conjugation length of the OPE chain, UV/Vis absorption spectroscopy served as a sensitive and convenient tool for probing the backbone conformation and interrogating the stability of relevant intramolecular hydrogen bonds.

Results and Discussion

Design and syntheses of OPEs: In addition to the original series of alkylated OPEs (**1a–c**), four series of analogous oligomers were synthesised (**2–5**, Scheme 1). In each series, oligomers of three different chain lengths were prepared. Oligomers with 3, 5, and 7 phenyl(ene) rings in the backbone were labelled **a**, **b**, and **c**, respectively. **2** and **3** were appended with tri(ethylene glycol) monomethyl ether (Tg) side chains. The difference between these two sets of oligomers was that a methylene linker was inserted between the amido carbonyl group and the nearest oxygen atom in the Tg side chain in **2**, whereas an ethylene spacer was incorporated in **3**.

In oligomers **4** and **5**, instead of a Tg side chain, alkoxy groups were attached to the amido functional moieties through a methylene or ethylene linker. These oligomers were designed to investigate the structure of the hydrogen bonds formed by back-folded OEG chains. These compounds would be useful for delineating whether one or more than one oxygen atom acted as the hydrogen-bond acceptor in such motifs. If **4** and **5** displayed similar behaviours to those of **2** and **3**, respectively, it would indicate that a single ether oxygen atom is sufficient to stabilise the hydrogen bond and enable OEG back-folding. On the other hand, if **4** and **5** displayed weakened hydrogen bonds, bifurcated hydrogen bonds would be implied in **2** and **3**, with the demand for the presence of two hydrogen-bond acceptors for maximal stability.[13]

After the attainment of a number of new monomers with different side chains (M2–M5 in Figure 1), the syntheses of oligomers **2–5** were accomplished by similar synthetic routes to that used for generating **1** (see the Supporting Information). Specifically, Sonogashira cross-coupling between aryl iodide and the terminal acetylene group was performed to assemble the OPE backbone. Trimethylsilyl protection–deprotection protocols were employed for the terminal acetylene groups to achieve step-wise chain extension, which offered monodisperse oligomers. The identity and purity of all studied oligomers were characterised by NMR spectroscopy, mass spectroscopy, and elemental analyses.

^{1}H NMR study of key monomers: The ^{1}H NMR spectra were first studied to characterise the hydrogen bonds in the monomers. All spectra were recorded in $CDCl_3$ (Figure 1). In M1, the amido NH groups (that is, protons H_a) generated a resonance with a chemical shift of approximately 7.8 ppm. However, in M2, in which the hexanamido groups were replaced with Tg-substituted 2-hydroxyacetamido groups, the corresponding H_a protons exhibited a distinct chemical shift of nearly 9.3 ppm. Such a significant change could not be solely explained by the inductive effect of different side chains. The chemical-shift value was concentration independent, so the marked downfield shift observed in M2 was attributed to an intramolecular hydrogen bond formed by

