ORGANIC
LETTERS

2008
Vol. 10, No. 13
2669−2672

Oligo(*p*-phenyleneethynylene)s with Hydrogen-Bonded Coplanar Conformation

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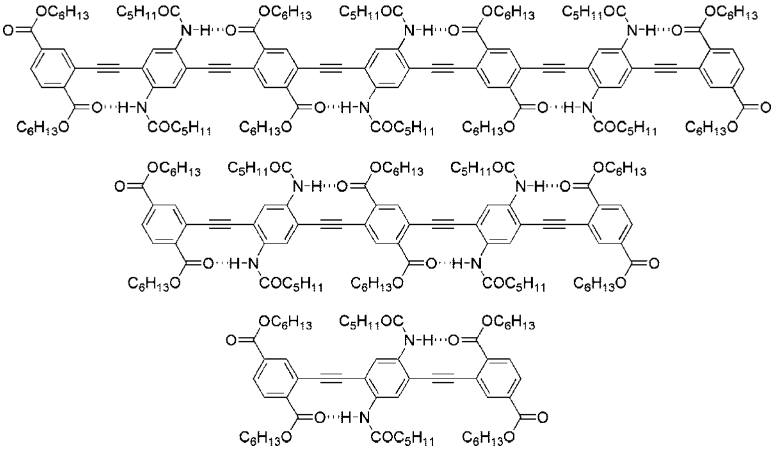
Received April 2, 2008

ABSTRACT



A series of monodispersed oligo(*p*-phenyleneethynylene)s were synthesized bearing intramolecular hydrogen bonds between side chains of adjacent phenylene units in the backbone. Thus, all repeating units of the molecules are constrained in a coplanar orientation. Such planarized conformation is considered favorable for single-molecule conductance. Photophysical characterization results show narrowed bandgaps and extended conjugation lengths, consistent with a rigid, planar backbone framework as a result of intramolecular hydrogen bonding.

Polymeric and oligomeric phenyleneethynylenes (PPEs and OPEs)[1] are a family of conjugated molecules that are highly diversified in structure and have found a range of applications in optoelectronics,[2] sensors,[3] supramolecular architecture constructions,[4] etc. More recently, with increased attention devoted to molecular and nanoscale electronics, OPEs are also intensively studied as promising molecular wire candidates due to their optimal electrical conducting properties.[5] However, although OPEs possess desirable backbone rigidity, the single bond joining the phenylene and ethynylene units in the molecules displays a low rotational barrier, rendering rapid torsional vibration of the phenylene units at room temperature.[6] Studies have shown that this

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[5] For recent examples of molecular conductance studies on OPEs and derivatives (including single-molecule studies) see: (a) Huber, R.; González, M. T.; Wu, S.; Langer, M.; Grunder, S.; Horhoiu, V.; Mayor, M.; Bryce, M. R.; Wang, C.; Jitchati, R.; Schönenberger, C.; Calame, M. *J. Am. Chem.*

10.1021/ol800753z CCC: $40.75

conformational disorder plays a detrimental role in the electrical conductance of OPEs, since the relative orientation of the phenylene units determines the extent of orbital overlapping and π-electron delocalization along the backbone.[7] By affecting the conjugation length and bandgap, the molecular conformation of the PE backbone inevitably affects the spectroscopic properties and energy migration characteristics along the molecules as well. Additionally, because rigid, planar aromatic structures tend to promote strengthened intermolecular interactions, the self-association behaviors are also influenced by the backbone shape. Effectively, the molecular dynamics of OPE/PPEs imposes critical influence over all their aforementioned applications.

Despite the great importance of the planar conformation of the PE structures, achieving precise control is challenging. Previous strategies employed to constrain or maneuver the relative orientation of the phenylene units in OPE/PPEs involve covalently tethering,[8a−c] implementing surfactant effect at the interface,[8d] increasing structural planarity in nematic liquid crystal solutions,[8e−g] exploiting steric interactions between backbone substituents,[8h] and introducing charges into the molecules.[8i,9] Our current study aimed to sythesize a series of OPEs with their conformation confined in the coplanar state by intramolecular H-bonds between the side chains of adjacent phenylene units. A side-chain H-bonding motif was previously introduced into *meta*-PE oligomers, conferring a coplanar orientation for the diphenylacetylene moieties.[10] With newly developed synthetic protocols, an analogous design is now implemented in the *para*-PE system. The syntheses of such a series of OPEs **1**−**3** are presented here. Their monodispersed, systematically extended chain lengths were designed to impart information of intramolecular H-bonding effects and facilitate future molecular-wire studies. Photophysical characterization of the oligomers provided evidence for the rigid, planar structures with extended effective conjugation lengths.

