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A Synthetic Strategy for the Construction of a Novel Series of Buckminsterfullerene (C_{60}) Ball-and-Chain Molecules Containing the Porphyrin Chromophore

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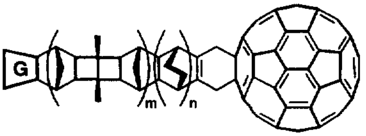
Abstract: A general method is described for synthesizing rigid "Ball-and-Chain" bichromophoric systems of the type C_{60}-{rigid bridge}-porphyrin **2**. Copyright © 1996 Elsevier Science Ltd

The rich redox properties and the photophysical behaviour, of the Buckminsterfullerene (C_{60}) molecule confer upon this species the exciting prospect that it and its functionalized derivatives might usefully participate in the long-range vectorial transport of excitation energy and of electrons.[1,2] In this respect, multichromophoric assemblies comprising functionalized C_{60} moieties and porphyrin units might serve as useful and interesting systems for modelling the primary photoinduced electron transfer events that take place in the photosynthetic reaction centre.[3-5] Such model electron transfer studies on porphyrin-C_{60} bichromophoric systems would ideally be carried out using structurally well-defined supramolecular assemblies in which the chromophores are held at fixed distances and orientations. In this manner an unambiguous profile of the dependence of the electron transfer dynamics on the distance and orientation of the chromophores may be determined.[4]



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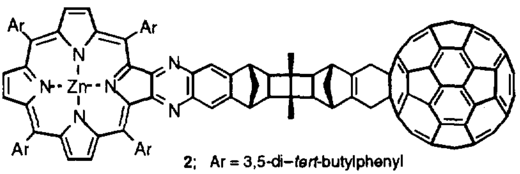
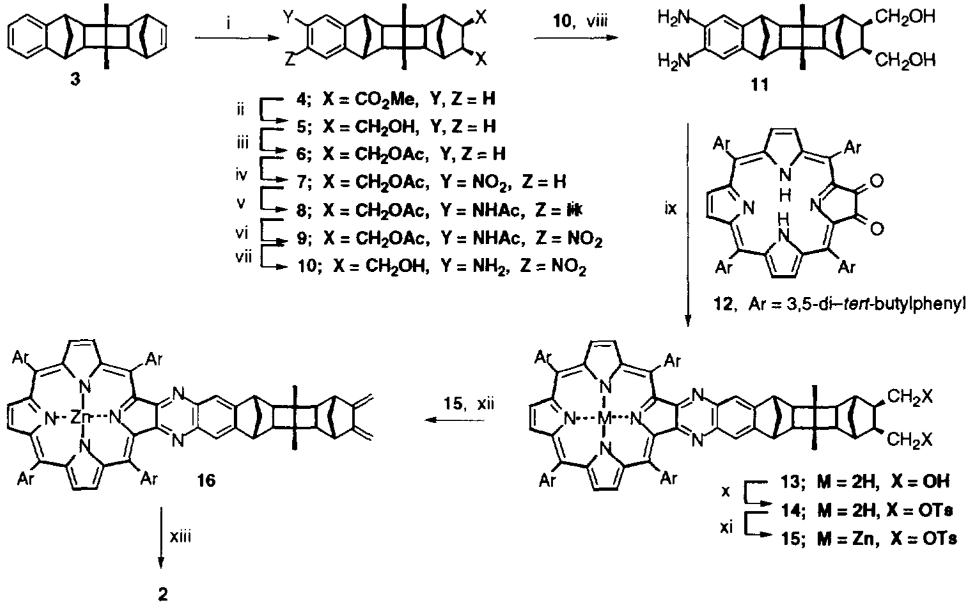


2; Ar = 3,5-di-*tert*-butylphenyl

We have recently communicated a novel approach to the construction of rigid covalently linked C_{60}-{rigid bridge}-(functional group, G) assemblies, which have the general structure shown by **1**.[6] These "ball-and-chain" systems contain a rigid hydrocarbon bridge comprising linearly fused norbornane and bicyclo[2.2.0]hexane units (norbornylogous bridge). Ball-and-chain systems, in which G is a a porphyrin group, should be ideal for studying the dynamics of electron and energy transfer processes between the C_{60} and porphyrin groups under spatially controlled conditions. We now report the first successful synthesis of a member of this series, namely **2**, in which the C_{60} and the porphyrin chromophores are attached to a norbornylogous bridge eight bonds in length. Recently, three covalently linked C_{60}-porphyrin systems,[5a-c] and one C_{60}–phthalocyanine system[5d] have been synthesized; however, the bridges used in those systems are quite short and are not synthetically amenable to systematic variation in length as is the norbornylogous bridge.