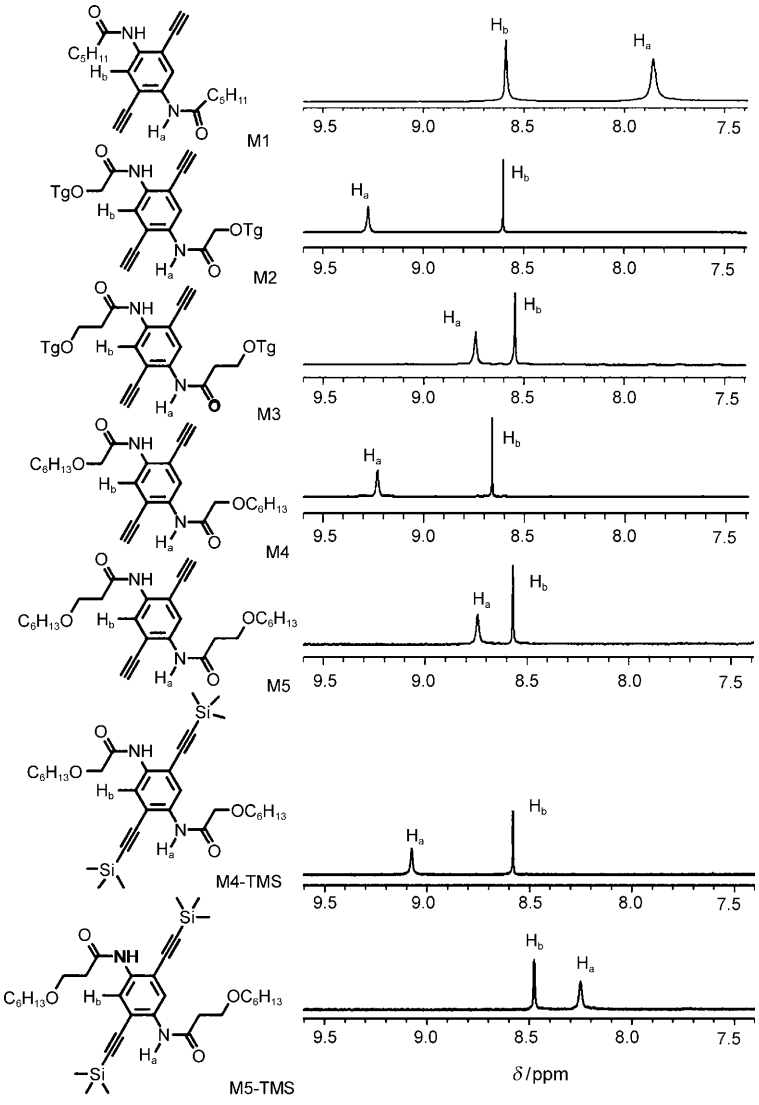
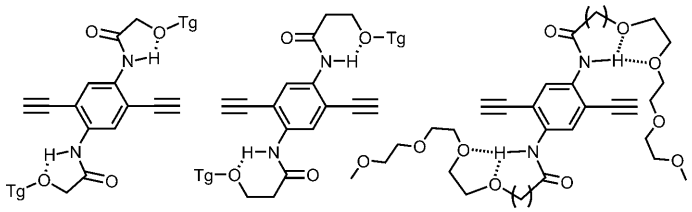


Figure 1. Chemical structures and the aromatic region of the ^{1}H NMR spectra of OPE monomers in $CDCl_3$.



Scheme 2. Intramolecular hydrogen-bonding motifs in M2 and M3 involving the back-folded OEG side chains forming five- or six-membered cyclic structures (left and middle, respectively). The bifurcated hydrogen-bonding motif (right) was evidenced to be unimportant for the current system.

the H_a protons. This result confirmed our prediction that the OEG side chains would fold back and form intramolecular hydrogen bonds with the contained ether oxygen atom(s) (Scheme 2). To further elucidate the properties of these hydrogen bonds, the ^{1}H NMR spectrum of M3 was then examined. Interestingly, the amido NH groups in M3 displayed a chemical shift of approximately 8.7 ppm, an intermediate value between those of corresponding protons in M1 and M2. The extent of downfield shift of hydrogen-bonded protons semi-quantitatively reflects the bond strength, so it was concluded that intramolecular hydrogen bonds were formed by the H_a protons in M3, but their strength was weaker than that of the hydrogen bonds in M2. Subsequently, the chemical shifts of the amido protons in M4 and M5 were compared. The NMR spectra showed that the H_a protons in M4 exhibited a similar chemical shift to that of M2, and M5 presented a similar spectrum to that of M3.

The information provided by ^{1}H NMR spectra of the monomers can be summarised as follows. First, because M2 and M4 exhibited similar chemical shifts, it was indicated that a single oxygen atom (the one nearest to the amido carbonyl group) played a dominant role in forming the hydrogen bond and driving the back-folding of the OEG chain. Any effect of the additional oxygen atoms was not detected. The similar chemical shifts displayed by the amido NH groups in M3 and M5 was also informative, in that no pronounced improvement in bond stability was manifested by the presence of additional hydrogen-bond acceptors, even in an hydrogen bond of attenuated strength. Essentially, these results suggested that the bifurcated hydrogen-bond motif was unimportant in these monomers (Scheme 2). This observation was different from that made by Meijer and co-workers with a benzene tricarboxamide, in which the presence of the second hydrogen-bond acceptor was critical for back-folding of the OEG side chain.[13] These results combined show that subtle changes in chemical structure strongly influence the hydrogen-bonding motif and its properties.

Furthermore, by correlating the amido NH chemical shifts with the structure differences between M2/M4 and M3/M5, it was evident that the five-membered ring formed in M2/M4 was more stable than the six-membered ring in M3/M5. The reason for this could be a smaller entropy cost for folding a shorter segment of aliphatic spacer. Additionally, because there is only one methylene unit in the five-membered ring, the torsion strain caused by unfavourable eclipsing or *gauche* interactions of CH bonds[12] is absent in M2 and M4 but present in M3 and M5. This must have greatly stabilised the hydrogen-bonding motif in the former group.