The synthetic routes of OPEs **1**−**3** are outlined in Scheme 1. The basic synthetic strategy was to join key intermediate 2,5-diethynyl-1,4-phenylenedihexanamide with (di)iodo-substituted dihexyl terephthalate via repetitive Sonogashira cross-coupling reactions and proper protection/deprotection protocols.[11] The NHs in the bisamide functionality and the carbonyl groups of the terephthalate acted as the H-bonding donor and acceptor, respectively, in the final OPEs. Such H-bonding motif was previously proven to hinder the rotational motion of the phenylene units in *m*-PE systems.[10] As the chain length increased from **1** to **3**, the solubility of the molecules was noted to decrease drastically and OPE **3** was only sparsely soluble in chloroform, the best solvent found.[12] Thus, the purfication of **3** was difficult and strenuous. This decrease in solubility suggested the presence of rigid, planar backbones,[13] which enhanced intermolecular interactions and self-association.

The formation of intramolecular H-bonds in OPEs **1**–**3** was confirmed by ^{1}H NMR spectroscopy. In intermediates **6** and **7** (as well as in compound **16**), the amide protons (N*H*) exhibited chemical shifts in the range of 7.8−8.0 ppm in CDCl$_3$, while all the amide protons in oligomers **1**−**3** displayed chemical shifts of ca. 9.0−9.2 ppm, indicating intramolecular H-bond formation in the latter. It was hoped that the formation and disruption of these H-bonds could be reversibly controlled by varying the solution temperature or by changing the solvent properties, thereby to study the molecular properties under different conformations. Yet, these intramolecular H-bonds proved to be robust. A minimal chemical shift change was observed with the N*H* proton in CDCl$_3$ by varied-temperature NMR technique ranging from 20 to 60 °C (Figure S1), or by titrating DMSO-d_6 into the CDCl$_3$ solution, indicating preservation of the H-bonds under these conditions.[14]

In order to delineate the effects of H-bonding, compounds

Soc. **2008**, *130*, 1080. (b) Moore, A. M.; Mantooth, B. A.; Donhauser, Z. J.; Yao, Y.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **2007**, *129*, 10352. (c) Yeganeh, S.; Galperin, M.; Ratner, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 13313. (d) Wang, C.; Batsanov, A.; Bryce, M. R.; Ashwell, G. J.; Urasinska, B.; Grace, I.; Lambert, C. J. *Nanotechnology* **2007**, *18*, 1. (e) Guo, X.; Small, J. P.; Klare, J. E.; Wang, Y.; Purewal, M. S.; Tam, I. W.; Hong, B. H.; Caldwell, R.; Huang, L.; O'Brien, S.; Yan, J.; Breslow, R.; Wind, S. J.; Hone, J.; Kim, P.; Nuckolls, C. *Science* **2006**, *311*, 356. (f) Seferos, D. S.; Blum, A. S.; Kushmerick, J. G.; Bazan, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 11260. (g) Xiao, X.; Nagahara, L. A.; Rawlett, A. M.; Tao, N. J. *J. Am. Chem. Soc.* **2005**, *127*, 9235.

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(8) (a) Crisp, G. T.; Bubner, T. P. *Tetrahedron* **1997**, *53*, 11899. (b) McFarland, S. A.; Finney, N. S. *J. Am. Chem. Soc.* **2002**, *124*, 1178. (c) Brizius, G.; Billingsley, K.; Smith, M. D.; Bunz, U. H. F. *Org. Lett.* **2003**, *5*, 3951. (d) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030. (e) Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 9670. (f) Nesterov, E. E.; Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 10083. (g) Ohira, A.; Swager, T. M. *Macromolecules* **2007**, *40*, 19. (h) Yang, J.-S.; Yan, J.-L.; Hwang, C.-Y.; Chiou, S.-Y.; Liau, K.-L.; Tsai, H.-H. G.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2006**, *128*, 14109. (i) Terashima, T.; Nakashima, T.; Kawai, T. *Org. Lett.* **2007**, *9*, 4195.

