# Design and Synthesis of Two (Pseudo)symmetric Giant Trichromophoric Systems Containing the $C_{60}$ Chromophore

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Diels−Alder reaction of $C_{60}$ with the 1,3-dienes *syn*-**5** and *syn*-**20** affords the giant trichromophoric systems *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** and *syn*-**$C_{60}$-9-DMN-6-DMA**, respectively, in which the three chromphores in each system are linked via rigid, hybrid saturated polynorbornane-bicyclo[2.2.0]-hexane ("norbornylogous") hydrocarbon bridges. The norbornylogous bridge is a strong mediator of electron and energy transfer via a through-bond coupling mechanism. Hence, the giant trichromophores described herein illustrate the necessary methodology for the synthesis of efficient molecular systems that are capable of generating long-lived charge-separated states. The 1,3-dienes *syn*-**5** and *syn*-**20** were prepared in a straightforward manner from two fragments containing a diene and a dienophile, and thus a simple building-block approach to such sophisticated systems is described. Semiempirical AM1 MO SCF calculations were carried out on the trichromophoric systems to quantify their ability to adopt two nondegenerate boat conformations, i.e., extended and folded conformers.

## Introduction

One of the most sought after goals in electron transfer is the rational design and successful construction of molecular photovoltaic devices,[1−3] i.e., those molecular systems that are capable of transducing photon energy into chemical potential through creation of a charge-separated state. The basic scheme for a bichromophoric donor−acceptor (**D**−**A**) molecular photovoltaic device is depicted in Figure 1.

Absorption of light by **D**−**A** leads to the (eventual) formation of the first excited state whose excitation energy is localized on either the **D** or **A** moiety. The locally excited state can then either decay nonproductively back to the ground state (with a rate $k_d$) or it may undergo desired electron transfer (ET) to give the charge-separated (CS) state $^+D-A^-$ (with a rate $k_{et}$). Left to itself, the CS state eventually undergoes charge recombination (with a rate $k_{cr}$). The amount of chemical potential stored during this process is given by the quantity ($h\nu + \Delta G°$).

The following criteria should be met when designing a molecular photovoltaic device:

(1) The quantum yield for the charge separation process should be as high as possible, that is, $k_{et} \gg k_d$.

(2) The lifetime, $\tau_{cr}$, of the CS state must be long enough that it is able to carry out "useful" chemical work.[3] In practice, $\tau_{cr}$ should be greater than 1 $\mu$s.

(3) The energy content of the CS state should be as high as possible, thereby ensuring maximum conversion of photonic energy into chemical potential. Thus, $|\Delta G°|$ should be small.

To meet requirement 1 above, the magnitude of $k_{et}$ should be greater than $10^{10}$ $s^{-1}$. This number follows from the observation that the lifetimes of the excited states of the majority of potentially useful chromophores are ca. $10^{-9}$ s. Thus, simultaneous satisfaction of requirements 1 and 2 means that the ratio of the rates of charge separation to charge recombination should be greater than $10^4$.

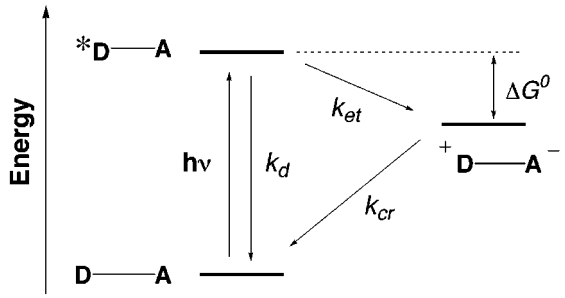


**Figure 1.** Energy diagram illustrating the possible pathways available in a photoinduced electron-transfer event within a molecule containing a donor (D) and acceptor (A).

We have been approaching this ratio using $C_{60}$-based chromophoric ball-and-chain systems **1(11)**[4] and **2(9)**[5] (Chart 1) in which the two chromophores are fused to our rigid polynorbornane-bicyclo[2.2.0]hexane bridges 11 and 9 $\sigma$-bonds in length, respectively. It is well-known that these bridges effectively mediate long-range ET processes very efficiently by a through-bond mechanism.[6]

Intriguingly, it was found not only that the efficiency of photoinduced CS in both **1(11)** and **2(9)** was very high

(1) *Molecular Electronics*; Jortner, J. J., Ratner, M., Eds.; *IUPAC Chemistry for the 21st Century*; Blackwell Science: Oxford, 1997.

(2) (a) Balzani, V. *Tetrahedron* **1992**, *48*, 10443. (b) Feringa, B. L.; Jager, W. F.; de Lange, B. *Tetrahedron* **1993**, *49*, 8267. (c) Anzai, J.; Osa, T. *Tetrahedron* **1994**, *50*, 4039. (d) Lehn, J.-M., Ed.; *Supramolecular Chemistry*; VCH: Weinheim, 1995; Chapter 8.

(3) Habib, J. L.; Soumillion, J. Ph. *J. Phys. Chem.* **1995**, *99*, 14223.

(4) (a) Lawson, J. M.; Oliver, A. M.; Rothenfluh, D. F.; An, Y.-Z.; Ellis, G. A.; Ranasinghe, M. G.; Khan, S. I.; Franz, A. G.; Ganapathi, P. S.; Shephard, M. J.; Paddon-Row, M. N.; Rubin, Y. *J. Org. Chem.* **1996**, *61*, 5032. (b) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055.

(5) (a) Ranasinghe, M. G.; Oliver, A. M.; Rothenfluh, D. F.; Salek, A.; Paddon-Row, M. N. *Tetrahedron Lett.* **1996**, *37*, 4797. (b) Bell, T. D. M.; Smith, T. A.; Ghiggino, K. P.; Ranasinghe, M. G.; Shephard, M. J.; Paddon-Row, M. N. *Chem. Phys. Lett.* **1997**, *268*, 223.

(6) Paddon-Row, M. N. *Acc. Chem. Res.* **1994**, *27*, 18.

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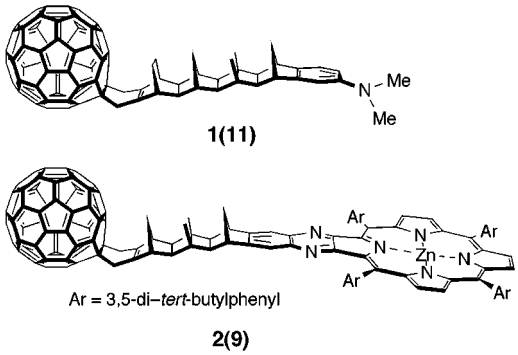
**Chart 1**




(>85%) but that subsequent CR was anomalously slow. The rate data (in PhCN solvent) for these systems are[4b,5b]

**1(11)**: $k_{et} = 6 \times 10^9\ s^{-1}$; $\tau_{cr} = 0.25\ \mu s$;

$$k_{et}{:}k_{cr} = 1.5 \times 10^3$$

**2(9)**: $k_{et} = 1 \times 10^{10}\ s^{-1}$; $\tau_{cr} = 0.42\ \mu s$;

$$k_{et}{:}k_{cr} = 4.2 \times 10^3$$

That the CR process is so slow is unprecedented for simple $C_{60}$-based bichromophoric systems,[7] and we have attributed this to the operation of orbital symmetry effects that are manifested in these (pseudo)symmetric systems.[4b,5b] Notwithstanding these promising results, it is necessary to increase the lifetime of the CS state even more. One way of achieving this is to increase the interchromophore separation. However, this cannot easily be done using simple bichromophoric systems without severely compromising the efficiency of formation of the CS state.

This problem can be circumvented by using polychromophoric systems, i.e., triads, tetrads, pentads, etc.,[8] that constitute a gradient of redox centers arranged within a spatially well-defined array. The principle behind this strategy is illustrated in eq 1 for the case of the covalently

$$D_2{-}D_1^*{-}A \rightarrow D_2{-}D_1^+{-}A^- \rightarrow {}^+D_2{-}D_1{-}A^- \qquad (1)$$

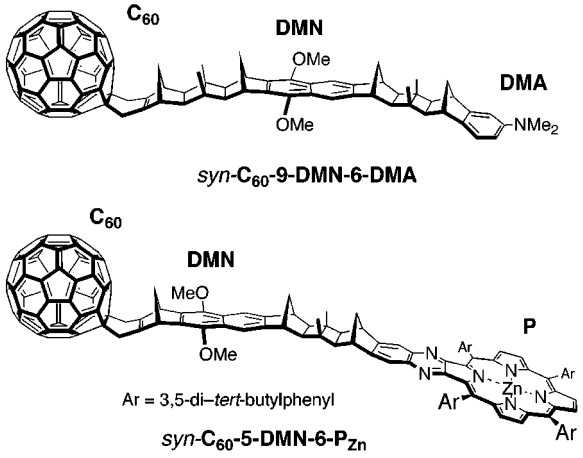
linked triad, $D_2{-}D_1{-}A$, in which $D_1$ is initially locally excited.

