

One-Pot Synthesis of Well-Defined Oligo- Butadiynylene-Naphthalene Diimides

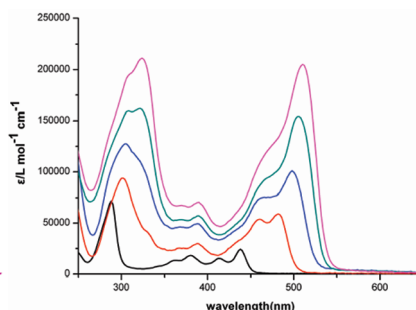
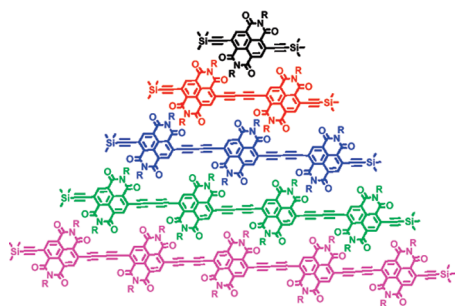
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Received June 3, 2010

ABSTRACT



A homogeneous series of well-defined oligo-butadiynylene-NDIs containing up to five naphthalene diimides (NDIs) moieties have been efficiently synthesized in one pot by oxidative homocoupling of 1,6-di((trimethylsilyl)ethynyl)naphthalene diimides in good yields.

Functional π -conjugated organic systems have attracted considerable attention in recent years, as they have potential applications in the emerging areas of molecular electronics and nanotechnology.¹ Of these conjugated systems, molecular wires are especially important and pave the way for the single-molecule devices.²

Molecular wires with ethynylenes have gained particular interest from experimental and theoretical viewpoints.³ However, butadiynylene aromatic systems, with the generic structure

(aryl-C \equiv C-C \equiv C-)_n, have rarely been explored.⁴ They are not only potential attractive substances for molecular wires but also can undergo topochemical reactions upon UV-irradiation or thermal-stimuli, leading unique butadiynylene supramolecules to potential chemosensors and photonic materials.⁵

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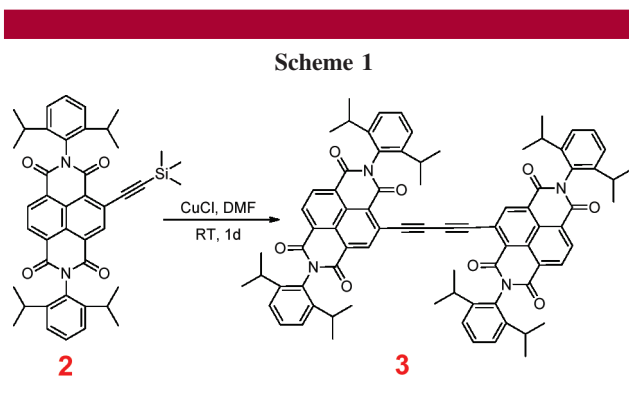
Generally, the synthesis of the molecular wires by traditional stepwise approaches or improved iterative divergent/convergent methods requires a long and repetitious processes. For example, the trimethylsilyl group is often employed as a protective group for the preparation of a substrate for the consequent Sonogashira or Glaser reaction, which is carried out after deprotection of the silyl group.⁶ Thereby the straightforward synthesis of these kinds of molecular wires became very significant.

Owing to their neutral, planar, chemically robust, redox-active, and electron-deficient properties, naphthalene diimides (NDIs) have been used extensively in supramolecular chemistry,⁷ electron-transfer systems,⁸ DNA sensors,⁹ and n-type organic field effect transistors (OFETs).¹⁰ The chemical modification of the NDIs can be achieved by two different methods. One is to introduce substituents at the N atoms of imide groups, and the other is functionalization of NDIs by core substitution; however, only substitution on the core will cause a significant effect on the optical and redox properties.¹¹

Herein we report the one-pot synthesis of a homologous series of soluble and linearly conjugated butadiynylene-NDI oligomers containing up to five naphthalene moieties by direct functionalization of 1,6-di((trimethylsilyl)ethynyl)-NDIs under extremely mild conditions. Moreover, the availability of a well-defined series of butadiynylene-NDIs allows us to assess the extent of electron delocalization along the backbone by comparing their optical spectra.

Initially, 1-bromonaphthalene diimides and 1,6-dibromonaphthalene diimides were synthesized following a known procedure.¹² Stille cross-coupling of bromo-NDIs with tributyl[(trimethylsilyl)ethynyl]stannane in the presence of Pd(PPh₃)₄ as a catalyst in toluene afforded the trimethylsilylethynyl-NDIs **2** and 1,6-di((trimethylsilyl)ethynyl)-NDIs

4.¹³ Subsequently, compound **2** was chosen as a model substrate to undergo homocoupling with a stoichiometric amount of CuCl in *N,N*-dimethylformamide (DMF) at room temperature¹⁴ to directly give corresponding symmetrical butadiynylene-NDIs in good yield (70%, 25% starting material can be recovered; Scheme 1).



