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Synthesis of a linear benzo[3]phenylene-[60]fullerene dyad

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Abstract—The synthesis of a new linear benzo[3]phenylene–[60]fullerene dyad 1 is achieved over 10 steps in 15% overall yield by using an efficient sequence combining a double cobalt(I)-mediated cyclotrimerization with a Bingel reaction. © 2005 Elsevier Ltd. All rights reserved.

The [N]phenylenes are linear polycyclic aromatic hydrocarbons constituted an alternation of N benzene units fused to N-1 cyclobutadiene rings. Similar to acenes, they are promising candidates for molecular electronics because of an extended π -conjugated system. As of today, several [N]phenylenes have been synthesized¹ and some of them have even been studied spectroscopically² and theoretically.³ However, to our knowledge the use of [N]phenylenes as photo- or electroactive materials have not been reported.

The small reorganization energy of fullerenes in electron transfer reactions makes them particularly attractive as electron accepting materials for energy conversion and storage.⁴ Blends of functionalized [60]fullerenes mixed together with conjugated polymers such as poly-*p*-phenylenevinylene allow to build photovoltaic cells with conversion efficiencies up to of a few percents.⁵ 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.⁶

In this context, the photoinduced electron transfer between fullerenes and a number of polycyclic hydrocarbons, which have been covalently linked as donor moieties to C_{60} has been extensively investigated.⁷ In contrast, the first synthesis of fullerene adducts with tetracenes has been recently published⁸ and to our knowledge, no example with [N]phenylenes has so far been reported. Encouraged by our recent successful execution of tetracene–[60]fullerene dyad and as part of our program devoted to the construction of photovoltaic cells, we turned our attention to a very efficient preparation of [60]fullerene adducts bearing a [3]phenylene moiety.

[N]Phenylenes generally absorb between 400 and 500 nm with high molar extinction coefficients, but for efficient photovoltaic conversion, absorption maximum around 500–550 nm is preferred. Since the addition of a fused benzene ring in the acene series tends to red-shift the absorption by 100 nm,⁹ we envisioned to covalently link C_{60} with various benzo[3]phenylenes acting as electron donors instead of the corresponding [3]phenylenes.

Because of the ability of C_{60} to easily achieve close spatial proximity with aromatic compounds via van der Waals interactions,⁸ a sterically demanding group such as trimethylsilyl has been introduced on the adduct to avoid a possible intramolecular π -stacking between benzo[3]phenylene and C_{60} . Indeed, π -stacking would render the separated charge state life-time too low and would be inhibitory for further charge separation and efficient photovoltaic effect. Thus, we report herein the successful synthesis of the newly designed C_{60} -benzo[3]phenylene dyad **1** prepared by Bingel reaction,¹⁰ which has been also recently employed to efficiently prepare [60]fullerene adducts bearing carbazole moieties¹¹ (Fig. 1).

Our strategy for the synthesis of the benzo[3]phenylene was based upon a classical iterative sequence including

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Figure 1. Newly designed C_{60} -benzo[3]phenylene dyad 1.

palladium-catalyzed alkynylations followed by cobaltcatalyzed cyclotrimerizations.¹² A Sonogashira coupling of trimethylsilylacetylene (TMSA) with **2**, obtained in 92% yield from commercially available naphthalene-2,3-diol,¹³ followed by desilylation of the triple bonds afforded diyne **3** in 83% yield over two steps (Scheme 1). The first [2+2+2] cyclization was performed by slow addition of a dilute solution of compound **3** in boiling bis(trimethylsilyl)acetylene (BTMSA),^{12b} under irradiation. The benzobiphenylene **4**, obtained in 94% yield, was then sequentially submitted to iododesilylation, palladium-catalyzed coupling and desilylation to furnish diyne **6** in 79% yield over three steps.