In this system, the ET process takes place in a sequence of rapid "hops" between adjacent chromophores that are spanned by a bridge short enough to guarantee that each hop occurs with near unit efficiency. The final result is charge separation over a sufficiently large distance that the unwanted charge-recombination step becomes acceptably slow.

It therefore seemed highly attractive to us to apply this multichromophore approach to our ball-and-chain molecules and to construct trichromophoric ball-and-chain systems. In this way, the combination of increased interchromophore separation, combined with orbital symmetry effects, should make for exceptionally long-lived giant CS states in such systems.

To this end, we have been exploring the synthetic viability of constructing such large trichromophoric ball-and-chain molecules. In this paper, we describe the successful synthesis of two such trichromophoric systems, namely, *syn*-**$C_{60}$-9-DMN-6-DMA** and *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** (Chart 2).[9] The synthesis of these particular trichromophoric systems was undertaken to test out the synthetic methodology rather than to construct an acceptable photovoltaic device. Thus, the use of the dimethoxynaphthalene (DMN) group as the central chromophore was based more on synthetic convenience than on its redox properties. Although this group could act as an intermediate vector of either positive or negative charge, its ability to do so in this situation is questionable.[10] It could, however, mediate charge separation between $C_{60}$ and the terminal donor chromophore (DMA or $P_{Zn}$) by a superexchange mechanism. The variety of groups that we are able to append to the termini of the norbornylogous framework,[6,11] and in particular with $C_{60}$ (Figure 2),[4] means that the methodology described herein can be utilized to form a series of multichromophoric systems with which to screen acceptable photovoltaic devices.

**Chart 2**




## Results and Discussion

**Synthetic Strategy.** The most reasonable retrosynthetic strategies for both *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** and *syn*-**$C_{60}$-9-DMN-6-DMA** are depicted in Schemes 1 and 2, respectively. The strategy involves dissection of the central dimethoxynaphthalene moiety into a *p*-benzoquinone, e.g., **4** or **7**, and a 1,3-diene, e.g., **3** or **6**. There is, of course, stereochemical ambiguity in the Diels–Alder reaction between **3** and **4** and between **6** and **7**, which ultimately gives rise to syn and anti stereoisomers (Scheme 3).[12–17] The ambiguity arises as a result of the

(7) Imahori, H.; Yamada, K.; Hasegawa, M.; Taniguchi, S.; Okada, T.; Sakata, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2626.

(8) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198.

(9) syn refers to the relative spatial disposition of the methano bridges of the two norbornane rings that are fused to the DMN group.

(10) On a more practical note, replacement of the methoxy groups of DMN with stronger donor groups, e.g., amino, would produce a good intermediate charge vector.

(11) (a) Patney, H. K.; Paddon-Row, M. N. *Synthesis* **1986**, 326. (b) Antolovich, M.; Oliver, A. M.; Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 2* **1989**, 783. (c) Golka, A.; Keyte P.; Paddon-Row, M. N. *Tetrahedron* **1992**, *48*, 7663. (d) Golka, A.; Craig, D. C.; Paddon-Row, M. N. *Aust. J. Chem.* **1994**, *47*, 101. (e) Atkinson, E. J.; Oliver, A. M.; Paddon-Row, M. N. *Tetrahedron Lett.* **1993**, *34*, 6147. (f) Black, A. J.; Wooster, T. T.; Geiger, W. E.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1993**, *115*, 7924. (g) Rothenfluh, D. F.; Oliver, A. M.; Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 2* **1996**, 639. (h) Craig, D. C.; Ghiggino, K. P.; Jolliffe, K. A.; Langford, S. J.; Paddon-Row, M. N. *J. Org. Chem.* **1997**, *62*, 2381. (i) Guylas, P. T.; Langford, S. J.; Lokan, N.; Ranesinghe. M. G.; Paddon-Row, M. N. *J. Org. Chem.* **1997**, *62*, 3088.

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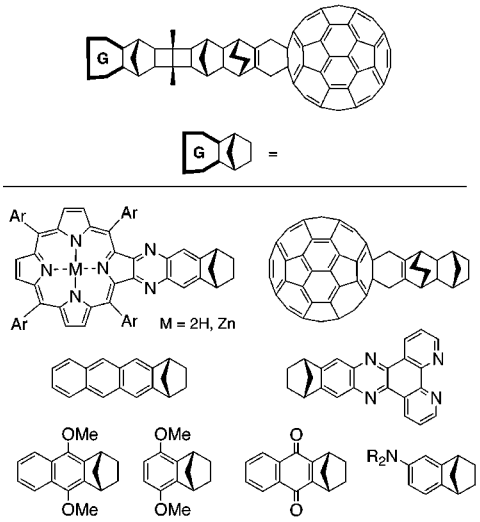
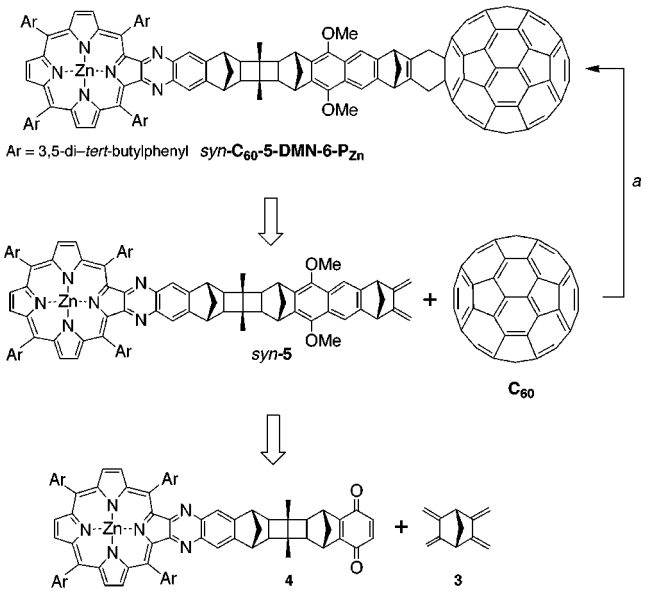



**Figure 2.** Some of the available chromophores that have been appended to the norbornylogous framework with $C_{60}$.

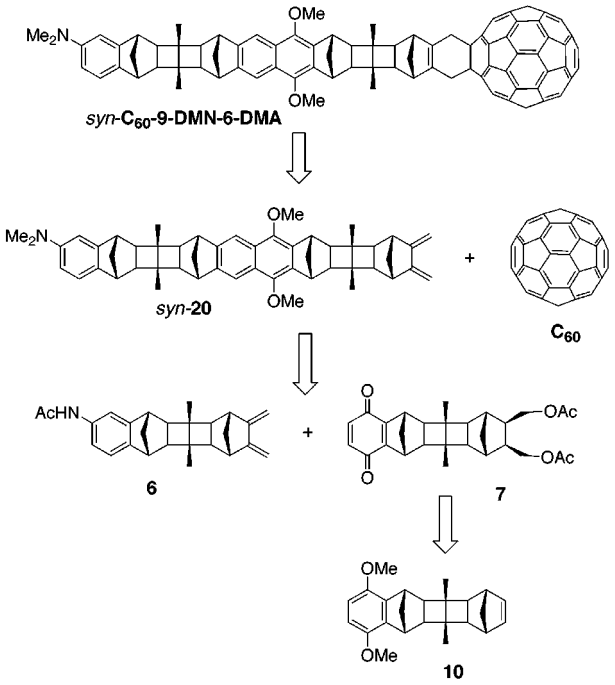
**Scheme 1. Retrosynthetic Considerations for *syn*-$C_{60}$-5-DMN-6-$P_{Zn}$ Lead to 3 and 4 as Key Intermediates**[a]




[a] Synthesis of *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** from *syn*-**5** and $C_{60}$: *a* 1,2-dichlorobenzene, 110 °C, 40 h, Ar.

fact that both the benzoquinone and diene fragments have two diastereotopic $\pi$-faces, which are differentiated by the neighboring methano bridges (Scheme 3) of the norbornane skeleton. The presence of two distinct $\pi$-faces in both quinone and diene fragments means that eight distinct transition states (**I**−**VIII**) may be accessed in the Diels−Alder reaction (Scheme 3). Aromatization of the eight possible cycloadducts will give rise to only two discrete diastereoisomers, namely, syn and anti.[9]

**Scheme 2. Adopted Retrosynthetic Analysis for *syn*-$C_{60}$-9-DMN-6-DMA**




The nature of the $\pi$-facial diastereoselectivity of cycloaddition reactions of the type discussed here has been investigated both computationally and experimentally.[13−17] In brief, norbornane-fused *p*-benzoquinones and exocyclic 1,3-dienes exhibit fairly strong exo and endo facial selectivities, respectively.[13−17] These selectivities are probably the result of a combination of stereoelectronic and torsional influences inherent in the rigid norbornane framework. Thus, in light of these earlier studies, it would be reasonable to assume the reaction between **3** and **4** and between **6** and **7** would proceed via the two pathways involving transition structures **I** and **VII** (Scheme 3) in which the $\pi$-facial diastereoselectivity requirements of both reactants are satisfied. Of these two transition structures, **VII** is energetically less preferred on steric grounds. Consequently, syn addition via transition structure **I** is predicted to predominate, and subsequent oxidative aromatization of the reaction mixture should therefore give rise to a preponderance of the syn stereoisomer.