Scheme 1 *Reagents and conditions*: (reactions at room temperature unless otherwise noted): i, CO, MeOH, THF, $CuCl_2$, Pd/C (10%), 2 days; ii, $LiAlH_4$, THF, reflux; iii, Ac_2O, Py, 2 days; iv, $Cu(NO_3)_2.3H_2O$, Ac_2O, CH_2Cl_2, 18 h; v, Zn, Ac_2O, AcOH, 30 °C, 5 days; vi, HNO_3, AcOH, CH_2Cl_2, 0 °C, 2 h; vii, $NH_2NH_2.H_2O$, 90 °C, 17 h; viii, $NH_2NH_2.H_2O$, EtOH, Pd/C (10%), reflux, 18h; ix, CH_2Cl_2/MeOH (1:1), reflux, 17 h; x, TsBr, Py, CH_2Cl_2, -5 °C, 3h; xi, $Zn(OAc)_2$, $CHCl_3$/MeOH (9:1), 30 min; xii, $KOBu^t$, DMSO, 2h; xiii C_{60}, *o*–dichlorobenzene, 110–115 °C, 16 h (Py = pyridine; Ts = *p*–$MeC_6H_4SO_2$; DMSO = dimethyl sulfoxide)

The synthesis is presented in Scheme 1. The key features are: (a) Construction of the norbornylogous bridge **11**, bearing an *o*–phenylenediamine moiety, (b) attachment of the porphyrin ring to **11**, using the porphyrin dione **12**,[7] to form **13**, and (c) the conversion of **13** into the novel porphyrin-diene **16**, which is expected to undergo Diels–Alder reaction with C_{60} by addition across a 6–6 ring junction of the latter molecule.[6]

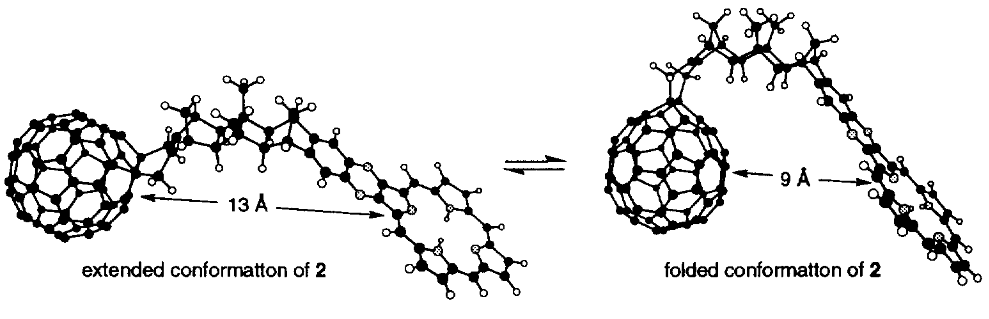
The six–bond benzo–bridge[8] **3** underwent *cis*–bismethoxycarbonylation[10] to give **4**[10c] which was converted into the bis–acetoxymethyl compound **6** using standard procedures. Nitration of this material occurred essentially exclusively at the 7–position to give **7**. Transformation to the anilide **8**, followed by nitration gave the *o*–nitroanilide **9** which was converted into the *o*–phenylenediamine–diol **11** by treatment with hydrazine hydrate, to yield the *o*–nitroaniline **10**, followed by reduction of this compound with hydrazine hydrate and Pd/C.

Condensation of **11** with tetrakis(3,5–di–*tert*–butylphenyl)porphyrin dione **12**[7a] proceeded smoothly to give **13** in high yield (92%). The diol **13** was transformed into the diene **16** through bistosylation, formation of the zinc porphyrin, and subsequent base induced bisdehydrotosylation.[11a] The overall yield of diene **16** from **3** is 18%. Heating a deoxygenated solution of **16** (1 eq) and C_{60} (2 eq) in *o*–dichlorobenzene at 110 - 115 °C gave the ball-and-chain system **2** (84%) as a purple solid (from CH_2Cl_2/petrol). Characterization of **2** was straightforward.[11b] In particular, the ^1H NMR spectrum of **2** revealed the presence of an AB quartet at δ 3.82 - 3.97, due to the allylic CH_2 groups of the cyclohexene ring, which is a characteristic feature of these types of molecules.[6] The presence of a resonance at δ 65 in the ^{13}C NMR spectrum of **2** also confirms that cycloaddition took place at the 6–6 ring junction of C_{60}.[5c,6]

The cyclic voltammetry data for **2** and the model systems, namely, the porphyrin-bridge molecule lacking the C_{60} group, and the C_{60}-bridge molecule lacking the porphyrin group, are presented in Table 1. The reversible potentials observed at *ca.* 0.89 and 1.14 V for **2**, correspond to oxidation of the porphyrin group, and the remaining three waves are due to reduction of the C_{60} group. Comparison of the reduction potentials for **2** with those for the model systems do not reveal the presence of significant interactions between the two chromophores in **2**, a conclusion which is also borne out by their electronic spectra. This is not surprising, given the large calculated (MM2 force-field) interchromophore separations of 9 and 13 Å for the folded and extended conformations of **2**, as shown below.

Table 1: Reduction potentials (*vs.* Ag/AgCl; 25 °C, in toluene/acetonitrile (4:1, 3.0 mL) containing $Bu_4N^+BF_4^-$ (0.1 M), scan rate of 100 mV s^{-1}).

