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

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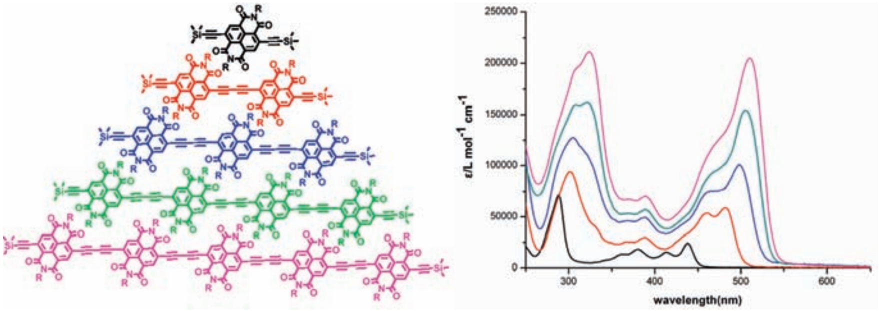
ABSTRACT



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

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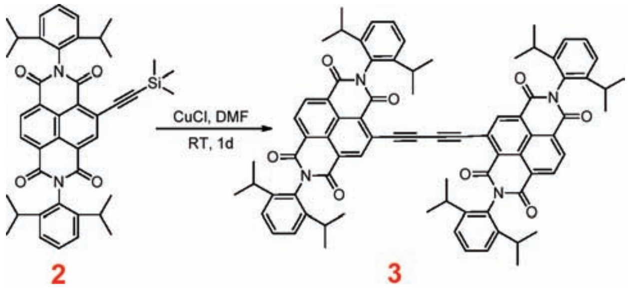
Generally, the synthesis of the molecular wires by traditional stepwise approaches or improved iterative divergent/convergent methods requires a long and repetitious processes. For example, the trimethylsilyl group is often employed as a protective group for the preparation of a substrate for the consequent 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 $Pd(PPh_3)_4$ 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 temperature[14] to directly give corresponding symmetrical butadiynylene-NDIs in good yield (70%, 25% starting material can be recovered; Scheme 1).

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; 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]

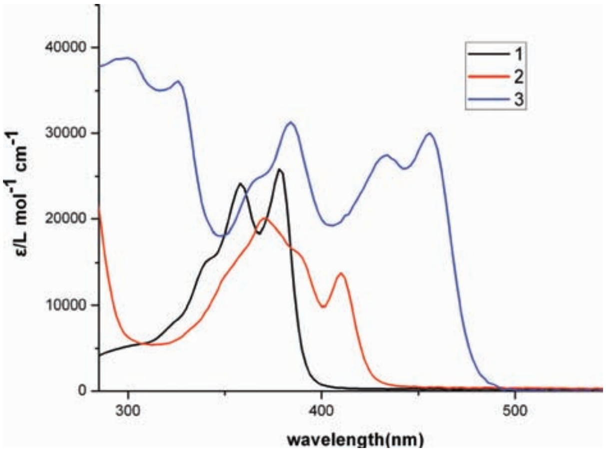


Figure 1. UV−vis absorption spectra of compounds **1** (unsubstituted NDI), **2**, and **3** in THF at room temperatue.