(9) Extensive efforts have also been made at attaining planar structures in oligo- and polyphenylenes; for examples of laddered polyphenylenes and derivatives, see: (a) Grimsdale, A. C.; Müllen, K. *Macromol. Rapid Commun.* **2007**, *28*, 1676. (b) Tour, J. M. *J. Org. Chem.* **2007**, *72*, 7477. For conformational control via noncovalent interactions, see: (c) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 8717. (d) Vetrichelvan, M.; Valiyaveettil, S. *Chem.−Eur. J.* **2005**, *11*, 5889.

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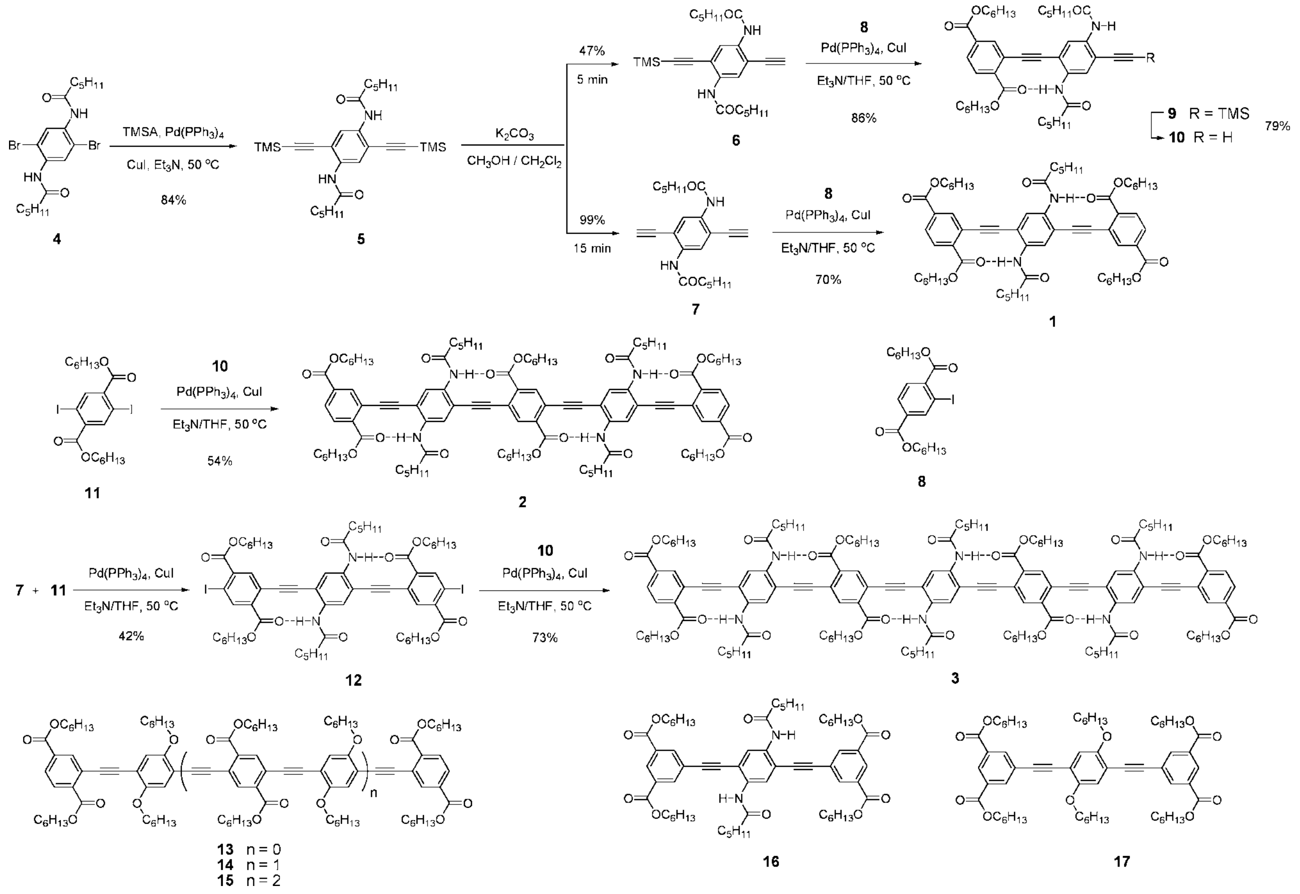
(11) By carefully controlling the amount of potassium carbonate and the reaction time, selectively cleaving one or both of the TMS groups in **5** can be achieved under respectively optimized conditions.

