ORGANIC LETTERS

2004
Vol. 6, No. 11
1689−1692

Hopping of a Single Hole in *hexakis*-[4-(1,1,2-Triphenyl-ethenyl)phenyl]benzene Cation Radical through the Hexaphenylbenzene Propeller

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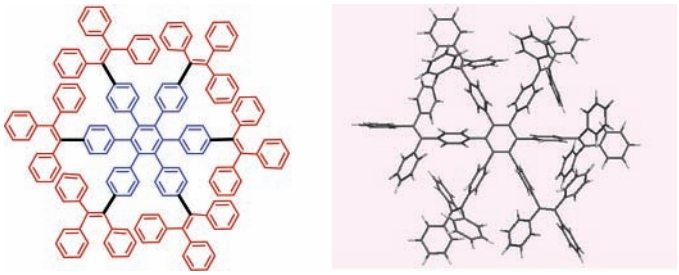
Received October 17, 2003

ABSTRACT



A versatile synthesis of a dendritic structure (5) is described in which six tetraphenylethylene moieties are connected to a central benzene ring in such a way that one of the phenyl rings of each tetraphenylethylene is also part of the propeller of the hexaphenylbenzene core. Observation of multiple oxidation waves in its cyclovoltammogram as well as an intense charge-resonance transition in the near-IR region in its cation radical spectrum suggests that a single hole delocalizes via electron transfer over six identical redox-active centers.

The ready availability of hexaphenylbenzene (**HPB**) and tetraphenylmethane (**TPM**) cores, and the ease of modification of their vertexes to incorporate suitable electro-active functionalities, makes them attractive starting points (or platforms) for the construction of nanometer-sized materials with novel light-emitting and charge-transport properties.[1] A key to successful design of such structures requires that the relative spatial organization of the electro-active units should allow effective electronic coupling among them. Accordingly, our interest in the hexaphenylbenzene core arises from the fact that it arranges its (six) functionalizable vertexes in a circular array around the central benzene ring in a propeller-shaped structure. Conceivably, such a cofacial arrangement of phenyl groups may allow an effective electronic coupling among the six aryl rings via an overlap of orbitals on carbon 1 of phenyls that lie cofacially at a close distance of 2.9 Å from each other (see structures **A** and **B** below).[2] The origin of such an interaction has its roots in our recent observations[3] of the effective electronic coupling between cofacially oriented aryl rings in a number of polyaromatic derivatives. For example, we have noted that a hole (formed by removal of a single electron) can hop between two cofacially oriented aryl moieties even at an angle of 120° in various ethanoanthracene derivatives as readily judged by the appearance of characteristic near-infrared (NIR) charge-resonance absorption bands in the absorption spectra of their cation radicals.[3]

(1) (a) Zimmermann, T. J.; Freundel, O.; Gompper, R.; Muller, T. J. J. *Eur. J. Org. Chem.* **2000**, 3305. (b) Keegstra, M. A.; De Feyter, S.; De Schryver, F. C.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 774. (c) Wang, S.; Oldham, W. J., Jr.; Hudock, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *124*, 5695 and references therein.

(2) Compare: Larson, E. M.; Von Dreele, R. B.; Hanson, P.; Gust, J. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 784.

(3) (a) Rathore, R.; Kochi, J. K. *Can. J. Chem.* **1999**, *121*, 913. (b) Rathore, R.; Abdelwhaed, S. H.; Guzei, I. A. *J. Am. Chem. Soc.* **2003**, *125*, 8712. (c) Rathore, R.; Johnson, R. S. Manuscript under preparation.

10.1021/ol036037g CCC: $27.50 © 2004 American Chemical Society
Published on Web 04/23/2004

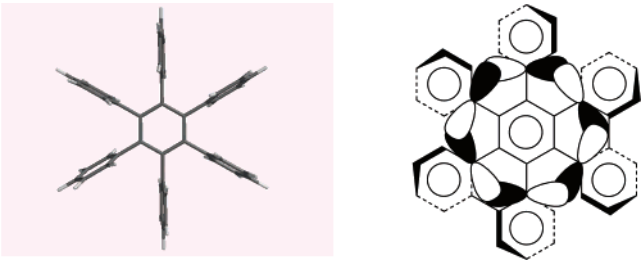


Figure 1. Structures showing the propeller arrangement (**A**, left) and orbital overlap among six phenyl groups (**B**, right) in hexaphenylbenzene.