Indeed, preferred syn adduct formation has been observed in a Diels−Alder reaction similar to those envisaged here.[12] Diels−Alder reaction between the diene **6** and the quinone **8** in the presence of lead(IV) dioxide led to the formation of a 72:28 mixture of the quinones *syn*-**9** and *anti*-**9**, respectively (Scheme 4).[12] Interestingly, the syn and anti diastereoisomers differ substantially in their shape; the syn isomer has a "U-shape", whereas the anti isomer has an "S-shape". A ramification of this difference in shape is that the two diastereomers of **DMA-6-DMN-8-DCV** were found to exhibit significantly different electron-transfer dynamics, which could be explained by the occurrence of solvent-mediated charge recombination taking place within the U-shaped cavity of the syn isomer.[18−20] Hence, the synthetic strategies

(13) Mehta, G.; Padma, S.; Pattabhi, V.; Pramanik A.; Chandraselhar, J. *J. Am. Chem. Soc.* **1990**, *112*, 2942.
(14) (a) Paquette, L. A.; Carr, R. V. C.; Bohm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Bohm, M. C.; Carr, R. V. C.; Gleiter R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218.
(15) Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3642.
(16) (a) Paquette, L. A. in *Stereochemistry and Reactivity of Systems Containing π-Electrons*; Watson, W. H., Ed.; Verlag: Deerfield Beach, FL, 1983; Chapter 2. (b) Gleiter R.; Bohm, M. C. *ibid*.; Chapter 4.
(17) Brown F. K.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 1971.
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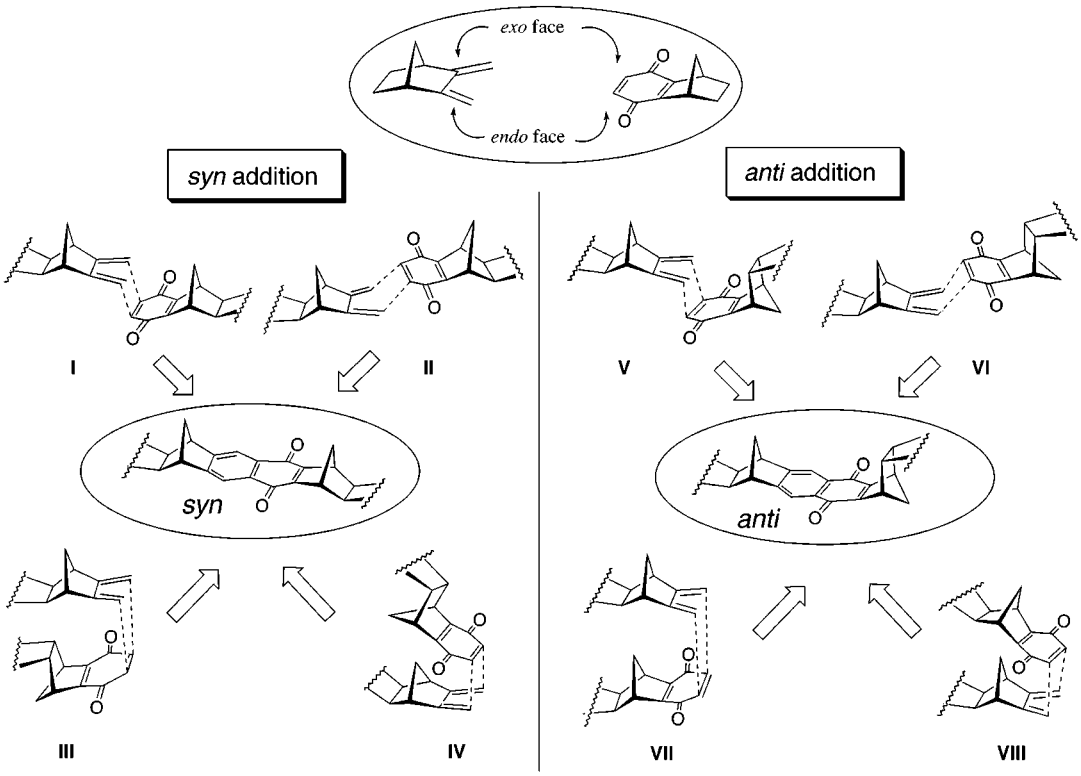
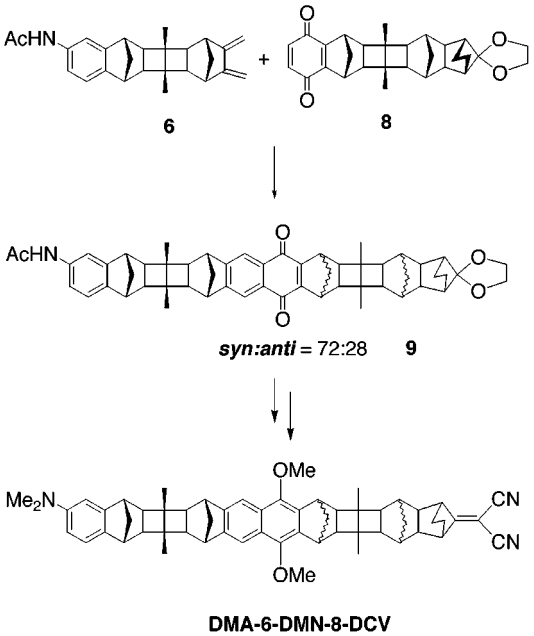
**Scheme 3. Eight Possible Intermediates Arising from the Diels–Alder Reaction between Norbornane-Based 1,3-Exocyclic Dienes and *p*-Benzoquinones**[a]




[a] The exo and endo faces of each species are indicated. Oxidation of the adducts gives rise to the two syn and anti diasteroisomers.

**Scheme 4**[a]




[a] The Diels–Alder rection of **6** and **8** gives rise to two separable diasteroisomers. Further transformations gives rise to the trichromophore **DMA-6-DMN-8-DCV**. A difference in ET dynamics was seen between the syn and anti isomers.

adopted in this paper have been applied to the preparation of one isomer, as a means of exploring this phenomena further.

**Synthesis.** The synthesis of *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** was achieved in a straightforward manner by heating a solution of the known[21] diene *syn*-**5** and $C_{60}$ (2 equiv) in dry, degassed 1,2-dichlorobenzene at 110 °C in the absence of light for 40 h. The desired cycloadduct *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** was obtained in 93% yield after chromatography on silica gel. An excess of $C_{60}$ was used to preclude the formation of any significant amount of higher addition products. Matrix-assisted laser desorption and ionization (MALDI) mass spectrometry yielded a peak centered at 2412 mass units, which is consistent with the molecular weight of *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$**. The $^1$H and $^{13}$C NMR spectra of the adduct are consistent with the proposed structure for *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$**. In particular, the allylic $CH_2$ protons of the cyclohexene ring that is fused to the $C_{60}$ unit appear as an AB quartet centered at $\delta$ 4.02, which is a hallmark of $C_{60}$ Diels–Alder monoadducts of the type *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$**.[4a] Also diagnostic are the $^{13}$C resonances at $\delta$ 61.3 and 66.3, which respectively correspond to the allylic $CH_2$ carbons of the cyclohexene ring and the $sp^3$ carbons within the $C_{60}$ framework.[4a]

Retrosynthetic considerations (Scheme 2) for *syn*-**$C_{60}$-9-DMN-6-DMA** give the diene **6** and the dimethoxybenzene system **10**, both having been previously synthesized.[4a,22] Stille–Vogel bismethoxycarbonylation[23] of

(20) Roest, M. R.; Verhoeven, J. W.; Schuddeboom, W.; Warman, J. M.; Lawson J. M.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1996**, *118*, 1762.

