Synthesis of the First Tetracene-[60]fullerene Dyad

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We report on a multistep synthesis of the newly designed tetracene-[60]fullerene dyad involing a Bingel reaction between the tetracene and C_{60} moieties. This strategy prevents the usual Diels–Alder reaction which would result in the loss of the tetracene aromaticity in the target dyad.

Introduction

The small reorganization energy of fullerenes in electron-transfer reactions makes them particularly attractive as electron-accepting materials for energy conversion and storage.[1] Blends of functionalized [60]fullerenes mixed together with conjugated polymers such as poly-*p*-phenylenevinylene allow for the building of photovoltaic cells with conversion efficiencies of up to 3.5%.[2–4] In these systems, a fast photoinduced electron transfer from the polymer donor moiety to the fullerene acceptor takes place, followed by a slow charge recombination. Similarly, donor-linked [60]fullerenes have been prepared in view of developing solid state photovoltaic systems.[5–8] A number of polycyclic aromatic hydrocarbons (PAHs) have also been covalently linked as donor moieties to C_{60}.[9–11] However, with the exception of perylene (E_{ox} = 0.85 V vs. SCE in MeCN),[11] they all exhibit energy transfer (instead of charge transfer) under photoexcitation due to a very high oxidation potential ($E_{ox} > 1.09$ V).

Surprisingly, higher acenes such as tetracene and pentacene possess electrochemical ($E_{ox} < 0.77$ V) and photophysical properties ($^{1*}E < 2.6$ eV), which are consistent with the required donor properties for photoinduced charge transfer. In particular, in contrast to other PAHs, they possess low oxidation potentials ($E_{ox} < 0.77$ V), low singlet excited-state energies ($1^{*}E < 2.6$ eV), and a strong absorption in the visible region. However, they probably have never been used as donors in C_{60}-donor dyads since they undergo [4+2] cycloadditions with the [6,6] bonds of C_{60}.[12–15] Since crystalline tetracene and pentacene possess excellent hole-transport properties and are currently studied as organic semiconductors in devices such as field-effect transistors,[16,17] it is interesting to develop synthetic strategies to obtain functionalized acenes.

We report here on the multistep synthesis of the newly designed tetracene-[60]fullerene dyad **1** (Figure 1). The 3,5-bis(dodecyloxy)benzylic group is introduced to ensure solubility of the dyad in organic solvents.

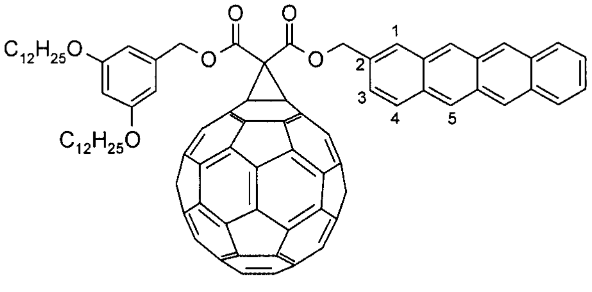

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Figure 1. Tetracene-[60]fullerene dyad **1**

Results and Discussion

Our strategy for the synthesis of the tetracene moiety is based upon the [2+2+2] cycloaddition of propargylic alcohol with the 1,7-diyne **7**. Preparation of the latter compound was performed in three steps (Scheme 1).

Bromination of commercially available 2,3-dimethylnaphthalene quantitatively gave compound **5**, which was then converted into the iodinated derivative in 85% yield. Copper coupling of acetylene Grignard with **6** led to **7** in 57% yield. The tetracene skeleton **8** was then obtained by rhodium-catalyzed [2+2+2] cycloaddition in the presence of 20% of the Wilkinson catalyst in 87% yield .[18] This cyclization of a 1,7-diyne allowed the generation of two six-membered rings in a single step with high yields for such a semi-intermolecular reaction.[19] The choice of rhodium as the

