Facile Synthesis of Multifullerene-OPE Hybrids via in Situ Ethynylation

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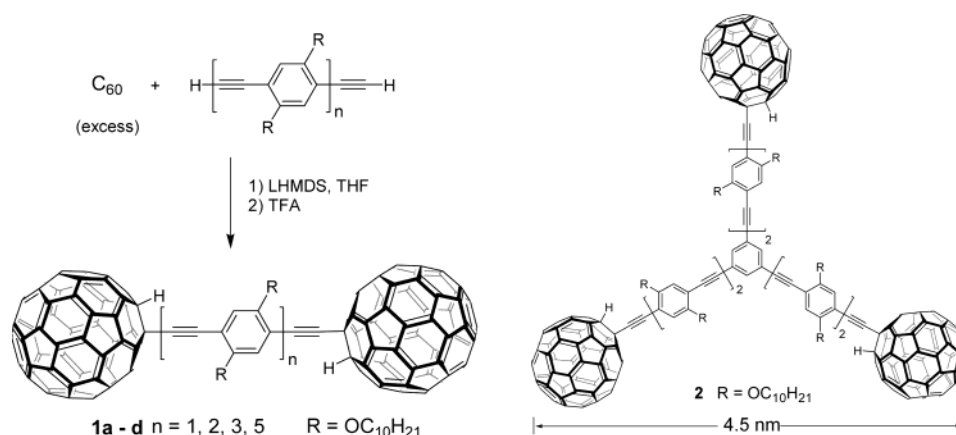
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ABSTRACT

A series of fullerene-terminated oligo(phenylene ethynylene)s (OPEs) (1a–d and 2) have been synthesized and further characterized by cyclic voltammetry (CV) and UV–vis spectroscopy. The key step in the syntheses is an effective one-pot reaction that allows the attachment of C_{60} to multiple terminal alkynes.

Buckminster [60]fullerene is a useful building block for making various molecular devices and nanoarchitectures due to its unique three-dimensional electron delocalization and small diameter (ca. 0.7 nm). So far, most well-defined multiple-fullerene-containing molecules are derived from methanofullerenes,[1] fulleropyrrolidines,[2] fullerene-acenes,[3] and ethynylated fullerenes.[4] Except for the dumbbell-type fullerenes,[4] there are few examples of multifullerene compounds in which fullerene molecules are directly attached via an acetylenic bond in a linear geometry. Lately, integrat-

ing fullerenes as terminal groups in conjugated oligomeric systems has gained attention; however, to our knowledge, the compounds made are limited to primarily mono- or bis-(fullerene) derivatives, and in most cases, the fullerenes are linked to the oligomers through more than one sp^3 carbon and in a nonlinear fashion.[5] In our research, we extended

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Scheme 1
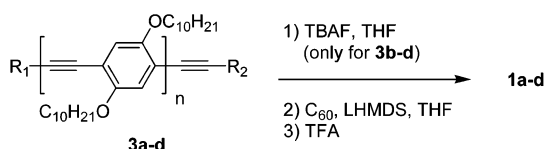
reactant	n	R_1	R_2	product	yield
3a	1	H	H	**1a**	42%
3b	2	TIPS	TMS	**1b**	24%
3c	3	TIPS	TIPS	**1c**	34%
3d	5	TIPS	TIPS	**1d**	60%

Scheme 2

the "fullerene dumbbells" with rigid conjugated oligo-(phenylene ethylene) (OPE) molecular wires, where only one sp^3 carbon is attached to the OPE. The significance of synthesizing **1** and **2** is not only for their interesting architecture but also the production of new candidates for organic photovoltaic devices,[6] third-order nonlinear optical materials,[7] and molecular electronics.[8] Ethynylated fullerenes are generally prepared via a method of lithium acetylide addition as first reported by Komatsu et al.[9] This ethynylation procedure has wide applicability, and a number of acetylene derivatives of C_{60} have been successfully prepared.[4,10] Nonetheless, as the original report claimed,[9] the yield of this type of reaction is highly dependent on experimental conditions.

In our numerous attempts to make multifullerene-OPE derivatives using the above procedure, the reactions gave very low yields of desired product. To overcome this synthetic difficulty, we devised a reproducible and effective approach, namely, an in situ-generated lithium acetylide addition in THF (Scheme 1). Interestingly, in our hands only lithium hexamethyldisilazide (LHMDS) has been found to be efficacious in generating multifullerene species. Many other bases, including n-BuLi, lithium diisopropylamide (LDA), and lithium 2,2,6,6-tetramethylpiperidide (LTMP), either failed to yield products or resulted in diminutive yields.