(12) OPEs **1**−**3** all have terephthalate as terminal units. Oligomers having phenylenedihexanamide as terminal units had very low solubility in common organic solvents or simply failed to be synthesized in a purified form due to extremely low solubilities. Such low solubilities likely resulted from intermolecular H-bonding formed by terminal amide groups not engaged in intramolecular H-bonding.

(13) Similar solubility was observed among oligomers **13**−**15**, confirming the solubility change in **1**−**3** is a result from planarization of the aromatic backbone, rather than merely from the chain extension.

(14) The chemical shift of H-bonded N*H* only changed by ca. 0.09 ppm as the temperature increased from 20 to 60 °C, compared to a 0.05 ppm shift for non-hydrogen bonded N*H* proton and ca. 0.02 ppm shift for aromatic protons. No significant chemical shift change was observed when

Scheme 1. Syntheses of Intramolecularly H-Bonded OPE **1**−**3** and Structures of Analogous Compounds without H-Bonds



13−**17** were subsequently synthesized as analogues of **1**−**3** without H-bonds for comparison studies. Oligomers **13**−**15** have identical chain lengths with **1**−**3**, respectively, but the amide side chains were replaced with alkoxy groups. Thus, intramolecular H-bonds were removed in **13**−**15**, while the electronic properties maintained comparable with those of **1**−**3**. Compound **16** has a similar structure with OPE **1**, except that the terephthalates were replaced with isophthalates, resulting in removal of the intramolecular H-bonds. Molecule **17** is a control molecule with two isophthalate terminal units and a dialkoxyphenylene in the middle. As the stretching modes of N−H and C═O bonds are sensitive to H-bonding, supportive evidence for intramolecular H-bonds in OPE **1**−**3** was given by IR spectroscopy, although it was complicated by the intermolecular H-bond formation in **16** under conditions for recording IR spectra (see the Supporting Information for details).

Subsequently, the photophysical properties of OPEs **1**−**3** and **13**−**17** were systematically examined to investigate the effect of H-bonds on the conformational charateristics depicted by the molecular spectroscopic features. As shown by the UV−vis absorption spectra in Figure 1, compound **17** has an absorption peak at 372 nm and **16** at 364 nm. Also, in this case by switching from dialkoxy to diamide group, the onset of the absorption band was blue-shifted. However, the opposite trend was observed in **1** and **13** upon an analogous functionality change. The absorption band of **1** was noticeably red-shifted relative to that of **13**. This difference in spectroscopy change was therefore reasonably attributed to another structural disparity between OPEs **1** and **13**, i.e., the intramolecular H-bonds in **1**. As the optical

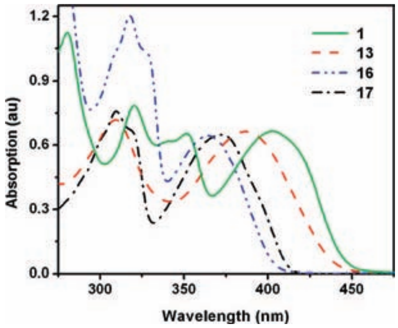


Figure 1. UV−vis absorption spectra of **1**, **13**, **16**, and **17**, normalized based on the longest-wavelength absorption maxima.

DMSO-d_6 was titrated into the $CDCl_3$ solution of **1** up to 15 vol%; high volume percentage of DMSO or methanol in chloroform solution caused the molecule to self-aggregate, as evidenced by the fluorescence quenching of the system, which would have further stabilized the coplanar conformation and the H-bonds.

spectra reflect the average property of a collective ensemble of a distribution of conformations, this could serve as the evidence supporting that the H-bonds effectively constrained the phenylene rings to adopt more planarized orientations, resulting in a more extended π-electron delocalization.