Additionally, the hydrogen bonds in M3 and M5 were found to be more sensitive to steric interference. If the terminal acetylene group was attached to a trimethylsilyl (TMS) group, as in M5-TMS (Figure 1), the resonance of the NH protons was further upfield shifted by approximately 0.5 ppm relative to that of M5, from 8.7 to 8.2 ppm. A similar chemical shift change was recorded between M3 and M3-TMS (spectrum not shown). On the other hand, upon TMS substitution, a much smaller extent of upfield shifting (<0.15 ppm) was displayed by M4-TMS (Figure 1) and M2-TMS (spectrum not shown). Apparently, such upfield shifting evidenced weakening of the intramolecular hydrogen bonds in these monomers. This was considered to be a result of steric repulsion caused by the bulky TMS group. One possible explanation for the larger susceptibility of the hydrogen bonds in M3 and M5 to steric interference could be that the six-membered cyclic hydrogen-bonding motif was intrinsically labile and easier to disrupt (see above). An additional reason might be that, due to the larger ring size, part of the side chain in M3-TMS or M5-TMS was forced to be in closer proximity to the TMS moiety, and this imposed greater steric strain that resulted in distortion and weakening of the hydrogen bonds. The latter explanation was supported by theoretical calculations simulating the energy-minimised molecular conformation of M5-TMS (Figure S1 in the Supporting Information).

Spectroscopic study of the OPEs in non-polar solvent: In spite of the different chemical shifts observed for the H_a protons in the monomers, all of the amido NH protons in the various oligomers exhibited a similar chemical shift of approximately 9.3 ppm. Such a value suggested that relatively stable hydrogen bonds were formed in all of these oligomers by the amido NH proton. In **1**, unambiguously, the intramolecular hydrogen bonds were formed between the amido NH proton and the ester carbonyl oxygen atom on adjacent phenyl(ene) rings. However, due to the presence of competing hydrogen-bond acceptors (namely the ether oxygen atoms from the side chains), the structure of the hydrogen-bonding motif became equivocal in oligomer series **2**–**5**. That is, although ^{1}H NMR spectroscopy gave explicit evidence for hydrogen-bond formation, it was incapable of identifying the hydrogen-bond acceptor.

Uniquely, UV/Vis absorption spectra provided critical information for the hydrogen-bond structure in the oligomers. In the previous study,[18] we showed that the effective conjugation length of the oligomers was extended by restraining the rotational motion of the phenylene units in the OPE backbone and confining them into a co-planar conformation by virtue of intramolecular hydrogen bonds. This was evidenced by a bathochromic shift of the absorption band, relative to that of analogous OPEs without such intramolecular hydrogen bonds. Shown in Figure 2 are the absorptions of

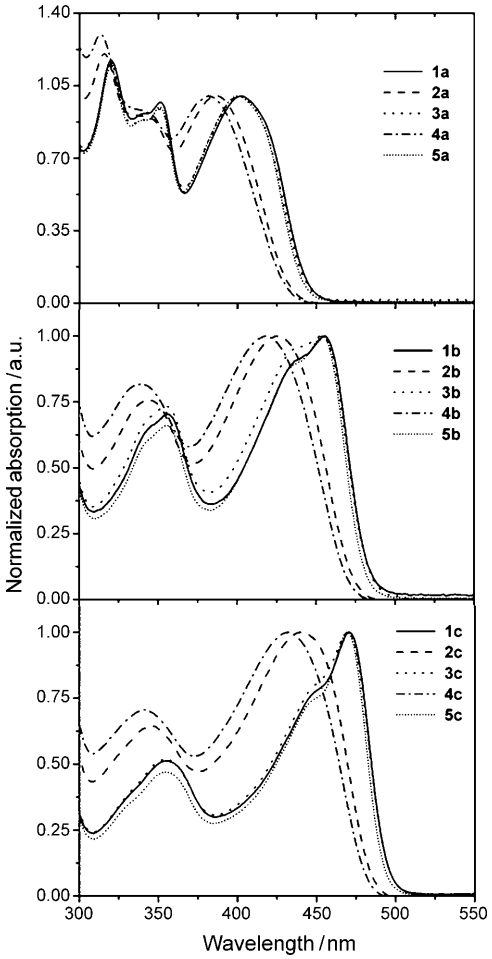


Figure 2. UV/Vis absorption spectra for OPE series **1**–**5** in chloroform.