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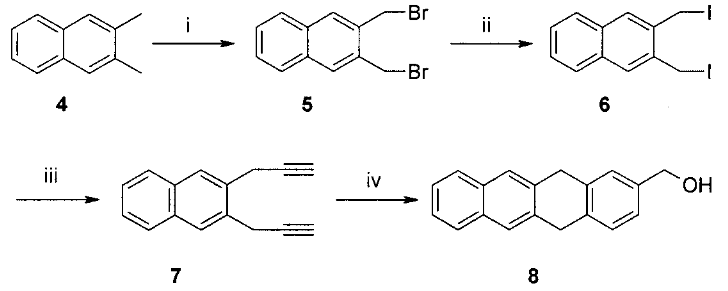
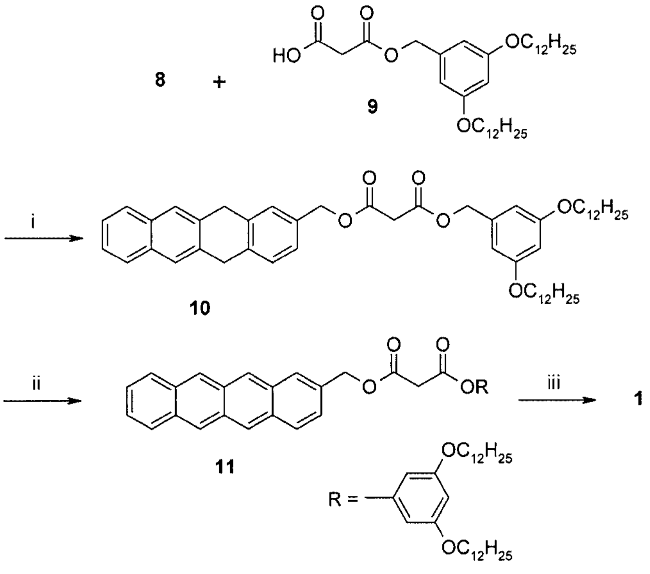


Scheme 1. Reagents and conditions: (i) NBS, AIBN, CCl_4, reflux (97%); (ii) NaI, acetone, reflux (85%); (iii) ethynylmagnesium bromide, CuI, THF, 60 °C, (57%); (iv) propargylic alcohol, $[RhCl(PPh_3)_2]$, toluene, reflux (87%)

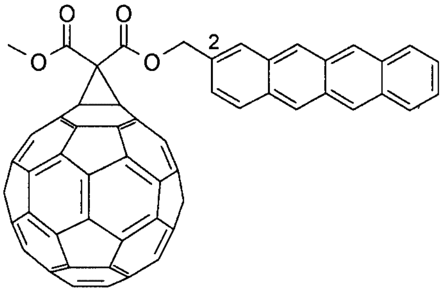
catalyst [instead of $CpCo(CO)_2$, for example] avoids the trimerization of both the 1,7-diyne and propargylic alcohol. In addition, the use of a ruthenium-based catalyst, as recently proposed by Yamamoto et al. for the efficient cyclization of 1,6-diynes, has not been adapted for use with 1,7-diynes.[20]

N,*N'*-dicyclohexylcarbodiimide(DCC)-mediated esterification of benzylic alcohol **8** with carboxylic acid **9** afforded malonate **10**. Compound **9** was introduced to ensure the solubility of the dyad in organic solvents, and was synthesized in 70% yield from 3,5-dihydroxybenzyl alcohol.[21] Aromatization of dihydronaphthacene derivative **10** was performed with DDQ to give the desired donor moiety in good yield. Finally, the reaction of C_{60} with compound **11** under Bingel conditions[22,23] afforded the target dyad **1** in 27% yield. The Bingel reaction can be carried out at room temperature thus avoiding the undesirable Diels–Alder side-reaction. After purification by flash chromatography, **1** was isolated as a black powder. The molecular structure of **1** is unambiguously confirmed by ^1H NMR, ^{13}C NMR and MALDI-TOF MS measurements (m/z = 1520.4). It should be noted that we also synthesized the insoluble analog of **1**, i.e. a C_{60}-tetracene dyad bearing a methyl group (R = CH_3) instead of the 3,5-bis(dodecyloxy)benzylic group, with the use of the same strategy. However, because of its insolubility, this compound was only characterized by mass spectroscopy.



Scheme 2. Reagents and conditions: (i) DCC, DMAP, CH_2Cl_2, 0 °C to room temperature (73%); (ii) DDQ, benzene, reflux (50%); (iii) C_{60}, I_2, DBU, toluene, room temperature (27%)

The ^1H NMR spectrum of **1** recorded in $CDCl_3$ at 293 K shows that all the signals are split. In particular, the two $-CH_2O-$ groups located on each side of the linker appear as four singlets in the δ = 5.4–5.7 ppm range. Although it was recently observed for an anthracene-C_{60} dyad that was synthesized by the Bingel reaction,[14] an intramolecular Diels–Alder reaction between the tetracene moiety and the fullerene can be ruled out here. Firstly, in the ^{13}C NMR spectrum of **1** in deuterated toluene, there is no signal for a primary carbon in the 15–100 ppm range and only three signals for quaternary carbons at δ = 67.5, 69.2, and 69.3 ppm, which correspond to the cyclopropane ring. It is well-known that the ^{13}C NMR signature of a Diels–Alder adduct between an acene and a fullerene is a resonance around 50–60 ppm for the bridging primary carbon of the acene moiety and a resonance around 70–80 ppm for the bridging quaternary carbon of the fullerene moiety. Moreover, in the ^1H NMR spectrum of **1**, singlets that correspond to the central rings of tetracene are deshielded by 0.2 ppm relative to the tetracene derivative **11**. In the case of a [4+2] C_{60}-tetracene adduct, the protons of the remaining central ring are shielded by 0.5 ppm.[11] Finally, in the 5.0–6.0 ppm range of the ^1H NMR spectrum, we only observe the signals for the two benzylic methylenes, and no signal that could be assigned to a Diels–Alder adduct is visible. The absence of a Diels–Alder reaction can be attributed to the position of the malonate linker on carbon 2 of tetracene (see Figure1), which prevents close overlap of the π-orbitals of the central rings of tetracene with those of the [6,6] bonds of the fullerene. This assumption is substantiated by ab initio calculations at the HF/3–21G level (Gaussian 03).[24] In order to facilitate these calculations, they have been performed without the introduction of the bulky solubilizing alkyl chains that were changed into a methyl group (dyads **12** and **13**). The Diels–Alder adduct of dyad **12** is 5 kcal·mol^{-1} less stable than dyad **12**, whereas the Diels–Alder adduct of dyad **13** is 27 kcal·mol^{-1} more stable than dyad **13** (see Figure 2).