Next, the absorption and fluorescence emission spectra of **1**−**3** were compared to those of **13**−**15** (Figure 2). It was found that, at all different chain lengths oligomers having intramolecular H-bonds (**1**−**3**) gave rise to absorption and emission peaks of longer wavelengths than those of corresponding oligomers without the H-bonds (**13**−**15**). Again, such a red-shifting trend substantiated the hypothesis that H-bonds may help planarize the backbone framework and extend the effective conjugation length. It was also noted that at given chain length the extent of red-shifting was more pronounced in the absorption spectra than in the emission spectra. It is reasonable that the H-bonds appear to be more effective in planarizing the ground-state structures. For those oligomers without H-bonds the equilibrium geometry of the lowest excited state, from which fluorescence originates, possibly has a more planarized structure than the average of disorded ground-state conformations. Thus, the red-shifting is to a less extent in the fluorescence spectra. The magnitudes of Stokes' shift provided further evidence for the backbone rigidity of **1**−**3**. Flexible molecules tend to undergo energy-dissipating internal conversions prior to fluorescent decay and thus typically possess larger Stokes' shifts. Here, OPEs **1**−**3** consistently exhibit smaller Stokes' shifts than corresponding **13**−**15**, presumably due to H-bonding entailed structural rigidity. For example, a rather small Stokes' shift of 1191 cm^{-1} was observed for **3**, as compared to a shift of 2681 cm^{-1} for **15** (Table 1). All the above evidence supported the argument that the intramolecular H-bonds effectively reduced the torsional motion of the phenylene rings in **1**−**3**, rendering more rigid and planar conformation.

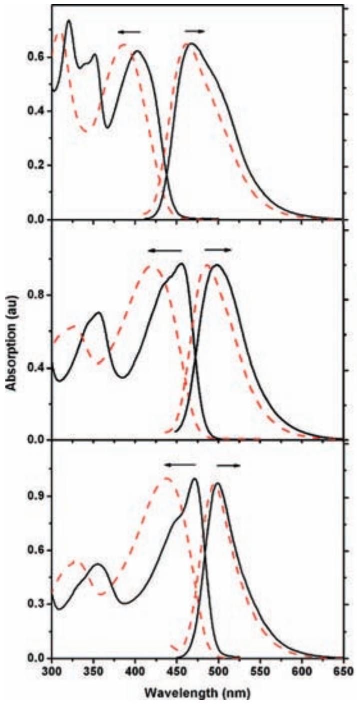


Figure 2. UV−vis absorption and fluorescence spectra of OPEs **1** (upper, solid), **2** (middle, solid), **3** (bottom, solid), **13** (upper, dashed), **14** (middle, dashed), and **15** (bottom, dashed), normalized based on λ_{ab} or λ_{em} in Table 1.

Table 1. Photophysical Characterizations of the OPEs

compounds	λ_{ab}/nm^{a} (ε/10^{4}M^{-1}cm^{-1})^{b}	λ_{em}/nm^{c}	($\lvert\lambda_{em}-\lambda_{ab}\rvert$)/nm (/cm^{-1})
1	402 (2.6)	468	66 (3508)
2	456 (7.1)	499	43 (1890)
3	471 (11)	499	28 (1191)
13	387 (2.6)	461	74 (4148)
14	419 (6.2)	486	67 (3290)
15	437 (10)	495	58 (2681)
16	364 (2.5)	420	56 (3663)
17	372 (3.2)	416	44 (2843)

[a] Absorption maximum of the longest-wavelength. [b] Extinction coefficient of λ_{ab}. [c] Emission maximum wavelengths.

In conclusion, a series of OPEs with repeating units intramolecularly H-bonded into coplanar conformation are synthesized. These OPEs will be further functionalized and studied, e.g., regarding their molecular conducting properties. As these planar conjugated structures demonstrated enhanced self-association tendency, the system will also be modified to explore their features and functions within ordered supramolecular architectures.

Acknowledgment. This work is supported by the National Natural Science Foundation of China (No. 20774005 and 50603001), the Ministry of Science and Technology of China (No. 2006CB921600), and Peking University.

Supporting Information Available: Synthetic procedures and characterization data of the oligomers, including the quantum yield information and discussion of IR spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org

OL800753Z