the newly synthesised oligomer series **2**–**5**, recorded in chloroform, relative to those of series **1**. A trend was discernible from these spectra: at a given chain length, oligomers of series **1**, **3** and **5** displayed very similar absorption energy, whereas series **2** and **4** showed hypsochromically shifted absorption bands. For example, OPEs **1c**, **3c**, and **5c** had nearly identical absorption maxima at approximately 470 nm, but the absorption peaks of **2c** and **4c** were at 440 and 430 nm, respectively. Such an absorption energy difference was also manifested by oligomers of shorter chain lengths. It was also noted that the absorptions of **2** and **4** were very similar to those of OPEs with non-planar conformations (that is, without hydrogen bonds).[19] On the basis of these results, we proposed that the disparate absorption energies reflected different backbone conformations. All of the studied OPEs were categorised into two sets, series **1**, **3** and **5** versus series **2** and **4**, depending on their absorption energy. The former group possessed a co-planar backbone conformation, whereas the latter existed in random, non-planar conformations, like regular OPEs.

Such a hypothesis was substantiated by additional experimental evidence. Series **1**, **3** and **5** generally exhibited higher extinction coefficients than corresponding oligomers of the same chain lengths in series **2** and **4** (Table 1). Moreover, for OPEs containing five or more phenyl(ene) units, distinct absorption band shapes were observed with the two sets of oligomers. Specifically, **1b/c**, **3b/c** and **5b/c** exhibited fine structures in their absorption spectra. By contrast, OPEs **2b/c** and **4b/c** gave broader and more featureless absorption bands. All of these differences indicated that oligomer series **3** and **5** possessed more rigid backbones than those of series **2** and **4**. It can be imagined that, if the rotational motion of the phenylene units were inhibited or suppressed, the OPE backbone would become less flexible. Hence, the absorption-band shape and extinction coefficient served as further evidence for constrained and rigidified backbones in series **1**, **3** and **5**, unlike those in series **2** and **4**.

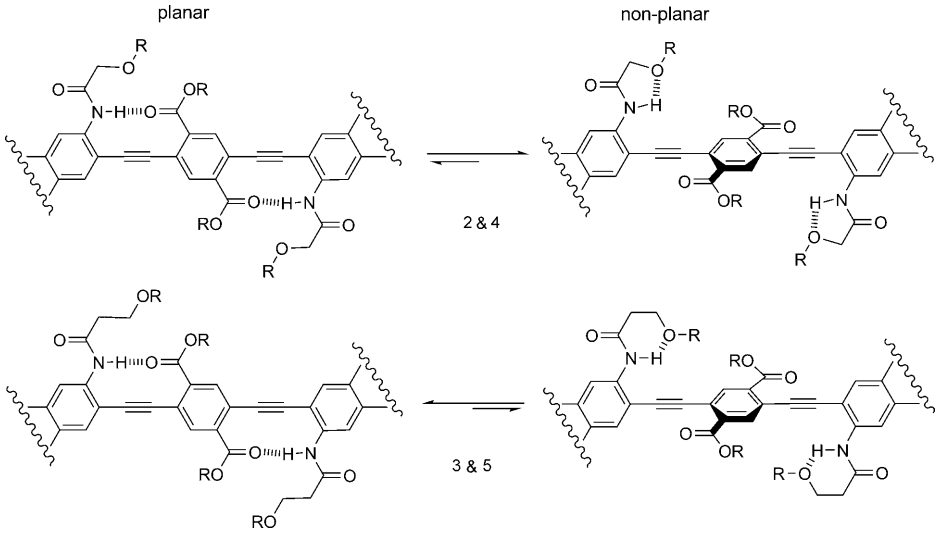
Table 1. Absorption data for the studied OPE oligomers.

Oligomer	λ_{max} [nm] (ε [10^4 $M^{-1}cm^{-1}$])[a]		λ_{max} [nm] (ε [10^4 $M^{-1}cm^{-1}$])[a]		λ_{max} [nm] (ε [10^4 $M^{-1}cm^{-1}$])[a]
1a	402 (2.6)[b]	**1b**	456 (7.1)[b]	**1c**	471 (11)[b]
2a	386 (2.1)	**2b**	425 (6.1)	**2c**	441 (8.3)
3a	401 (3.0)	**3b**	451 (7.5)	**3c**	469 (12)
4a	382 (2.3)	**4b**	417 (6.2)	**4c**	431 (7.3)
5a	401 (3.1)	**5b**	452 (7.7)	**5c**	468 (11)

[a] The precision of the extinction coefficient (ε) was approximately $\pm 15\,\%$. [b] Taken from reference [18].