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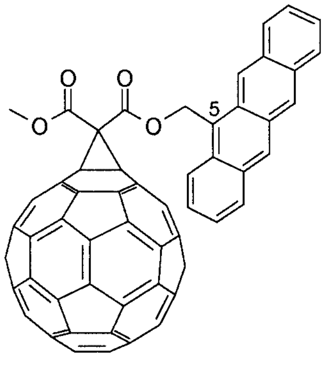

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Figure 2. Tetracene-[60]fullerene dyads **12** and **13**

The splitting of all ^{1}H NMR signals of **1** suggests the coexistence of two rotational isomers, as already reported for C_{60}-tetrathiafulvalene triads.[25] Besides, the substantial low-field shift of δ = 0.2–0.5 ppm for all tetracene protons can be explained by a π-stacking conformation in which the acene and the C_{60} moieties achieve close spatial proximity due to van der Waals attraction. Both π-stacking and the coexistence of conformers in **1** would be a common consequence of the flexibility of the malonate linker. It should be noted that intramolecular π-stacking has also been observed in C_{60}-porphyrin and C_{60}-pyrene dyads.[26,27]

π-Stacking in dyad **1** is also supported by its structureless UV/Vis absorption spectrum and the strong fluorescence quenching of the tetracene moiety. A solution of **1** in toluene is a purple–red and its absorption spectrum consists of a monotonous broad band extending over the 440–600 nm range. Besides, under UV irradiation, the typical vibronic feature of tetracene fluorescence in the 400–500 nm region disappears (Figure 3). This indicates that a charge or energy transfer (intra- or intermolecular) takes place in solution. However, since no emission band is observed in the 650–900 nm range, it cannot be concluded that charge transfer takes place in solution. If charge transfer effectively occurs, π-stacking would yield excited states that have short lifetimes, which would be inhibitory for further charge separation and efficient photovoltaic effect in the solid state. However, recent studies show that the charge separation lifetime of the phthalocyanine-[60]fullerene dyad may be considerably longer in the solid state than in solution.[5] We are currently investigating the photophysical properties of **1**.

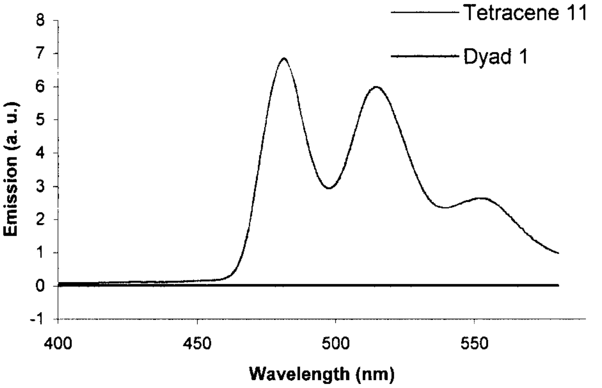

Figure 3. Fluorescence emission spectra of tetracene **11** and dyad **1** in dichloromethane (λ_{ex} = 300 nm. [c] = 9.5 × 10^{-6} M)

Conclusion

In conclusion we have successfully synthesized the first C_{60}-tetracene dyad with the use of an original route that includes a rhodium-catalyzed [2+2+2] cycloaddition and a Bingel reaction. Compound **1** has been fully characterized, which shows, in particular, that the C_{60} and tetracene moieties do not undergo Diels–Alder reaction and that **1** probably adopts a π-stacking conformation. We are presently using this new approach to synthesize a series of substituted C_{60}-tetracene and C_{60}-[N]phenylene analogs.[28]

Supporting Information (see also the footnote on the first page of this article): The details of the synthesis and characterization (^{1}H and ^{13}C NMR, FT-IR, elemental analysis) of all compounds reported here are provided.

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