(21) Jolliffe, K. A.; Bell, T. D. M.; Ghiggino, K.; Langford, S. J.; Paddon-Row, M. N. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 916.

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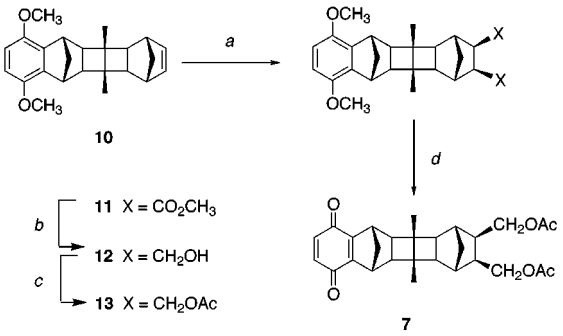
(23) (a) James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810. (b) Stille, J. K.; Divakaruni, R. *J. Org. Chem.* **1979**, *44*, 3474. (c) Mahaim, C.; Carrupt, P.-A.; Hagenbuch, J.-P.; Florey, A.; Vogel, P. *Helv. Chim. Acta* **1980**, *63*, 1149. (d) Jolliffe, K. A.; Paddon-Row, M. N. *Tetrahedron* **1995**, *51*, 2689.

**Scheme 5**[a]




[a] *a* $CuCl_2$, CO, MeOH, Pd/C; *b* $LiAlH_4$, THF; *c* $Ac_2O$, py, DMAP; *d* AgO, 6 N $HNO_3$.

olefin **10** ($CuCl_2$, CO, Pd/C, MeOH) gave the corresponding diester **11** in high yield (Scheme 5). Reduction of the diester ($LiAlH_4$, THF) to the corresponding diol **12** and acetylation ($Ac_2O$, py) gave the diester **13**, which could be easily oxidized (AgO, $HNO_3$) to the corresponding quinone **7**, again in high yield.

Heating a THF solution of diene **6** and quinone **7** in the presence of $PbO_2$ led to the formation of the naphthoquinone diester **14** in 61% yield as an inseparable mixture of syn and anti diastereomers (Scheme 6). The purpose of the $PbO_2$ was to oxidize the initial cycloadduct directly to the naphthoquinone. At this stage, it was necessary to reductively bismethylate the naphthoquinone group to the corresponding dimethoxynaphthalene derivative, hopefully separate the two diastereoisomers, and then introduce the 1,3-diene functionality. Reductive bismethylation ($Na_2S_2O_4$, KOH, $Me_2SO_4$) followed by saponification of the two ester groups (MeOH, NaOMe) gave the DMN-based diol **16** in 86% yield. Separation of the two diastereomers by means of column chromatography gave pure *syn*-**16** and *anti*-**16** in a 2:1 ratio. Although we cannot assign syn or anti stereochemistry to either stereoisomer with absolute certainty, precedence from similar Diels–Alder reactions,[13,22,24–26] together with the observed 2:1 ratio of isomers produced, strongly suggests that the major isomer has syn stereochemistry. Conversion of the putative *syn*-**16** diol to the corresponding *syn*-**18** diene was achieved in two steps by means of standard procedures (Scheme 6). Deprotection of the acetamide *syn*-**18** (KOH, aquous EtOH) followed by reductive alkylation ($CH_2O$, $NaCNBH_3$) of the amine gave *syn*-**20** in 81% yield. Finally, diene *syn*-**20** was heated with $C_{60}$ (2 equiv) in dry, degassed 1,2-dichlorobenzene at 120–125 °C under an inert atmosphere for 12 h to yield the corresponding triad *syn*-**$C_{60}$-9-DMN-6-DMA** in 45% yield after chromatography. The $^1H$ and $^{13}C$ NMR spectra of the adduct are consistent with the proposed structure, i.e., the presence of the AB quartet of allylic proton resonances centered at $\delta$ 3.97 and carbon resonances at $\delta$ 61.3 and $\delta$ 65.2 attributable, respectively, to the two equivalent allylic carbons and the pair of equivalent $sp^3$ carbons within the $C_{60}$ framework.[4a] Unfortunately, *syn*-**$C_{60}$-9-DMN-6-DMA** did not give a parent ion using MALDI mass spectrometry.[4a] Nevertheless, the assigned structure for this triad is secure.

**Conformational Analysis.** Neither *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** nor *syn*-**$C_{60}$-9-DMN-6-DMA** is completely rigid, because the flexing of the cyclohexene ring in these systems gives rise to two conformations, namely, "extended" and "folded" (Figure 3). Because these conformers may influence the dynamics of ET differently, it was of interest to calculate their relative energies and geometries. Geometry optimizations were carried out at the semiempirical AM1 theoretical level[27] by means of the Spartan suite of programs.[28] In the case of *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$**, the four aryl groups of the zinc–porphyrin were omitted for reasons of computational feasibility. Although no symmetry constraints were applied to the geometry optimizations, the extended and folded conformations of both *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** and *syn*-**$C_{60}$-9-DMN-6-DMA** possess approximate $C_s$ symmetry. Heats of formation of the conformers are summarized in Table 1, and the profiles of their optimized geometries are shown in Figure 3.

Both the extended and folded conformations are approximately "U-shaped". However, in the case of the extended conformation, the fullerene unit points away from the cavity, whereas in the case of the folded conformation, the fullerene occupies part of the cavity. As a result of these differences, the separation, $R$,[29] between the terminal chromophores is only ca.10 Å in the folded conformers compared to ca. 16 Å in the extended conformers. This sizable difference in interchromophore separation between the folded and extended conformers may have consequences for the dynamics of ET processes in these molecules. Thus, the smaller separation between the terminal chromophores in the folded conformation may permit solvent-mediated ET to take place between the $C_{60}$ and the porphyrin (or DMA) groups, thereby creating a "short-circuit" for both CS and CR processes.[17–19,30] This situation is far less likely to occur in the case of the extended conformer.

The folded and extended conformers for each system have nearly identical heats of formation, with the extended conformation being marginally preferred by less than 0.2 kcal/mol (Table 1).[31] This is borne out by the fact that the cyclohexene folding angle, $\theta$, (the angle between the two mean planes of the cyclohexene ring), has nearly the same magnitude, 139.5 ± 0.5° (Table 1), in the two conformations of either system, which indicates the lack of electrostatic interactions between the terminal chromophores in the folded conformation. How-

(24) Pilet, O.; Vogel, P. *Helv. Chim. Acta* **1981**, *64*, 2563.

(25) The synthetic sequence adopted for the preparation of *syn*-**5** from **3** and **4**, NMR analysis justifying stereochemistry, and characterization data will be shortly presented: Jolliffe, K. A.; Ball, G.; Langford, S. J.; Paddon-Row, M. N.; Oliver, A. M.; Salek, A., unpublished results.

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(27) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

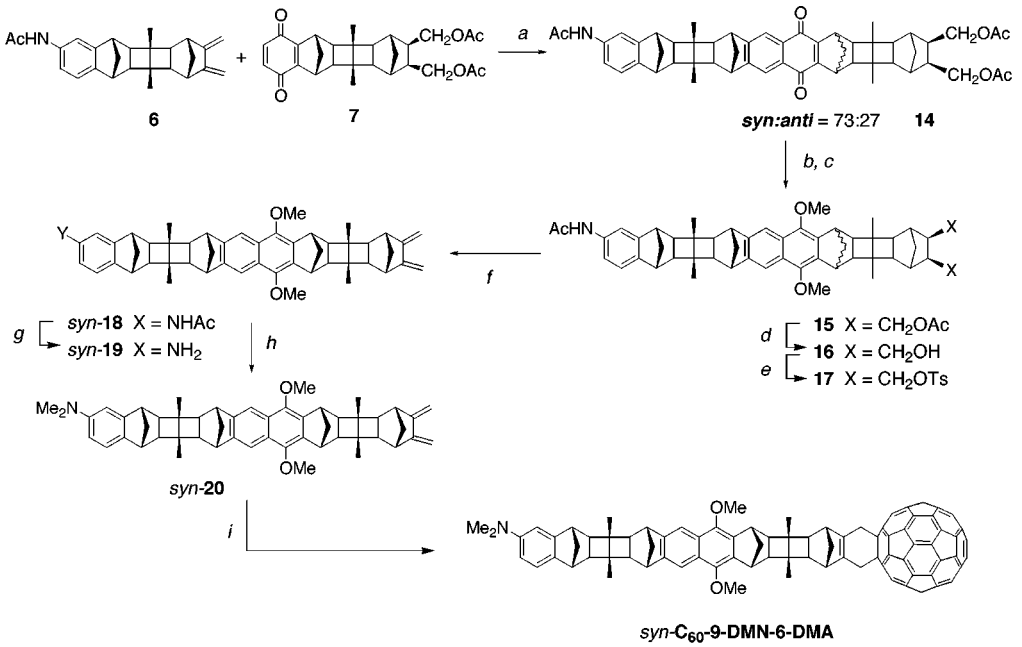
(28) Spartan, version 4.0; Wavefunction, Inc.: Irvine, CA.