Additionally, the emission spectra of these OPEs manifested a similar trend to the absorption spectra. Series **1**, **3** and **5** exhibited emission bands of longer wavelengths than series **2** and **4**, for compounds with corresponding chain lengths (Figure S2 in the Supporting Information), which further verified the above proposition that the former series possessed longer effective conjugation lengths than the latter series, consistent with different backbone conformations.

Varied backbone conformations entailed by competitive hydrogen-bonding motifs: By correlating the oligomer backbone conformations, inferred from optical spectra, with the intramolecular hydrogen-bond stability, characterised by ^{1}H NMR spectroscopy, a legitimate rationale for the experimental observations was reached. In the oligomers **2**–**5**, the ester carbonyl groups competed with ether oxygen atoms in the side chains as hydrogen-bond acceptors. Hydrogen bonds among neighbouring phenylene units existed in OPE series **1**, **3** and **5** and led to the co-planar backbone conformation. On the other hand, such hydrogen bonds must be disrupted in series **2** and **4**, because the backbones were non-planar. But the chemical shifts of the amido NH protons suggested that these protons were also hydrogen-bonded in **2** and **4**. A plausible explanation is that they were bonded to oxygen atoms in the side chains, rather than to the carbonyl groups. Essentially, the results indicated that the intramolecular hydrogen bonds formed by the amido NH proton and the ester carbonyl oxygen atom were of intermediate stability, between those of the five- and six-membered cyclic hydrogen-bonding motifs formed within the side chains (Scheme 3). Different combinations of hydro-



Scheme 3. Illustration of different OPE backbone conformations controlled by competitive intramolecular hydrogen bonds.

gen-bond donors and acceptors brought about varied bonding motifs, backbone conformations, and spectroscopic features.

UV/Vis study and backbone conformation analyses in polar protic solvent: All of the aforementioned absorption spectra were recorded in the non-polar solvent chloroform, which is non-disruptive to hydrogen bonds. Subsequently, we carried out a study interrogating the hydrogen-bond stability, as well as the backbone conformation, in a polar protic solvent that may interfere with the intramolecular hydrogen bonds. Methanol was chosen for the experiment because of its potent capability to form hydrogen bonds, both as a donor and acceptor. It was considered that, because the longer OPEs contained a larger number of intramolecular hydrogen bonds, their backbone conformation should be more sensitive to solvent perturbation. Therefore, the investigation was focused on oligomer series **c**. As expected, the Tg side chains afforded adequate solubility for oligomers **2c** and **3c** in methanol. A comparison of the UV/Vis spectra recorded in chloroform and methanol revealed the following results. For both **2c** and **3c**, a minor wavelength difference was displayed between the spectra measured in the two different solvents (Figure 3). This difference was attributed to the solvent-polarity effect. Particularly for oligomer **3c**, which adopted a co-planar conformation in chloroform, if methanol molecules had broken up any of the hydrogen bonds between the phenylene units, the effective conjugation length of the oligomer would be shortened, which would cause a blueshift in the absorption spectrum. If most or all of the intramolecular hydrogen bonds were disrupted in **3c**, the oligomer should exist with a non-planar backbone conformation and hence would exhibit an absorption spectrum similar to that of OPE **2c**. However, the experiment showed that the evident wavelength difference persisted between the absorption maxima of **2c** and **3c** in methanol. The fact that the absorptions of **3c** in chloroform and methanol were of similar energy indicated that this oligomer retained the co-planar conformation in the polar protic solvent, which implies that the hydrogen bonds were reserved among the phenylene units. A slight broadening and tailing effect observed for the absorption of **3c** in methanol suggested the occurrence of minor intermolecular aggregation of this molecule at a concentration of $<10^{-5}$ M, whereas no evidence for intermolecular aggregation was detected for **2c** at a similar concentration. This stronger tendency for self-association also corroborated the theory of a rigid, planar backbone structure in **3c**.