The UV-vis spectra of unsubstituted compound **1** (*N,N'*-bis(2,6-diisopropylphenyl)-1,4,5,8-naphthalenetetracarboxylic acid diimides), **2**, and **3** in THF were shown in Figure 1;

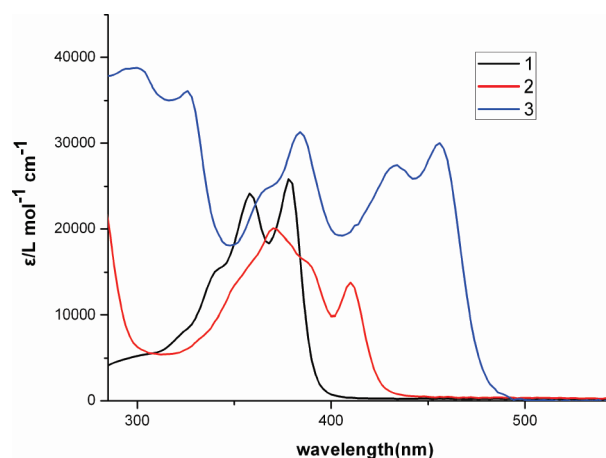


Figure 1. UV-vis absorption spectra of compounds **1** (unsubstituted NDI), **2**, and **3** in THF at room temperature.

in contrast with the white compound **1**, the maximum absorption of **2** is bathochromically shifted from 378 to 410 nm. Compared to compound **2**, the butadiynylene-NDI **3** causes a larger shift of about 46 nm, as a reflection of the extended conjugation length.¹⁵

The redox properties of compounds **1**, **2**, and **3** were studied by cyclic voltammogram in dichloromethane (in V vs Ag/

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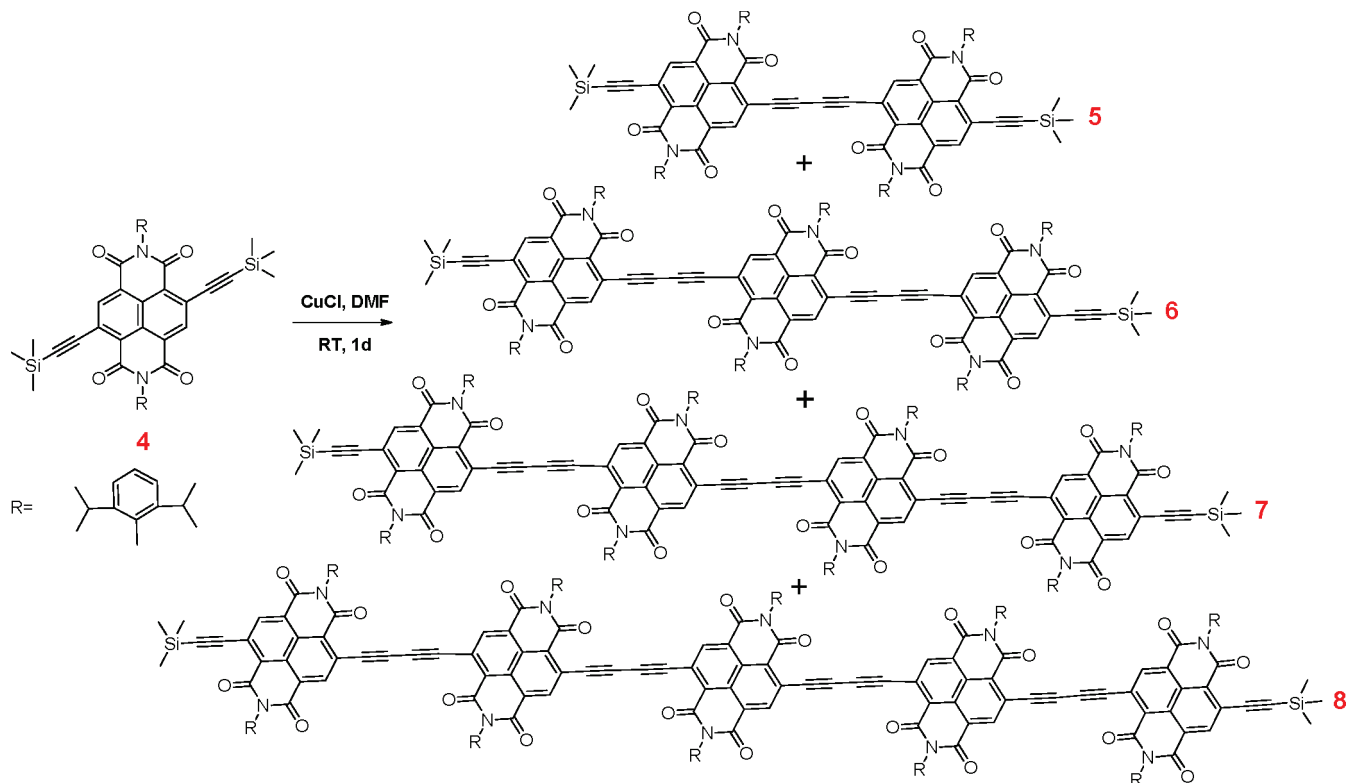
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Scheme 2