As in the approach of linear [3]phenylenes, the second bimolecular cyclotrimerization has been reported to be generally less efficient than the first one,^{12b} we anticipated that an intramolecular cyclization could be a higher yielding alternative. Thus, we considered to prepare linear benzo[3]phenylenes via an intramolecular cycloaddition through temporary silicon tethers. The use of disposable tethers in the sequence of the cyclization followed by the displacement of the silicon group allows the chemo- and regioselective formation of polysubstituted arenes.¹⁴



Scheme 1. Reagents and conditions: (a) TMSA, $PdCl_2(PPh_3)_2$, CuI, Et₂NH, Δ , 30 h. (b) KOH, MeOH, rt, 30 min, 83% from 2. (c) BTMSA, $CpCo(CO)_2$, *o*-xylene, Δ , *hv*, 94%. (d) ICl, CCl_4 , 0 °C to rt, 45 min, 81%. (e) TMSA, $PdCl_2(PPh_3)_2$, CuI, Et₂NH, Δ , 1 h. (f) KOH, MeOH, 30 min, 97% over two steps.



Scheme 2. Reagents and conditions: (a) 1. MeMgBr, THF, rt, 1 h; 2. $(CH_2O)n$, rt, 4 h. (b) NBS, CH_2Cl_2 , rt, 30 min. (d) 7, Et_3N , DMAP, CH_2Cl_2 , rt, 3 h.

Preparation of the quite stable trivne 8 was carried out from 6 following Scheme 2. The silvlated tether was introduced according to the reported procedure for the construction of unsymmetrical silaketals and silyl ethers.¹⁵ Our first attempts to cyclize 8 with only a catalytic amount of CpCo(CO)₂ were quite unsuccessful, only traces of the cycloadduct 9 were observed. As for linear [4]phenylene,¹⁶ we suppose that CpCo was complexed to the cycloadduct, thus consuming the catalyst and requiring a stoichiometric amount of the complex. Therefore, the target benzo[3]phenylene 9 was obtained in 27% yield by using one equivalent of $CpCo(CO)_2$ (Scheme 3). Thus, the opening of the silylether was carried out with MeLi and led quantitatively to benzo[3]phenylene 10. However, the overall yield for its formation is 5.4% from 2,3-dihydroxynaphthalene and appears not satisfying for synthetic purposes.

At the same time, the bimolecular cyclization of diyne **6** with silylated propargylic alcohol was attempted¹⁷ (Scheme 4).

Indeed, in the presence of a stoichiometric amount of $CpCo(CO)_2$, the bimolecular cycloaddition led surprisingly to higher yield than the intramolecular one. The cycloadduct **11** was obtained in 61% yield, boosting



Scheme 3. Reagents and conditions: (a) $CpCo(CO)_2$ (1 equiv), toluene, hv, Δ . (b) MeLi, 0 °C, THF.



Scheme 4. Reagents and conditions: (a) $CpCo(CO)_2$ (1.1 equiv), *o*-xylene, hv, Δ .



Scheme 5. Reagents and conditions: (a) DCC, DMAP, CH_2Cl_2 , 0 °C to rt, 20 h. (b) C_{60} , I_2 , toluene, rt, 6 h.

the overall yield of the sequence to 34%. N,N'-Dicyclohexylcarbodiimide mediated esterification of benzylic alcohol **11** was performed with carboxylic acid **12**, which was prepared in 70% yield from 3,5-dihydroxybenzyl alcohol,¹⁸ the presence of the 3,5-bis(dodecyloxy)benzylic substituents ensuring the solubility of the dyad in organic solvents. Thus, malonate **13** derived from **11** was obtained in 82% yield (Scheme 5).

Finally, the reaction of C_{60} with 13 under Bingel conditions¹⁰ afforded the target dyad 1 in 52% yield.¹⁹ In ¹H NMR spectrum, the resonance of the protons of the trimethylsilyl group of 1 is deshielded from 0.30 to 0.35 ppm as compared to 13, which probably indicates the close spatial proximity of C_{60} with the silicon group, which plays exactly the part as it was devoted.