Only a short ethylene linker, rather than a long, nonpolar alkylene segment, was incorporated between the hydrogen-bonding motif and Tg side chains in **3c**, so diffusion of methanol molecules to the vicinity of the hydrogen bonds should not be difficult. Hence, the shielding effect of a nonpolar local environment cannot be the reason for the failure of methanol to break up the intramolecular hydrogen bonds.[10] It may thus be concluded that the intrinsic stability of the intramolecular hydrogen bonds in **3c** sufficed for resisting interference from the solvent molecules. As the five-membered cyclic hydrogen-bonding motif was proven to be even more robust, it is therefore reasonable to infer that the

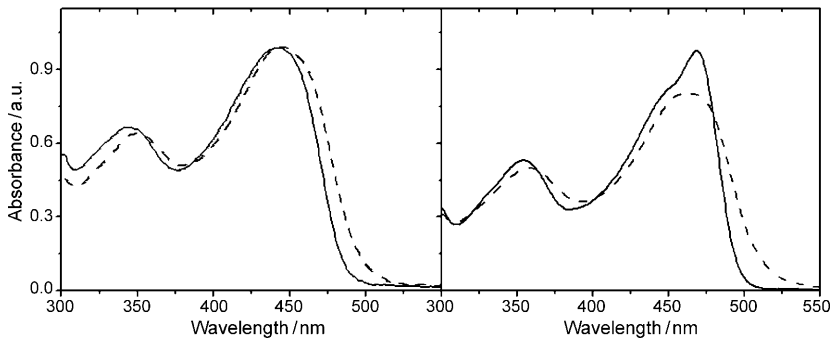


Figure 3. UV/Vis absorption spectra of **2c** (left) and **3c** (right) in chloroform (solid lines) and methanol (dashed lines).

intramolecular hydrogen bonds in **2c** were not disrupted by methanol either.

Conclusion

By designing and implementing competitive intramolecular hydrogen bonds, conjugated OPEs with controlled backbone conformations, either co-planar or random, were achieved. Additionally, the specific structure and stability of the hydrogen-bonding motifs involving back-folded OEG side chains were elucidated.

This was realised by incorporating two types of intramolecular hydrogen bonds into the OPEs. One of them was placed between adjacent phenyl(ene) units in the OPE backbone. When such hydrogen bonds were formed, all of the phenylene units in the OPE were constrained into a co-planar conformation. The other type existed within the side chains of the bisamidophenylene rings and did not entail the co-planar conformation. The two motifs demanded the same set of amido NH protons as the hydrogen-bond donors. Therefore, they were in competition and only one of them could be formed in the oligomers. Ester carbonyl groups on alternative phenylene units acted as acceptors in the first type of hydrogen bonds. Ether oxygen atoms in side chains attached to the amido groups served as the second type of acceptors. Depending on the length of the alkylene linker between the amido NH donor and ether oxygen acceptor in the side chain, either five- or six-membered rings were formed with the second type of hydrogen bonds. The experimental results showed that, in the studied OPEs, the five-membered cyclic hydrogen-bonding motif formed by the back-folded side chain was the most stable, whereas the six-membered analogue was rather labile. Hydrogen bonds formed between phenylene units by the ester carbonyl oxygen atom and the amido NH proton were of intermediate strength. Such a relative stability order allowed control over the OPE backbone conformation. The hydrogen bonds among phenylene rings were either disrupted, if they competed with five-membered-ring hydrogen bonds in the side chains, or they could be maintained, in which case the six-membered-ring hydrogen bonds within side chains yielded. Even in the protic solvent methanol, the intramolecular hydrogen bonds among phenylene units and those of five-membered cyclic structures were preserved. As the relative orientation of the phenylene units in the OPEs was governed by these hydrogen bonds, different backbone conformations were exhibited, either co-planar or random, depending on the side-chain structure.

More structural information regarding the hydrogen-bonding motif involving back-folded OEG side chains was acquired from the current study. It was uncovered that a single hydrogen-bond acceptor was sufficient to effect back-folding of the side chain; the additional oxygen atoms in the OEG unit did not improve the hydrogen-bond stability. No direct evidence for bifurcated hydrogen bonds was obtained. This was different from an independently studied hydrogen bond that also involved back-folded OEG chains.[13] The combined results thus implied that subtle structural variations may completely alter the hydrogen-bonding motif and its properties.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (project nos. 20774005 and 51073002), the Ministry of Science and Technology of China (no. 2011CB606106) and the Fok Ying-Tung Educational Foundation (no. 114008).