AgCl, see the Supporting Information). Compounds **1** and **2** showed two well-separated reversible reduction waves. Compared with NDI **1** (−0.58 and −1.15 V), the reduction potentials of NDI **2** (−0.52 and −1.06 V) are less negative, which can be attributed to an extension of the LUMO orbitals by the introduction of the ethynyl substituents. For NDI **3**, the second reduction waves were split into two waves (−0.40, −0.90, and −1.02 V), indicating the substantial electronic interaction between the two NDIs through the butadiynylene spacer.¹⁶

We then anticipated that 1,6-dibromo-NDIs would be used as a building block of larger butadiynylene-NDI arrays. Thus, we examined the homocoupling of compound **4** under the same conditions (Scheme 2). As expected, the 1,6-dibromo-NDIs gave directly corresponding homogeneous symmetrical butadiynylene-NDIs (Scheme 2) in good yields: **5** (32%), **6** (25%), **7** (16%), and **8** (7%). These novel oligomers could be further endowed with terminal functionality suitable for molecular wires, or attractive precursors of butadiynylene monomers to form a unique poly-butadiynylene structure.

The availability of the series of poly-butadiynylene-NDIs oligomers gives us the opportunity to assess the extent of electron delocalization along the backbone by comparing their optical spectra. The solution UV–vis absorption spectra of these homogeneous oligomers with different length units in THF are shown in Figure 2; various butadiynylene-NDIs showed broad and well-defined absorption bands that shifted bathochromically¹⁷ with the increasing number of NDI units with the longest maximum at 438, 482, 498, 506, and 510

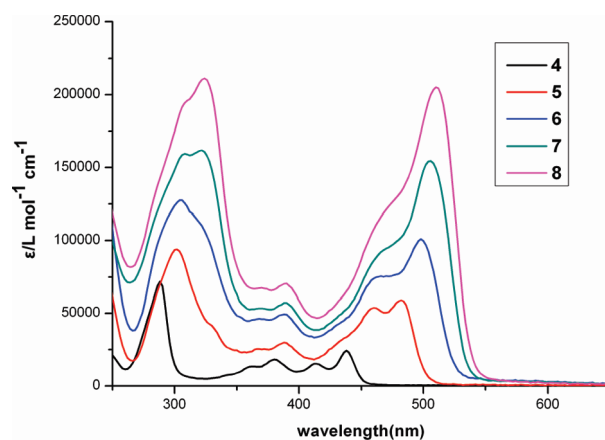


Figure 2. UV–vis absorption spectra of compounds **4**, **5**, **6**, **7**, and **8** in THF at room temperature.

nm for **4**, **5**, **6**, **7**, and **8**, respectively, as a reflection of extended conjugation length of the NDI core. However, the bathochromic shifts were not linearly proportional to the enlargement of the molecular length; the interval value of the bathochromic shifts (44, 16, 8, 4 nm) reveals that an effective conjugation length approaches saturation.¹⁸ The molar extinction coefficients of various oligo-butadiynylene-

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NDIs exhibited an approximate linear increase with the increasing number of NDI units (about 40000–50000 M⁻¹ cm⁻¹ per unit), whereas the fluorescences were too weak to be detected.

In summary, we have successfully synthesized well-defined oligo-butadiynylene-NDIs containing up to five naphthalene moieties in one pot by an efficient strategy of oxidative homocoupling of 1,6-di((trimethylsilyl)ethynyl)-NDIs. Further endowments with terminal functionality suit-

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able for molecular wires and construction of related single molecular devices are currently underway.

Acknowledgment. We thank the National Natural Science Foundation of China, 973 Program (Grant 2006CB932101), Chinese Academy of Sciences, and BASF SE for financial support of this research.

Supporting Information Available: Experimental procedure and characterization of new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL101280E