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

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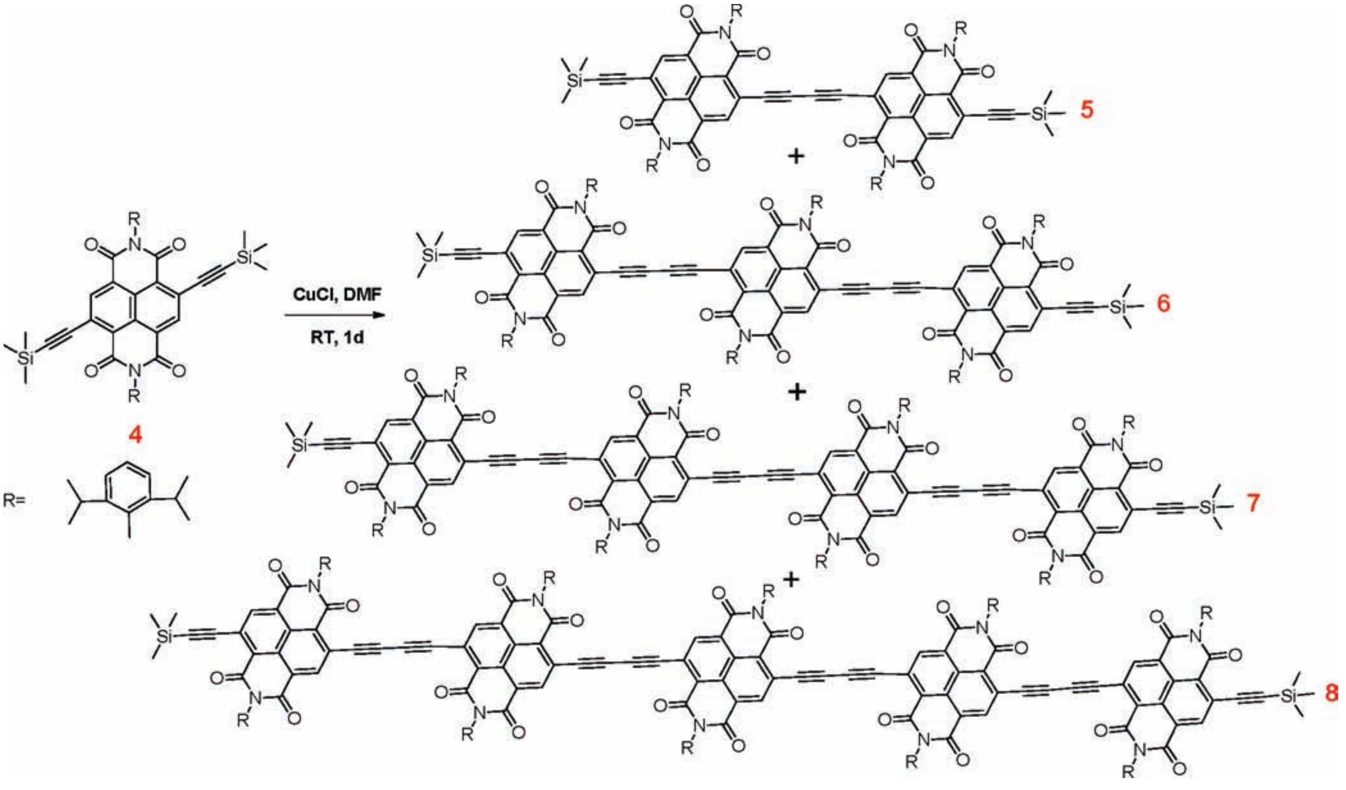
Scheme 2



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 oligomes 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 bathochromically[17] with the increasing number of NDI units with the longest maximum at 438, 482, 498, 506, and 510 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-

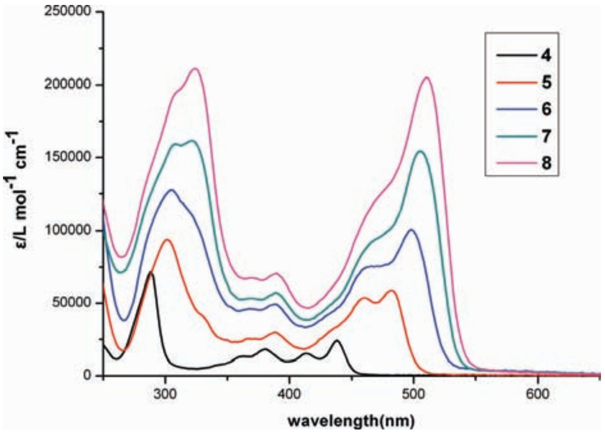


Figure 2. UV−vis absorption spectra of compounds **4**, **5**, **6**, **7**, and **8** in THF at room temperatue.

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

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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.

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