[1] a) L. Brunsveld, B. J. B. Folmer, *Chem. Rev.* **2001**, *101*, 4071–4097; b) A. W. Bosman, R. P. Sijbesma, E. W. Meijer, *Mater. Today* **2004**, *7*(4), 34–39; c) W. H. Binder, R. Zirbs, *Adv. Polym. Sci.* **2007**, *207*, 1–78; d) L. Bouteiller, *Adv. Polym. Sci.* **2007**, *207*, 79–112; e) G. ten Brinke, J. Ruokolainen, O. Ikkala, *Adv. Polym. Sci.* **2007**, *207*, 113–177; f) A. J. Wilson, *Soft Matter* **2007**, *3*, 409–425; g) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Shenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687–5754; h) W. S. Horne, S. H. Gellman, *Acc. Chem. Res.* **2008**, *41*, 1399–1408; i) J. S. Nowick, *Acc. Chem. Res.* **2008**, *41*, 1319–1330; j) X. Zhao, Z.-T. Li, *Chem. Commun.* **2010**, *46*, 1601–1616.

[2] For recent representative examples, see: a) D. González-Rodríguez, P. G. A. Janssen, R. Martín-Rapún, I. De Cat, S. De Feyter, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2010**, *132*, 4710–4719; b) O. Khakshoor, A. J. Lin, T. P. Korman, M. R. Sawaya, S.-C. Tsai, D. Eisenberg, J. S. Nowick, *J. Am. Chem. Soc.* **2010**, *132*, 11622–11628; c) S. H. Choi, I. A. Guzei, L. C. Spencer, S. H. Gellman, *J. Am. Chem. Soc.* **2010**, *132*, 13879–13885; d) B. Isare, M. Linares, L. Zargarian, S. Fermandjian, M. Miura, S. Motohashi, N. Vanthuyne, R. Lazzaroni, L. Bouteiller, *Chem. Eur. J.* **2010**, *16*, 173–177; e) Y. Chen, Z. Guan, *J. Am. Chem. Soc.* **2010**, *132*, 4577–4579; f) P. J. M. Stals, M. M. J. Smulders, R. Martín-Rapún, A. R. A. Palmans, E. W. Meijer, *Chem. Eur. J.* **2009**, *15*, 2071–2080; g) H. Shao, T. Nguyen, N. C. Romano, D. A. Modarelli, J. R. Parquette, *J. Am. Chem. Soc.* **2009**, *131*, 16374–16376; h) A. Ciesielski, G. Schaeffer, A. Petitjean, J.-M. Lehn, P. Samori, *Angew. Chem.* **2009**, *121*, 2073–2077; *Angew. Chem. Int. Ed.* **2009**, *48*, 2039–2043; i) S. Mahesh, R. Thirumalai, S. Yagai, A. Kitamurab, A. Ajayaghosh, *Chem. Commun.* **2009**, 5984–5986; j) J. J. Mousseau, L. Xing, N. Tang, L. A. Cuccia, *Chem. Eur. J.* **2009**, *15*, 10030–10038; k) W. Feng, K. Yamato, L. Yang, J. S. Ferguson, L. Zhong, S. Zou, L. Yuan, X. C. Zeng, B. Gong, *J. Am. Chem. Soc.* **2009**, *131*, 2629–2637; l) X.-N. Xu, L. Wang, Z.-T. Li, *Chem. Commun.* **2009**, 6634–6636; m) S. Yagai, S. Hamamura, H. Wang, V. Stepanenko, T. Seki, K. Unoike, Y. Kikkaw, T. Karatsu, A. Kitamura, F. Würthner, *Org. Biomol. Chem.* **2009**, *7*, 3926–3929.

[3] a) J. H. K. K. Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma, E. W. Meijer, *Nature* **2000**, *407*, 167–170; b) R. W. Sinkeldam, M. H. C. J. van Houtem, K. Pieterse, J. A. J. M. Vekemans, E. W. Meijer, *Chem. Eur. J.* **2006**, *12*, 6129–6137.

[4] V. G. H. Lafitte, A. E. Aliev, P. N. Horton, M. B. Hursthouse, K. Bala, P. Golding, H. C. Hailes, *J. Am. Chem. Soc.* **2006**, *128*, 6544–6545.

[5] P. G. A. Janssen, A. Ruiz-Carretero, D. González-Rodríguez, E. W. Meijer, A. P. H. J. Shenning, *Angew. Chem.* **2009**, *121*, 8247–8250; *Angew. Chem. Int. Ed.* **2009**, *48*, 8103–8106.