(29) $R$ is defined to be the distance between the center of the non-$C_{60}$ terminal chromophore and the surface of the $C_{60}$ moiety.

(30) (a) Clayton, A. H. A.; Ghiggino, K. P.; Lawson, J. M.; Paddon-Row, M. N. *J. Photochem. Photobiol., A* **1994**, *80*, 323. (b) Kumar, K.; Lin, Z.; Waldeck, D. H.; Zimmt, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 243.

(31) Shephard, M. J.; Paddon-Row, M. N. *Aust. J. Chem.* **1996**, *49*, 395. Within this reference, AM1 level conformational analysis studies on $C_{60}$–cyclohexene–norbornolygous bridge bichromophoric systems predict that the extended conformer is usually slightly preferred (by less than 0.3 kcal/mol) and that the cyclohexene folding angle, $\theta$, varies little (137–140°) between conformations and between systems. At the ab initio HF/3-21G level (using AM1 optimized geometries) there is a mixed preference between the folded and the extended conformations, depending on the system, and the relative energies between the two conformations are predicted to be ca. 1–5 kcal/mol larger than the AM1 results.

**Scheme 6**[a]




[a] *a* $PbO_2$, THF, 90 °C, sealed tube, 2 d; *b* $Na_2S_2O_4$, THF, 40 °C, 2 h; *c* KOH, $Me_2SO_4$, 3−4 h; *d* Na, MeOH, Ar, 2 h, separate isomers. To syn isomer: *e* *p*-TsBr, $CH_2Cl_2$, py, −5 °C, 2 h; *f* $^t$BuOK, THF, Rt, Ar, 2 h; *g* KOH, EtOH; *h* 40% aq. HCHO, $NaBH_3CN$, MeCN, THF, AcOH; *i* $C_{60}$, 1,2-dichlorobenzene, 120−125 °C, sealed tube, 12 h.

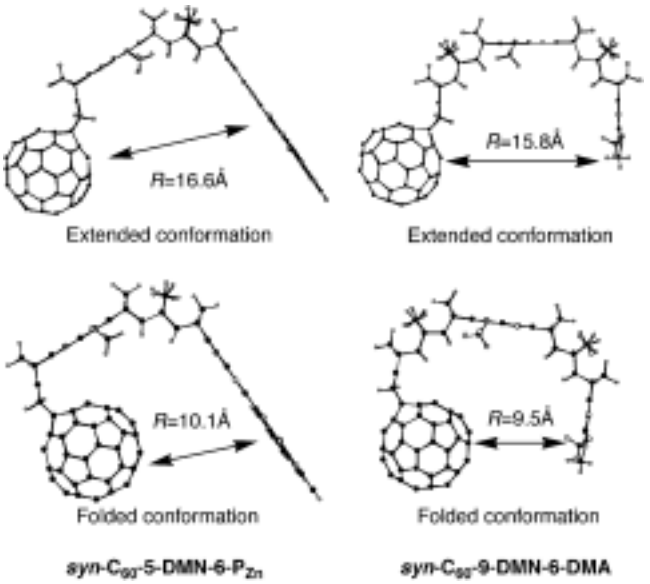



**Figure 3.** AM1 level optimized geometries for the folded and extended conformations of the *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** and *syn*-**$C_{60}$-9-DMN-6-DMA** systems. *R* is the closest separation between the $C_{60}$ and the center of the non-$C_{60}$ terminal chromophore.

ever, the AM1 method may underestimate favorable long-range electrostatic interactions between the two terminal chromophores, which would tend to favor the folded conformation.

Experimentally, the crystal structure of the $C_{60}$-dimethoxybenzene analogue of **1(11)** showed that the extended conformation is preferred, although this preference may be due to crystal packing effects.[32] A $^1$H NMR line-shape analysis of this bichromophore indicated that both conformers are present in solution and that one is preferred by ca. 0.65 kcal/mol over the other (at 173 K).[32] In the case of 61-hydroxy-1,9-(methano[1,2]benzo-methano)fullerene[60], the free-energy difference between the two conformers is also small and was determined to be 0.19 kcal/mol.[33] An estimation of the barrier height to interconversion between the folded and extended conformers was not calculated for *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** and *syn*-**$C_{60}$-9-DMN-6-DMA** because the AM1 method is known to underestimate its magnitude.[31] NMR analysis of these systems was also not possible due to encountered solubility problems at low temperatures in $CD_2Cl_2$ or $CD_3COCD_3$ solution.

If *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** and *syn*-**$C_{60}$-9-DMN-6-DMA** are found to undergo photoinduced ET to give the giant CS states *syn*-$^-$**$C_{60}$-5-DMN-6-$P_{Zn}^+$** and *syn*-$^-$**$C_{60}$-9-DMN-6-DMA**$^+$, respectively, then the harpooning mechanism[34] should convert the CS extended conformations into the Coulomb-stabilized folded conformations. Therefore, these CS states may experience very rapid charge recombination, because it could proceed via a solvent-mediated pathway in the folded conformations.

**Conclusions.** We have describe the successful synthesis of two trichromophoric ball-and-chain systems, namely, *syn*-**$C_{60}$-9-DMN-6-DMA** and *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$,** in which the three chromphores in each system are linked via rigid, norbornylogous hydrocarbon bridges. In both cases, the ball-and-chain systems are prepared by a convergent approach, in which the central chromophore is built using Diels−Alder chemistry. The nature of the norbornane-based exocyclic-1,3-dienes and dienophiles employed in the Diels−Alder reaction gives rise to the formation of syn and anti adducts, which may be separated. The results of AM1 calculations carried out on these systems indicate that the extended and folded

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**Table 1. AM1 Calculated Heat of Formation, $\Delta H_f$,[a] Interchromophore Separation, *R*, and Cyclohexene Folding Angle, $\theta$,[b] for the Folded and Extended Conformers of *syn*-$C_{60}$-5-DMN-6-$P_{Zn}$ and *syn*-$C_{60}$-9-DMN-6-DMA**

| system | conformation | $\Delta H_f$ (kcal/mol)[a] | *R* (Å) | $\theta$ (deg)[b] |
|---|---|---|---|---|
| *syn*-$C_{60}$-5-DMN-6-$P_{Zn}$ | extended | 1373.12 (0.0) | 16.6 | 139.0 |
| | folded | 1373.26 (0.14) | 10.1 | 139.9 |
| *syn*-$C_{60}$-9-DMN-6-DMA | extended | 1125.80 (0.0) | 15.8 | 139.2 |
| | folded | 1125.84 (0.04) | 9.5 | 140.0 |

[a] Values in parentheses are the relative energies (in kcal/mol) between the extended and folded conformations for both systems. [b] The (acute) angle between the two mean planes of the cyclohexene ring.

conformations for each trichromophore are essentially energetically degenerate and that the terminal chromophores in the folded conformation in each system are sufficiently close to each other to allow the possibility for solvent-mediated CS and CR processes to take place.

## Experimental Section

**General.** Chemicals were purchased from Aldrich and used as received. Solvents were dried, and reagents were purified where necessary using literature methods.[35] Compounds **6** and **10** were prepared according to published literature.[22] Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with Merck 5735 Kieselgel 60F. Column chromatography was carried out using Kieselgel 60 (0.040−0.063 mm mesh, Merck 9385). Melting points are uncorrected. Microanalyses were carried out by Dr. H. Pham of the School of Chemistry, UNSW. Low-resolution mass spectra (MS) were obtained using either electron impact (EIMS) or matrix-assisted laser desorption (MALDI) mass spectrometry in conjunction with a 3,5-dihydrobenzoic acid matrix recoded in the negative ion mode with relatively low laser power. Nuclear magnetic resonance (NMR) spectra were recorded at 300 MHz for proton frequency and 75 MHz for carbon frequency using the DEPT pulse sequence.