The reasons for the success of LHMDS are mechanistically unclear; however, LHMDS may first react with the fullerene to form a somewhat more soluble and reactive intermediate.[11] A series of the C_{60}-terminated phenylene ethynylene oligomers **1a−d** have been successfully prepared based on this newly developed methodology (Scheme 1). A general procedure is to treat a well-sonicated mixture of alkyne and excess C_{60} (ca. 2 equiv per terminal alkyne) with LHMDS (ca. 4 equiv) in dry THF and under a nitrogen atmosphere. An indication that the reaction is proceeding is the formation of a deep green-black color. In general, the reaction proceeds smoothly at ambient temperature and is completed within 1 h. Afterward, it is quenched with excess trifluoroacetic acid (TFA) to give a brownish slurry. The crude product is then purified through a silica flash column. In our work, the terminal OPEs were obtained from deprotection of their silyl-protected OPE precursors followed by silica gel purification for **3a** and **4**. The deprotected **3b−d** were pure enough to use without further purification. Our procedure has also been successfully applied to the synthesis of an octupolar tris-(fullerene)-OPE hybrid **2** (Scheme 2). Surprisingly, the yield of **2** was similar to the yields for the bis(fullerene)-OPE hybrids **1a−d**. The preparation of compounds containing higher numbers of fullerene species is presently underway in our laboratories.

The OPE precursors **3a−d** and **4** were prepared by Sonogashira coupling via an iterative synthetic approach as illustrated in Scheme 3. Hydroquinone was alkylated with

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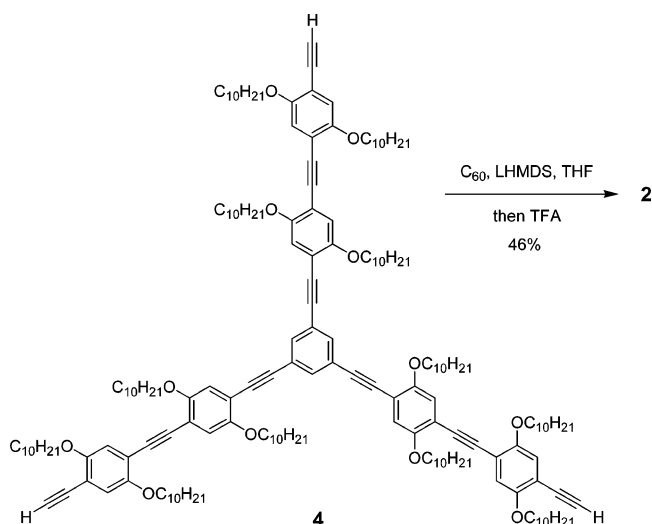
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(11) In a blank test, in which LHMDS was added into a solution of fullerene in THF, we observed a color change (black green) similar to that which occurred in normal fullerene ethynylation reactions. However, so far, efforts to identify the intermediate have not been successful.