The UV–visible spectrum of the dyad **1** is given in Figure 2 and fits well with the sum of the absorption spectra of the donor, **13** and methano[60]fullerene. This observation indicates the absence of significant interaction between benzo[3]phenylene and C₆₀ moieties in the ground state. However, a small red-shift is observed in the absorption maximum of **13** ($\lambda_{max} = 452 \text{ nm}$) as compared to [3]phenylene ($\lambda_{max} = 432 \text{ nm}$).^{12b} Such a small shift has already been observed with naphthelynocyclobutabenzene and is probably due to the partial electron localization in linear [*N*]phenylene. Finally, in agreement with what has already been reported for linear [3]phenylene,^{2a} compounds **11**, **12**, **13** and dyad **1** are not fluorescent.



Figure 2. UV-visible absorption spectra of 1 (—) and 13 (- - -) in THF ($c = 10^{-3} \text{ mol } L^{-1}$).

In summary, by using an efficient sequence combining a double cobalt(I)-mediated cyclotrimerization together with a Bingel reaction, we succeeded in synthesizing a new linear benzo[3]phenylene–[60]fullerene dyad, which was obtained over 10 steps in 15% overall yield from naphthalene-2,3-diol. The photophysical properties of dyad 1 are currently under study in solution and the solid state as well as its use in photovoltaic solar cells. Beside further substitution on the central six-membered ring should induce a lowering of the energy of the first excited state. Therefore, we are now working on the preparation of benzo[3]phenylene derivatives absorbing at wavelengths longer than 500 nm.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet. 2005.09.174 (experimental procedures and characterization data of the compounds **3–10**).

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- 19. Typical procedure for the preparation of 11: In a flamedried flask under argon, a solution of diyne 6 (0.165 g, 0.66 mmol), 3-(trimethylsilanyl)-prop-2-yn-1-ol (0.190 g, 1.49 mmol, 2.25 equiv) and CpCo(CO)₂ (85 μ L, 1 equiv) in *o*-xylene (5 mL) and THF (3 mL) was added with a syringe pump to boiling degassed *o*-xylene (5 mL). Light from a projector lamp (300 W, 50% of its power) was directed at the reaction mixture during the addition. After the mixture was refluxed and irradiated for an additional 15 min, the solvents were removed by vacuum transfer. Flash chromatography (toluene/AcOEt 9/1) of the crude

mixture gave after a successive recrystallization in benzene **11** (0.153 g, 61%). $R_{\rm f}$ (toluene/AcOEt 9/1) = 0.35. FT-IR (ATR) 2952, 1412, 1179, 1094, 868, 836, 748 cm⁻¹. ¹H NMR (400 MHz, C₆D₆) δ 0.21 (s, 9H), 4.31 (s, 2H), 6.23 (s, 1H), 6.26 (s, 1H), 6.44 (s, 1H), 6.47 (s, 1H), 6.64 (s, 1H), 6.72 (s, 1H), 7.10 (m, 4H). ¹³C NMR (100 MHz, C₆D₆) δ 0.66, 65.5, 111.2, 111.6, 113.1, 113.2, 116.7, 120.8, 126.2, 128.4, 129.3, 135.2, 146.4, 148.4, 151.0, 152.7. UV–vis (THF) $\lambda_{\rm max}$ 311, 327, 337, 353, 396, 425, 453. HMRS calcd: 378.1447. Found: 378.1439.