***syn*-$C_{60}$-5-DMN-6-$P_{Zn}$.** To a degassed solution of diene *syn*-**5**[21] (50 mg, 0.03 mmol) in *o*-dichlorobenzene (4 mL) was added $C_{60}$ (52 mg, 0.07 mmol). The reaction mixture was heated to 110 °C in the dark under argon for 40 h. After cooling to room temperature, the reaction mixture was chromatographed on silica (toluene), and the two major bands collected. The faster moving purple band was identified as the excess $C_{60}$ (23 mg). The lower running and major green-brown band was also collected, and removal of the solvent gave *syn*-**$C_{60}$-5-DMN-6-$P_{Zn}$** as a green-brown powder (66 mg, 93%): mp >300 °C;$^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.03 (6H, s), 1.43 (18H, s), 1.48 (18H, s), 1.52 (36H, s), 1.71 (1H, d, $J$ = 6.1 Hz), 1.85 (2H, s), 2.01 and 2.04 (2H, ABq, $J$ = 6.1 Hz), 2.62 and 2.75 (2H, ABq, $J$ = 6.8 Hz), 3.52 (2H, s), 3.54 (2H, s), 3.69 (6H, s), 3.98 and 4.08 (4H, ABq, $J$ = 15.4 Hz), 4.24 (2H, s), 7.52 (2H, s), 7.62 (2H, s), 7.77 (2H, t, $J$ = 1.8 Hz), 7.87 (2H, t, $J$ = 1.8 Hz), 7.92 (2H, bs), 8.08 (2H, t, $J$ = 1.6 Hz), 8.11 (2H, t, $J$ = 1.6 Hz), 8.43 (2H, bs), 8.88 (2H, s), 9.01 and 9.07 (2H, ABq, $J$ = 4.7 Hz); $^{13}$C NMR ($CDCl_3$, 500 MHz) $\delta$ 9.1, 29.6, 30.8, 31.6, 31.7, 31.8, 32.0, 34.8, 34.9, 34.9, 40.2, 41.7, 42.4, 42.6, 43.5, 51.3, 51.6, 53.3, 53.4, 61.5, 64.6, 66.3, 115.3, 119.4, 120.2, 120.7, 120.7, 124.1, 126.1, 128.4, 129.2, 129.2, 129.5, 131.2, 131.5, 132.1, 134.0, 134.7, 134.7, 138.5, 139.2, 140.7, 140.7, 140.8, 140.9, 141.2, 141.5, 141.7, 141.7, 141.9, 142.7, 142.9, 142.9, 143.1, 143.2, 144.6, 144.8, 147.4, 148.3, 148.4, 148.4, 148.9, 149.6, 149.9, 150.2, 152.2, 152.9, 155.7, 156.2; MALDI MS *m*/*z* 2412 $[M + 2]^+$.

**Diester 11.** To a suspension of olefin **10**[4a] (5.0 g, 14.5 mmol), anhydrous copper(II) chloride (7.7 g, 57 mmol), and anhydrous NaOAc (4.7 g, 57 mmol) in dry MeOH (450 mL) and THF (350 mL) was added 10% Pd/C (300 mg), and the flask was flushed with carbon monoxide. A balloon of carbon monoxide was attached, and the mixture was stirred at room temperature for 2 days. Once complete, the mixture was poured into water (200 mL) and $CH_2Cl_2$ (200 mL), and the resulting suspension was filtered through a pad of filter aid. The aqueous layer was extracted with $CH_2Cl_2$ (3 × 200 mL), and the organic layers were combined and washed with water (100 mL) and a saturated sodium carbonate solution (100 mL) until the blue color disappeared. The organics were dried over anhydrous $Na_2SO_4$, and the solvent was removed under reduced pressure to yield an off-white solid. This solid was recrystallized from EtOH to give **11** as a white solid (5.6 g, 83%): mp 248−250 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (6H, s), 1.53 (1H, d, $J$ = 9.2 Hz), 1.68 (2H, m), 1.96 (4H, m), 2.09 (1H, d, $J$ = 9.2 Hz), 2.47 (2H, s), 2.55 (2H, $J$ = 1.8 Hz), 3.49 (2H, s), 3.61 (6H, s), 3.79 (6H, s), 6.67 (2H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.3, 32.5, 40.1, 40.1, 43.3, 43.7, 49.8, 49.7, 51.4, 51.6, 56.0, 109.0, 136.5, 147.7, 173.5; EI MS *m*/*z* 466 ($M^+$), 435, 176. Anal. Calcd for $C_{28}H_{34}O_6$: C, 72.1; H, 7.4. Found: C, 72.4; H, 7.4.

**Diacetate 13.** A solution of diester **11** (5.0 g, 10.7 mmol) in dry THF (50 mL) was added to a suspension of lithium aluminum hydride (0.82 g, 21.5 mmol) in dry THF (100 mL), and the mixture was heated at reflux overnight. Once complete, the reaction mixture was cooled in an ice bath, and the excess $LiAlH_4$ was quenched by the slow addition of water (2 mL), a NaOH solution (15%, 5 mL), and more water (5 mL). The mixture then was heated at reflux for 30 min, cooled to room temperature, and filtered through a small plug of filter aid. The filtrate was evaporated to give diol **12** as a white solid, which was not purified and was used as is in the following step: $^1$H NMR ($CDCl_3$) $\delta$ 0.81 (s, 6H), 1.30 (d, $J$ = 9.0 Hz, 1H), 1.42 (d, $J$ = 9.0 Hz, 1H), 1.52 (d, $J$ = 8.5 Hz, 1H), 1.70 (d, $J$ = 8.5 Hz, 1H), 1.82 (m, 2H), 1.88 (s, 2H), 1.95 (s, 2H), 2.00 (s, 2H), 3.46 (s, 2H), 3.58−3.70 (m, 4H), 3.76 (s, 6H), 6.58 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.2, 31.6, 40.0, 40.5, 43.2, 47.4, 49.6, 52.1, 55.9, 63.3, 108.9, 136.5, 147.6.

To an ice-cold solution of diol **12** (4.3 g) in THF (100 mL) were added acetic anhydride (10 mL), pyridine (10 mL), and DMAP (50 mg). The mixture was allowed to warm to room temperature and stirred overnight. Water (200 mL) was added, and the product was extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layer was washed with water (100 mL), saturated copper sulfate solution (100 mL), sodium bicarbonate solution (10%, 100 mL), and brine (100 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed, and the white solid was purified by column chromatography (hexane/ethyl acetate) and then recrystallized from MeOH to give **13** (4.8 g, 90%): $^1$H NMR ($CDCl_3$) $\delta$ 0.87 (s, 6H), 1.42 (m, 2H), 1.52 (d, $J$ = 9.0 Hz, 1H), 1.72 (d, $J$ = 9.0 Hz, 1H), 1.81 (m, 2H), 1.97 (s, 2H), 1.99 (s, 2H), 2.04 (s, 6H), 2.06 (s, 2H), 3.47 (s, 2H), 3.78 (s, 6H), 3.93−4.04 (m, 4H), 6.59 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.3, 21.0, 30.1, 39.7, 40.1, 43.1, 43.2, 43.4, 49.7, 51.9, 55.9, 63.9, 108.9, 136.5, 147.7, 170.9. Anal. Calcd for $C_{28}H_{34}O_6$: C, 72.8; H, 7.7. Found C, 72.5; H, 7.9.

**Quinone 7.** To a solution of **13** (2.0 g, 4.1 mmol) in dioxane (10 mL) was added silver(II) oxide (2.0 g, 16.2 mmol), followed by a dilute nitric acid solution (6 N, 4 mL) dropwise over 10 min. The reaction mixture was stirred at room temperature for another 10 min or until all the silver oxide dissolved. Water (25 mL) and $CHCl_3$ (25 mL) were added, and the product was extracted with $CH_2Cl_2$ (2 × 100 mL). The organic layer was dried over anhydrous $Na_2SO_4$, and the solvent was removed to give a yellow oil, which was purified by column chromatography ($CH_2Cl_2$) to give **7** as a yellow solid that decomposed on prolonged standing (1.7 g, 91%): $^1$H NMR ($CDCl_3$) $\delta$ 0.81 (s, 6H), 1.39−1.51 (m, 3H), 1.56 (d, $J$ = 10.2 Hz, 1H), 1.80 (m, 2H), 1.94 (s, 2H), 1.98 (s, 2H), 2.02 (s, 6H), 2.08 (s, 2H), 3.36

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(s, 2H), 3.88−4.04 (m, 4H), 6.54 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.2, 20.9, 30.0, 39.7, 40.9, 41.4, 43.0, 43.4, 48.3, 51.8, 63.7, 67.0, 136.1, 151.3, 170.8, 183.9; EI MS *m*/*z* 464 ($M^+$), 421, 378, 344, 275.