Scheme 3 [a]
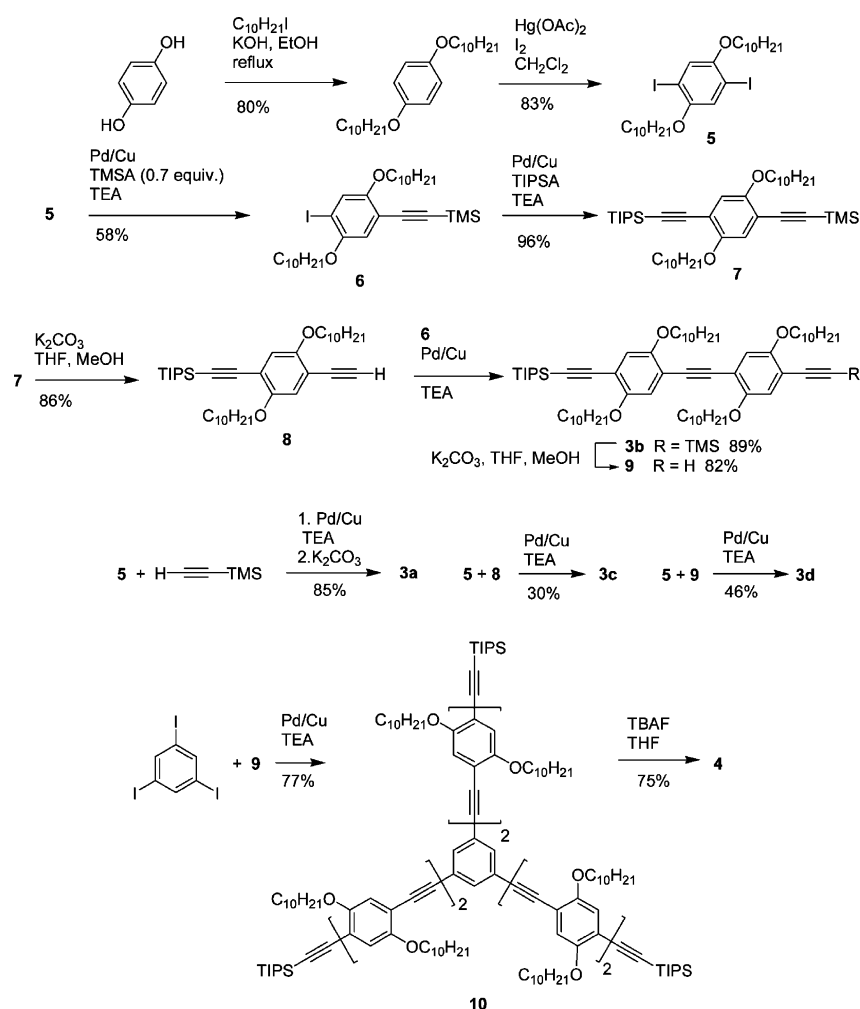
^{a} Pd/Cu = PdCl$_2$(PPh$_3$)$_2$, CuI.

1-iododecane in the presence of KOH in refluxing EtOH to give 1,4-bis(decyloxy)benzene, which was then iodinated to yield the building block **5** in an overall yield of 66%.[12] Cross-coupling of **5** with only 0.7 equiv of trimethylsilylacetylene (TMSA) afforded the monoiodide **6**. Then, cross-coupling of **6** with triisopropylsilylacetylene (TIPSA) gave monomer **7**, which was selectively deprotected using K$_2$CO$_3$ to afford monomer **8**. Compound **8** was further cross-coupled with **6** to give **3b**, which was then treated with K$_2$CO$_3$, affording OPE dimer **9**.

With all these building blocks in hand, the synthesis of OPE oligomers was readily achieved through a convergent coupling strategy. Diiodide **5** was cross-coupled with excess TMSA under Sonogashira conditions, followed by deprotection with K$_2$CO$_3$ yielding OPE monomer **3a** in 85% yield. In the same manner, cross-coupling of **5** with **8** and of **5** with **9** afforded OPE trimer **3c** and pentamer **3d**, respectively. Finally, dimer **9** was coupled with triiodobenzene to give the trigonal OPE **10**, which was deproteced with TBAF to afford **4**.

The electrochemical behavior of these multifullerene-OPE hybrids has been characterized by cyclic voltammetry (CV). Typical CVs for **1a** and **2** in comparison with pristine C$_{60}$ are shown in Figure 1. The most pronounced feature of Figure 1 is the close resemblance of CV curves for the mutilfullerene-OPEs to C$_{60}$. Although it is possible for there to be electronic communication between fullerene moieties,[13] only three couples of reversible redox waves are observed in the accessible potential window of the solvent under the present conditions for all cases (Supporting Information). These results suggest that electronic interactions between fullerene cages in the CV time scale are absent or very weak, a conclusion that is in line with the earlier report on acetylene-connected dumbbell-type fullerenes.[4] Detailed redox potential data of **1a−d** and **2** are summarized in Table 1. The three redox waves (I−III) observed for **1a−d** and **2** all shift toward more negative potentials relative to pristine