Typical procedure for the preparation of 13: At 0 °C, N,N'dicyclohexylcarbodiimide (DCC, 0.051 g, 0.25 mmol, 1.5 equiv) was added to a solution of $12^{8,18}$ (0.140 g, 0.25 mmol, 1.5 equiv) and **11** (0.059 g, 0.16 mmol, 1 equiv) in presence of 4-DMAP (0.01 g, 0.08 mmol, 0.5 equiv) in CH₂Cl₂ (8 mL). After being stirred for 1 h, the mixture was warmed up to rt and was stirred for an additional 5 h. After having removed the solvents in vacuo, the crude residue was purified by flash chromatography (PE/AcOEt 95/5 then 9/1) to give 13 as a viscous solid (0.118 g, 82%). $R_{\rm f}$ (PE/AcOEt 8/2) = 0.8. FT-IR (ATR) 2921, 2852, 1734, 1597, 1463, 1326, 1249, 1129, 869, 838, 754 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.30 (s, 9H), 0.89 (t, J = 6.6 Hz, 6H), 1.26 (m, 32H), 1.43 (m, 4H), 1.76 (m, 4H), 3.50 (s, 2H), 3.91 (t, J = 6.6 Hz, 4H), 5.06 (s, 2H), 5.11 (s, 2H), 6.41 (m, 3H), 6.48 (d, *J* = 2.3 Hz, 2H), 6.55 (s, 1H), 6.67 (m, 3H), 7.19 (dd, J = 6.6, 3.0 Hz, 2H), 7.36 (dd, J = 6.6, 3.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 0.3, 14.2, 22.8, 26.1, 29.3, 29.4, 29.5, 29.7, 32.0, 41.6, 67.3, 67.5, 68.1, 101.1, 106.4, 111.2, 111.6, 113.2, 117.3, 120.6, 126.1, 128.4, 135.1, 137.2, 140.2, 141.2, 146.2, 149.1, 151.1, 151.3, 151.4, 152.4, 153.3, 160.5, 166.2, 166.4. UV-vis (THF) λ_{max} (ϵ) 311 (78,000), 338 (22,800), 354 (28,200), 426 (19,200), 452 (30,600).

Typical procedure for the preparation of 1: To a solution of C_{60} (0.136 g, 0.19 mmol, 1.5 equiv), iodine (0.035 g, 0.14 mmol, 1.1 equiv), 13 (0.116 g, 0.13 mmol, 1 equiv) in freshly distilled toluene (100 mL) was added DBU (0.048 g, 0.32 mmol, 2.5 equiv). After being stirred for 6 h at rt, the reaction mixture was concentrated in vacuo to 25% of the initial volume, filtered on silica gel pad and then concentrated. The crude residue was purified by flash chromatography (toluene/PE 1/1) to furnish 1 (0.107 g, 52%). $R_{\rm f}$ (toluene/PE 1/1) = 0.1. FT-IR (ATR) 731, 839, 1228, 1463, 1597, 1746, 2851, 2923 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.35 (s, 9H), 0.88 (t, J = 6.9 Hz, 6H), 1.29 (m, 32H), 1.41 (m, 4H), 1.74 (m, 4H), 3.89 (t, J = 6.6 Hz, 4H), 5.38 (s, 2H), 5.42 (s, 2H), 6.42 (s, 1H), 6.45 (s, 2H), 6.57 (m, 2H), 6.63 (s, 1H), 6.69 (m, 3H), 7.21 (m, 2H), 7.38 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 0.8, 14.3, 22.9, 26.3, 29.4, 29.5, 29.6, 29.8, 29.9, 32.1, 52.0, 68.3, 69.1, 71.5, 101.8, 107.1, 111.4, 111.9, 113.4, 118.0, 120.7, 126.3, 135.2, 136.6, 139.2, 140.7, 141.0, 141.9, 142.0, 142.3, 143.1, 143.9, 144.6, 144.8, 145.0, 145.1, 145.2, 145.3, 145.4, 146.3, 149.6, 151.3, 151.4, 151.6, 152.5, 153.3, 160.6, 163.4, 163.6. MS (FAB, m/z) 720 [C^{+•}₆₀], 1642 [M^{+•}]. UV-vis (THF) λ_{max} (ε) 313 (113,000), 327 (81,300), 354 (47,900), 403 (12,300), 426 (22,000), 453 (32,000).