[6] Y.-X. Xu, G.-T. Wang, X. Zhao, X.-K. Jiang, Z.-T. Li, *Langmuir* **2009**, *25*, 2684–2688.

[7] A. L. Hofacker, J. R. Parquette, *Angew. Chem.* **2005**, *117*, 1077–1081; *Angew. Chem. Int. Ed.* **2005**, *44*, 1053–1057.

[8] S. Nygaard, C. N. Hansen, J. O. Jeppesen, *J. Org. Chem.* **2007**, *72*, 1617–1626.

[9] E. Obert, M. Bellot, L. Bouteiller, F. Andrioletti, C. Lehen-Ferrenbach, F. Boue, *J. Am. Chem. Soc.* **2007**, *129*, 15601–15605.
[10] I. Yoshikawa, J. Sawayama, K. Araki, *Angew. Chem.* **2008**, *120*, 1054–1057; *Angew. Chem. Int. Ed.* **2008**, *47*, 1038–1041.
[11] T. F. A. de Greef, M. M. L. Nieuwenhuizen, P. J. M. Stals, C. F. C. Fitié, A. R. A. Palmans, R. P. Sijbesma, E. W. Meijer, *Chem. Commun.* **2008**, 4306–4308.
[12] T. F. A. de Greef, M. M. L. Nieuwenhuizen, R. P. Sijbesma, E. W. Meijer, *J. Org. Chem.* **2010**, *75*, 598–610.
[13] P. J. M. Stals, J. F. Haveman, R. Martín-Rapún, C. F. C. Fitié, A. R. A. Palmans, E. W. Meijer, *J. Mater. Chem.* **2009**, *19*, 124–130.
[14] a) J. M. Tour, *Chem. Rev.* **1996**, *96*, 537–554; b) U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605–1644; c) U. H. F. Bunz, *Adv. Polym. Sci.* **2005**, *177*, 1–52.
[15] For recent examples of studies on OPEs and derivatives as molecular conductors, see: a) J. Terao, Y. Tanaka, S. Tsuda, N. Kambe, M. Taniguchi, T. Kawai, A. Saeki, S. Seki, *J. Am. Chem. Soc.* **2009**, *131*, 18046–18047; b) Z. Ng, K. P. Loh, L. Li, P. Ho, P. Bai, J. H. K. Yip, *ACS Nano* **2009**, *3*, 2103–2114; c) X. Chen, Y.-M. Jeon, J.-W. Jang, L. Qin, F. Huo, W. Wei, C. A. Mirkin, J. Am. Chem. Soc. 2008, 130, 8166–8168; d) R. Huber, M. T. González, S. Wu, M. Langer, S. Grunder, V. Horhoiu, M. Mayor, M. R. Bryce, C. Wang, R. Jitchati, C. Schönenberger, M. Calame, J. Am. Chem. Soc. 2008, 130, 1080–1084; e) A. M. Moore, B. A. Mantooth, Z. J. Donhauser, Y. Yao, J. M. Tour, P. S. Weiss, *J. Am. Chem. Soc.* **2007**, *129*, 10352–10353; f) S. Yeganeh, M. Galperin, M. A. Ratner, *J. Am. Chem. Soc.* **2007**, *129*, 13313–13320; g) C. Wang, A. Batsanov, M. R. Bryce, G. J. Ashwell, B. Urasinska, I. Grace, C. J. Lambert, *Nanotechnology* **2007**, *18*, 044005.
[16] J. M. Seminario, P. A. Derosa, *J. Am. Chem. Soc.* **2001**, *123*, 12418–12419.
[17] K. Okuyama, T. Hasegawa, M. Ito, N. Mikami, *J. Phys. Chem.* **1984**, *88*, 1711–1716.
[18] W. Hu, N. Zhu, W. Tang, D. Zhao, *Org. Lett.* **2008**, *10*, 2669–2672.
[19] A minor difference was observed between spectra of OPEs **2** and **4**, the reason for which is not completely clear so far. A tentative explanation was proposed as follows. Alkyl chains are less flexible than OEG chains and, under the back-folded conformation, this lower flexibility induced more severe steric interactions with the backbone, neighbouring phenylene units and/or side groups and caused an averagely larger dihedral angle among adjacent backbone phenylene units in **4** than in **2**. This brought about the blueshifted absorption of **4**.

Received: December 14, 2010
Revised: January 22, 2011
Published online: May 9, 2011