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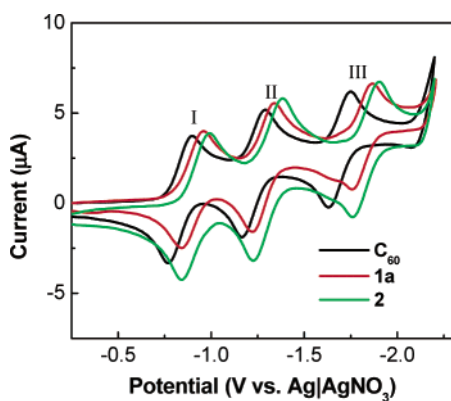
Figure 1. Cyclic voltammograms of C_{60}, **1a**, and **2** in 0.1 M TBABF$_4$/*o*-dichlorobenzene at room temperature. The working electrode was glassy carbon, and the counter electrode was a Pt wire; the nonaqueous reference electrode was Ag|AgNO$_3$. The formal potential of 2 mM ferrocene in 0.1 M TBABF$_4$ and acetonitrile was 70 mV vs this Ag|AgNO$_3$ reference electrode. Scan rate was 10 mV/s.

C_{60}. This is probably because of the inductive effect from the electron-withdrawing OPE moiety and/or the decrease of π-delocalization on the fullerene cage due to the introduction of two sp^3 carbon atoms.[9] The formal potentials of the first redox wave I cathodically shift with the increasing chain length of the OPEs.

The electronic absorption properties of these multifullerne-OPEs were studied by UV–vis spectroscopy. In the UV–vis spectra (Figure 2), a bathochromic shift of the lowest energy absorption maxima (λ_{max}) from **1a** to **1d** is observed, which is due to the increasing π-conjugation path in OPEs. The same degree of shift of λ_{max} is observed in the corresponding OPE precursors; data that appear to rule out electronic communication between fullerenes and OPE backbones. A characteristic absorption of C_{60} derivatives centered around ca. 430 nm[10a] is observed as in the UV–vis profiles of **1a** and **1b**, whereas such a feature becomes less pro-

Table 1. Results of Cyclic Voltammetry

| compd | formal potential^a, $E_{1/2}$ | | |
	I	II	III
C_{60}	−0.832	−1.227	−1.691
1a	−0.901	−1.281	−1.813
1b	−0.905	−1.288	−1.814
1c	−0.906	−1.286	−1.813
1d	−0.909	−1.292	−1.814
2	−0.918	−1.304	−1.831

^{a} Formal potentials are calculated as averages of oxidation and reduction peak potentials. Potentials are given in volts vs a nonaqueous reference electrode, Ag|AgNO$_3$. The formal potential of 2 mM ferrocene in 0.1 M TBABF$_4$ and acetonitrile is 70 mV vs this Ag|AgNO$_3$ reference electrode.
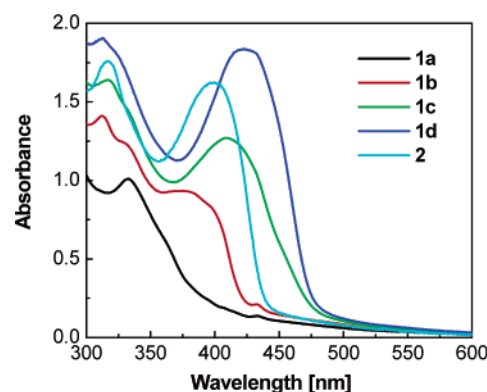

Figure 2. Electronic absorption spectra of **1a–d** and **2** as measured in *o*-dichlorobenzene.

nounced in the absorption curves of **1c** and **1d** because the strong absorption of OPEs predominate in this region. The analytical data confirm that there is no significant electronic communication or charge-transfer interaction between the fullerenes and OPEs occurring in the ground state, which is in agreement with our CV data as well as results in the report on monofullerene-OPE hybrids.[5a] Additionally, fluorescence quenching was detected under a UV lamp for all the fullerene-OPE hybrids compared to their strongly fluorescent OPE precursors. This observation suggests that stronger electronic interactions are taking place between the fullerene cages and OPE backbones in the photoexcited state.[14]

In conclusion, an efficient and practical synthetic method for directly attaching C_{60} to multiple terminal alkynes has been developed using an in situ acetylide addition reaction with LHMDS as the base. This method has enabled us to synthesize a series of multifullerene-OPE hybrid molecules with satisfactory yields. Spectroscopic and electrochemical studies on these molecules did not show detectable electronic communication between the OPE and fullerene moieties in the ground state.

Supporting Information Available: Experimental details along with spectroscopic data for all new molecules synthesized and CVs of compounds **1b–d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL049447T

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