***syn*- and *anti*-14.** A solution of **7** (0.81 g, 1.77 mmol), **6**[22] (0.65 g, 1.76 mmol), and lead dioxide (1.0 g) in dry THF (5.0 mL) was placed in a sealed tube and heated at 90 °C for 2 days. After cooling to room temperature, the reaction mixture was diluted by with EtOAc (25 mL) and filtered through a small plug of silica to remove the lead oxide residue. The filtrate was evaporated to dryness, and the crude product was purified by column chromatography (1:1 EtOAc/light petroleum) to give the cycloadduct **14** as a mixture of syn and anti isomers (900 mg, 61%). This was carried through to next step without further purification: $^1$H NMR ($CDCl_3$) $\delta$ 0.84 (s, 6H), 0.87 (s), 0.99 (s, 6H), 1.47 (m, 4H), 1.63 (m, 3H), 1.74 (s, 2H), 1.81 (m, 6H), 1.95 (s, 2H), 1.98 (s, 2H), 2.02 (s, 6H), 2.03 (s, 6H), 2.07 (s, 3H), 2.11 (s, 2H), 3.18 (d, $J$ = 6.5 Hz, 1H), 3.24 (d, $J$ = 6.18 Hz, 2H), 3.38 (s, 2H), 3.43 (m, 1H), 3.49 (s, 2H), 4.08−3.89 (m, 4H), 7.04 (s, 1H), 7.05 (s, 1H), 7.23 (s, 1H), 7.40 (d, 1H), 7.79 (m, 2H).

To a solution of the diastereomeric mixture *syn*- and *anti*-**14** (0.90 g, 1.09 mmol) in THF (10 mL) were added water (20 mL), sodium dithionate (4.5 g), tetra-*n*-butylammonium iodide (50 mg), and sodium bicarbonate (2.0 g). The resultant mixture was stirred and heated at 40 °C for 2 h. Once complete, the reaction mixture was cooled to room temperature, solid KOH (900 mg) was added, and the reaction mixture was stirred for 2 h at room temperature. Once this time elapsed, excess dimethylsulfate (15 mL) was added, and the reaction mixture was stirred at room temperature for 3−4 h. The excess dimethylsulfate was quenched by adding ammonium hydroxide solution (15 N, 50 mL). The mixture was extracted with $CH_2Cl_2$ (2 × 100 mL). The combined $CH_2Cl_2$ layers were washed with water (100 mL), sodium bicarbonate solution (10%, 100 mL), and brine (100 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave the diastereomeric mixture of *syn*- and *anti*-**15** as a brown solid. $^1$H NMR ($CDCl_3$) $\delta$ 0.91 (s, 6H), 1.01 (s, 6H), 1.40−1.90 (m, 8H), 1.94 (s, 2H), 1.98 (s, 2H), 2.02 (s, 6H), 2.04, (s, 2H), 2.08 (s, 2H), 2.11 (s, 2H), 2.16 (s, 2H), 3.32 (m, 2H), 3.38 (s, 2H), 3.60 (s, 2H), 3.93 (s, 6H), 4.02−4.04 (m, 4H), 7.04 (m, 2H), 7.14 (m, 1H), 7.37 (s, 1H), 7.77 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.4, 14.1, 19.7, 20.9, 22.6, 24.3, 28.2, 30.1, 39.7, 40.3, 40.4, 42.5, 42.7, 42.9, 43.0, 43.2, 43.6, 43.7, 43.9, 50.1, 50.4, 50.7, 51.9, 53.4, 54.5, 58.6, 61.6, 63.9, 71.6, 112.7, 113.5, 116.9, 120.6, 126.4, 134.1, 135.6, 143.8, 144.4, 145.7, 148.5, 168.2, 170.9.

Diacetate **15** was dissolved in dry MeOH (10 mL) and treated with sodium metal (10 mg) with stirring, under argon for 2 h. The reaction was quenched by adding water (50 mL) and extracted into $CHCl_3$ (2 × 100 mL). The $CHCl_3$ layer was washed with water (100 mL) and brine (100 mL) and dried over anhydrous $Na_2SO_4$; the solvent was removed to give a mixture of *syn*-**16** and *anti*-**16** as a white solid. The diastereomers were successfully purified by column chromatography (EtOAc/light petroleum; 1:1). ***anti*-16**, white solid (201 mg, 23%): $^1$H NMR ($CDCl_3$) $\delta$ 0.80 (s, 6H), 0.99 (s, 6H), 1.23 (d, $J$ = 7.2 Hz, 1H), 1.33 (d, $J$ = 7.2 Hz, 1H), 1.50−2.00 (m, 8H), 1.89 (s, 2H), 1.93 (s, 2H), 2.00 (s, 2H), 2.06 (s, 3H), 2.16 (s, 2H), 3.19 (s, 2H), 3.32−3.40 (m, 2H), 3.55 (s, 2H), 3.57 (s, 1H), 3.60−3.77 (m, 3H), 3.93 (s, 6H), 7.00 (s, 2H), 7.36 (s, 1H), 7.50 (s, 1H), 7.76 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.4, 24.3, 26.3, 31.6, 40.3, 40.5, 42.8, 42.9, 43.2, 43.6, 43.8, 43.9, 47.5, 50.2, 50.4, 50.7, 52.2, 61.7, 63.3, 112.7, 113.7, 117.1, 120.7, 126.5, 134.2, 135.2, 144.4, 145.7, 149.0, 168.4. ***syn*-16**, white solid (530 mg, 63%): $^1$H NMR ($CDCl_3$) $\delta$ 0.86 (s, 6H), 0.99 (s, 6H), 1.35 (d, $J$ = 8.0 Hz, 1H), 1.45 (d, $J$ = 8.0 Hz, 1H), 1.60−1.75 (m, 4H), 1.80−2.10 (m, 4H), 1.84 (s, 2H), 1.91 (s, 2H), 1.94 (s, 2H), 1.98 (s, 2H), 2.10 (s, 3H), 3.21 (s, 1H), 3.23 (s, 1H), 3.37 (s, 2H), 3.59 (s, 2H), 3.70 (m, 4H), 3.94 (s, 6H), 7.02 (s, 2H), 7.20 (s, 1H), 7.37 (s, 2H), 7.77 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.4, 24.2, 31.5, 40.4, 42.8, 43.2, 43.6, 43.7, 47.4, 50.2, 50.6, 50.7, 52.2, 53.4, 61.7, 63.2, 112.6, 113.7, 117.2, 120.6, 126.4, 134.2, 135.3, 143.9, 144.4, 145.7, 148.4, 168.7. Anal. Calcd for $C_{52}H_{59}O_5N$: C, 80.3; H, 7.6; N, 1.8. Found: C, 79.6; H, 7.6; N, 1.7.

**Diene *syn*-18.** To a solution of *syn*-**16** (225 mg, 0.29 mmol) in $CH_2Cl_2$ (10 mL) at −5 °C were added *p*-toluenesulfonylbromide (275 mg, 1.16 mmol) and pyridine (1 mL), and the reaction was stirred at −5 °C for 2 h. Water (50 mL) was added, and the product was extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic layer was washed in turn with dilute HCl (1.0 M, 50 mL), water (50 mL), a saturated copper sulfate solution (50 mL), and brine (50 mL) and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent gave ditosylate, a white solid that was purified by column chromatography (dichloromethane) to yield *syn*-**17** as a white solid (250 mg, 79%): $^1$H NMR ($CDCl_3$) $\delta$ 0.80 (s, 6H), 0.97 (s, 6H), 1.25 (m, 1H), 1.5−1.7 (m, 2H), 1.70−2.00 (m, 7H), 1.81 (s, 2H), 1.91 (s, 2H), 1.96 (s, 2H), 2.04 (s, 2H), 2.06 (s, 3H), 2.43 (s, 6H), 3.18 (s, 2H), 3.35 (s, 2H), 3.56 (s, 2H), 3.81−3.90 (m, 4H), 3.92 (s, 6H), 7.00 (s, 2H), 7.34 (m, 5H), 7.75 (m, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.3, 9.4, 14.9, 21.5, 24.2, 30.1, 37.3, 39.3, 40.2, 42.6, 42.8, 43.1, 43.5, 43.9, 50.1, 50.4, 50.5, 50.6, 51.3, 51.5, 61.6, 66.2, 69.4, 112.6, 113.5, 116.9, 120.5, 126.4, 127.7, 129.8, 132.6, 133.9, 135.3, 143.7, 144.3, 144.9, 145.7, 148.4, 168.3.