Molecule	$E^1_{1/2}$/V	$E^2_{1/2}$/V	$E^3_{1/2}$/V	$E^4_{1/2}$/V	$E^5_{1/2}$/V
model 1: Porphyrin–bridge lacking the C_{60} group.	1.11	0.89	–	–	–
model 2: C_{60}–bridge lacking the porphyrin group.	–	–	–0.58	–1.01	–1.40
2	1.14	0.89	–0.58	–1.03	–1.47



The synthetic strategy described here is quite general and allows for the facile construction of a broad spectrum of C_{60}–{rigid bridge}–porphyrin ball-and-chain systems possessing bridges of variable, but precisely defined length *and configuration*[9c] using established synthetic techniques.[4b,9] Such systems are being synthesized by us. Meanwhile, the photophysical studies of **2** are under current investigation.

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11. (a) Selected spectroscopic data for **16**: UV-VIS (CHCl$_3$) λ_{max} (log ε) /nm 444 (5.26), 533 (3.80), 569 (4.26), 612 (4.13). ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.07 (s, 6H), 1.57 (s, 18H), 1.59 (s, 18H), 1.62 (s, 36H), 1.62 (d, J=11 Hz, 1H), 1.81 (d, J=11 Hz, 1H), 1.87 (d, J=9.75 Hz, 1H), 2.07 (d, J=9.72 Hz, 1H), 2.17 (bs, 4H), 2.81 (s, 2H), 3.55 (s, 2H), 4.79 (s, 2H), 5.11 (s, 2H), 7.56 (s, 2H), 7.84 (bt, 2H), 7.97 (bs, 2H), 8.00 (s, 2H), 8.04 (bs, 2H), 8.15 (s, 2H), 8.16 (s, 2H), 8.96 (s, 2H), 9.04-9.09 (ABq, J=5.0 Hz, 4H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 9.54, 31.79, 31.97, 35.0, 35.07, 42.94, 43.83, 44.50, 45.58, 50.76, 50.92, 100.16, 118.58, 120.30, 120.46, 120.73, 124.21, 128.39, 129.44, 131.35, 132.11, 140.95, 141.95, 142.02, 142.11, 148.47, 148.93, 149.68, 149.90, 150.25, 151.46, 152.40. MS (MALDI) *m/z* 1466.5 (M$^+$+1), 379, 294.5. Analysis: calculated for $C_{100}H_{114}N_6Zn$ C, 81.96 ; H, 7.84, N, 5.73. Found C, 81.80; H, 7.93, N, 5.50.

    (b) Selected spectroscopic data for **2**: UV-VIS (CHCl$_3$) λ_{max} (log ε) /nm 264 (4.75), 328 (4.57), 446.4 (5.07), 532.8 (3.75), 569.6 (4.14), 612 (4.02). ^{1}H NMR (300 MHz, CDCl$_3$/CS$_2$) δ 1.15 (s, 6H),1.44 (s, 18H), 1.50 (s, 18H), 1.54 (s, 36H), 1.75 (m, 2H), 1.91 (d, J=9 Hz,1H), 2.10 (d, J=9 Hz, 1H), 2.17 (s, 2H), 2.23 (s, 2H), 3.20 (s, 2H), 3.58 (s, 2H), 3.82-3.97 (ABq, J=14.4 Hz, 4H), 7.50 (s, 2H), 7.77 (t, 2H), 7.87 (t, 2H), 7.88 (m, 2H), 7.97 (t, 2H), 8.07 (m, 2H), 8.09 (m, 2H), 8.87 (s, 2H), 8.94 (d, J=4.6 Hz, 2H), 8.97 (d, J=4.6 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$/CS$_2$) δ 9.56, 31.70, 31.74, 31.88, 34.75, 34.79, 34.88, 40.60, 42.95, 43.06, 43.51, 43.98, 46.28, 49.84, 50.85, 65.05, 118.77, 120.21, 120.61, 120.76, 122.24, 124.18, 124.19, 128.36, 128.42, 129.32, 131.33, 132.08, 134.44, 135.56, 139.28, 139.42, 140.68, 140.90, 141.03, 141.16, 141.49, 141.55, 141.59, 141.69, 141.88, 141.92, 142.09, 142.29, 143.69, 143.84, 144.28, 144.38, 144.50, 144.54, 144.69, 144.71, 144.83, 145.13, 145.17, 145.33, 145.41, 145.70, 146.63, 148.30, 148.92, 149.54, 149.65, 150.14, 152.41, 157.32, 157.49. MS (MALDI) *m/z* 2187.5 (M$^+$+1), 1668.2, 1645.4, 1467.0, 379.4. Analysis: calculated for $C_{160}H_{114}N_6Zn$: C, 87.91; H, 5.37; N, 3.84. Found C, 87.05; H, 5.73; N 3.30. Note that the ^{1}H and ^{13}C NMR spectra reveal that the *tert*-butyl groups associated with each of the two aromatic rings closest to the quinoxaline group are non–equivalent (*eg* the ^{1}H NMR signals at δ 1.44 and 1.50 integrate for 18H each) which is due to restricted rotation.

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