To a solution of the ditosylate *syn*-**17** (250 mg, 0.23 mmol) in dry DMSO (10 mL) was added a solution of potassium *tert*-butoxide (1.3 M, 1 mL, 1.3 mmol) in dry THF, and the reaction mixture was stirred at room temperature under argon for 2 h. Water (50 mL) was added, and the product was extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL) and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent gave a white solid that was purified by column chromatography (EtOAc/light petroleum; 1:1) to yield *syn*-**18** as a white solid (124 mg, 75%): $^1$H NMR ($CDCl_3$) $\delta$ 0.94 (s, 6H), 1.01 (s, 6H), 1.45 (m, 1H), 1.60 (m, 2H), 1.70 (m, 2H), 1.80−1.90 (m, 4H), 1.97 (s, 4H), 2.06 (s, 2H), 2.06−2.07 (m, 1H), 2.08 (s, 3H), 2.13 (s, 2H), 2.73 (s, 2H), 3.22 (s, 2H), 3.39 (s, 2H), 3.62 (s, 2H), 3.94 (s, 6H), 4.74 (s, 2H), 5.07 (s, 2H), 7.01 (s, 2H), 7.10 (s, 1H), 7.37 (s, 1H), 7.78 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.4, 24.3, 34.9, 40.4, 42.9, 43.2, 43.6, 43.7, 43.9, 44.3, 45.4, 50.2, 50.4, 50.5, 50.6, 100.1, 112.7, 113.6, 117.0, 120.6, 126.4, 134.2, 135.2, 143.9, 144.4, 145.7, 148.5, 151.3, 168.1. Anal. Calcd for $C_{52}H_{55}O_3N$: C, 84.2; H, 7.5; N, 1.9. Found: C, 84.2; H, 7.3; N, 1.6.

**Diene *syn*-19.** A suspension of *syn*-**18** (120 mg, 0.16 mmol) and KOH (2.5 g) in EtOH (25 mL) and water (2 mL) was heated at reflux overnight under argon. The reaction mixture was cooled to room temperature, diluted with water (50 mL), and extracted with $CH_2Cl_2$ (3 × 50 mL). The combined $CH_2Cl_2$ extracts were washed with water (50 mL), a saturated sodium bicarbonate solution (50 mL), and brine (50 mL) and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent gave a white solid that was purified by column chromatography (EtOAc/light petroleum; 1:1) to give *syn*-**19** (105 mg, 93%): $^1$H NMR ($CDCl_3$) $\delta$ 0.96 (s, 6H), 1.02 (s, 6H), 1.46 (d, $J$ = 9.2 Hz, 1H), 1.58−1.76 (m, 4H), 1.82 (d, $J$ = 9.2 Hz, 1H), 1.86 (s, 2H), 1.88−1.92 (m, 1H), 1.96 (s, 2H), 1.95−1.97 (m, 1H), 2.08 (s, 2H), 2.16 (s, 2H), 2.75 (s, 2H), 3.17 (s, 2H), 3.40 (s, 2H), 3.63 (s, 2H), 3.95 (s, 6H), 4.78 (s, 2H), 5.08 (s, 2H), 6.34−6.37 (dd, $J$ = 2.0, 8.2 Hz, 1H), 6.55 (d, $J$ = 2.0 Hz, 1H), 6.90 (d, $J$ = 8.19 Hz, 1H), 7.79 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.5, 9.5, 9.6, 35.0, 40.5, 42.9, 43.0, 43.1, 43.3, 43.6, 43.6, 41.0, 44.3, 45.4, 50.4, 50.6, 50.7, 50.8, 50.9, 61.7, 109.0, 111.5, 112.7, 121.0, 126.5, 134.2, 138.4, 144.0, 144.5, 145.8, 149.19 151.4.

**Diene *syn*-20.** To a solution of *syn*-**19** (105 mg, 0.16 mmol) in MeCN (5 mL) and THF (5 mL) under argon were added formaldehyde solution (40%, 0.128 mL, 1.57 mmol), sodium cyanoborohydride (30 mg, 0.50 mmol), and 2 drops of acetic acid. The reaction mixture was stirred at room temperature for 2 h (progress of the reaction was checked by TLC). Once complete, the reaction mixture was diluted with water (50 mL) and extracted with $CH_2Cl_2$ (2 × 50 mL). The $CH_2Cl_2$ extracts were washed with water (50 mL) and bicarbonate solution (10%, 50 mL) and dried ($MgSO_4$), and the solvent was removed. The crude product was purified by column chromatography (EtOAc/light petroleum 3:7) as eluant to give *syn*-**20** (85 mg, 81%) as an oil:$^1$H NMR ($CDCl_3$) $\delta$ 0.95 (s, 6H), 1.02 (s, 6H), 1.46 (d, $J$ = 10.2 Hz, 1H), 1.59−1.76 (m, 5H), 1.82−2.0 (m,

2H), 1.90 (s, 2H), 1.97 (s, 2H), 2.06 (s, 2H), 2.15 (s, 2H), 2.74 (s, 2H), 2.88 (s, 6H), 3.18 (s, 1H), 3.20 (s, 1H), 3.38 (s, 2H), 3.62 (s, 2H), 3.94 (s, 6H), 6.42 (dd, $J$ = 2.0, 8.2 Hz, 1H), 6.67 (d, $J$ = 2.0 Hz, 1H), 7.00 (d, $J$ = 8.2 Hz, 1H), 7.77 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.5, 9.5, 9.6, 35.0, 40.5, 41.3, 42.8, 42.9, 43.1, 43.2, 43.3, 43.7, 44.3, 44.4, 45.4, 50.6, 50.6, 50.7, 50.8, 51.0, 61.7, 100.1, 107.0, 109.4, 112.7, 120.8, 126.5, 134.2, 144.5, 145.9, 148.9, 151.4. EI MS $m/z$ 727 ($M^+$), 529, 379.

***syn*-$C_{60}$-9-DMN-6-DMA.** To a degassed solution of diene *syn*-**20** (52 mg, 0.08 mmol) in *o*-dichlorobenzene (5 mL) in a pressure tube was added $C_{60}$ (113 mg, 0.16 mmol). The reaction mixture was stirred and heated in an oil bath at 120−125 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with light petroleum (100 mL), and the resulting precipitate was collected by filtration under argon. The residue was dissolved in $CS_2$ (2 mL) and $CHCl_3$ (25 mL) and filtered, and the filtrate was evaporated to dryness giving a dark brown solid. The solid was quickly purified by column chromatography (toluene/$CHCl_3$; 1:1) under argon pressure to give ***syn*-$C_{60}$-9-DMN-6-DMA** (46 mg, 45%) as a dark brown powder that started to decompose on exposure to air. Repurification by chromatography (toluene/$CHCl_3$; 1:1) reduced the yield to 27 mg:$^1$H NMR ($CDCl_3$) $\delta$ 1.08 (s, 6H), 1.13 (s, 6H), 1.7−2.0 (m, 2H), 2.09 (s, 2H), 2.16 (s, 2H), 2.29 (s, 2H), 2.36 (s, 2H), 2.87 (s, 6H), 2.88 (s, 2H), 3.22 (s, 2H), 3.39 (s, 2H), 3.69 (s, 2H), 3.94 (s, 3H), 3.95 (s, 3H), 3.95 and 4.00 (ABq, $J$ = 2.0 Hz, 4H), 6.25 (d, $J$ = 2.0 Hz, 1H), 6.55 (dd, $J$ = 2.0, 8.2 Hz, 1H), 6.87 (d, $J$ = 8.2 Hz, 1H), 7.70 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 9.49, 14.0, 14.2, 17.0, 22.9, 23.3, 26.0, 29.4, 29.8, 30.1, 32.0, 40.5, 40.6, 41.1, 42.3, 42.7, 42.8, 43.1, 43.2, 43.7, 44.4, 46.6, 49.8, 50.8, 50.9, 51.1, 51.2, 51.3, 51.7, 61.3, 65.2, 112.8, 120.8, 120.9, 125, 126.8, 127.4, 128.6, 130.3, 130.5, 133.56, 134.62, 135.5, 136.2, 139.8, 140.3, 140.8, 140.9, 141.1, 141.5, 141.8, 141.9, 142.1, 142.8, 143.1, 144.0, 144.1, 144.2, 144.3, 144.7, 144.8, 147.0, 148.5, 157.0.

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