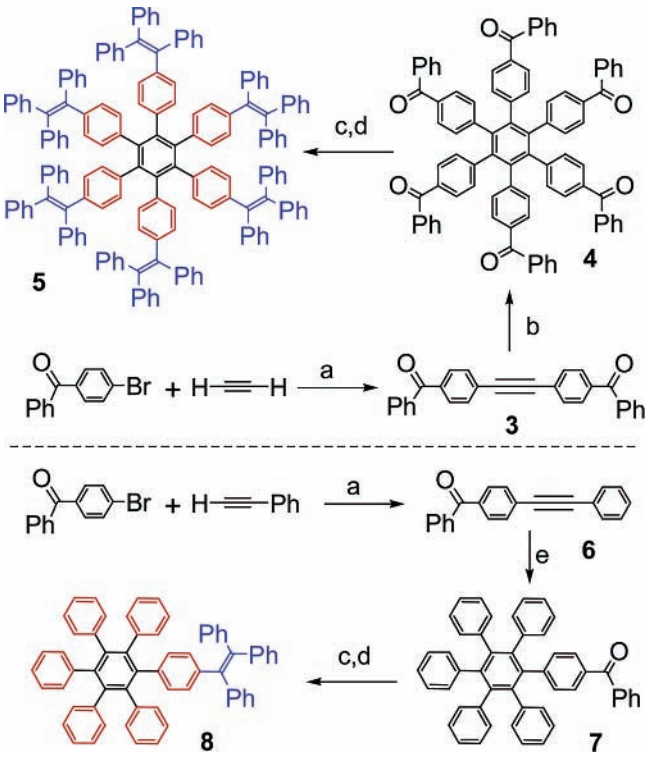
Interestingly, however, we[4] and others[5] have recently shown that the incorporation of electro-active aryl groups on the vertexes of the **HPB** core [such as *hexakis*(4-methyl-2,5-dimethoxy-biphenyl)-benzene, **1**] did not show any significant electronic interaction among each other in their cation radicals.[4] Such a conclusion was supported by the fact that (i) the cyclic voltammogram of **1** showed a single reversible (six-electron) wave and (ii) the UV−vis absorption spectra of **1** at various oxidation states (i.e., $\mathbf{1}^{+\bullet}$ to $\mathbf{1}^{6+\bullet}$) were identical to the absorption spectrum of the cation radical of 4,4′-dimethyl-2,5-dimethoxybiphenyl (**2**, a model compound). The lack of electronic coupling between various aryl groups in **1** was attributed to the fact that the hole is completely localized on the dimethoxytolyl (*p*-hydroquinone ether) moiety.[4] It was thus envisioned that incorporation of an electro-active group that allows the hole to reside over the phenyl groups that constitute the propeller of the hexaphenylbenzene core may allow an effective electronic coupling among the electro-active groups.

We now report that such a criteria could be met in a polychromophoric molecule **5** in which the six tetraphenylethylene moieties are connected to a central benzene ring. The choice of this electro-active moiety stems from the fact that one of the phenyl rings of each tetraphenylethylene unit is also part of the propeller of hexaphenylbenzene core (see structure **5**, Scheme 1) as well as the fact that it has rich electrochemical and excited-state properties; furthermore, it has been extensively utilized as an electron-transfer catalyst in a variety of polymerization and coupling reactions.[6]

Accordingly, this report constitutes the synthesis of dendritic donor **5** (Scheme 1) as well as a model compound **8**, containing only one tetraphenylethylene moiety (Scheme 1), and delineation of the hopping of a single hole over six tetraphenylethylene moieties in its monocation radical ($\mathbf{5}^{+\bullet}$) by electrochemical and optical measurements as follows.

As shown in Scheme 1, the synthesis of **5** was accomplished via a three-step route. Thus, bis(4-benzoylphenyl)acetylene (**3**), obtained by a Pd-catalyzed coupling of commercially available 4-bromobenzophenone with gaseous acetylene in 65% yield, was trimerized in refluxing dioxane in the presence of a cobalt catalyst to the previously unknown *hexakis*(4-benzoylphenyl)benzene (**4**).

Scheme 1. Synthesis of Polychromophoric Donor **5** and a Model Tetraphenylethylene Donor **8**[a]



[a] Conditions: (a) $(PPh_3)PdCl_2$, CuI, CH_3CN/piperdine (2:1), reflux; (b) $Co_2(CO)_8$, dioxane, reflux; (c) diphenylmethyl lithium (generated from *n*-BuLi and diphenyl-methane in ether); (d) *p*-toluenesulfonic acid in toluene; (e) tetraphenylcyclopentadienone, Ph_2O, reflux.

A reaction of freshly prepared diphenylmethyllithium (obtained by a reaction of *n*-butyllithium with diphenylmethane in ether at 0 °C) with **4** afforded the hexaalcohol, which was dehydrated directly by refluxing in toluene in the presence of a catalytic amount of *p*-toluenesulfonic acid, to afford a highly soluble *hexakis*-tetraphenylethylene derivative **5** in >90% yield. The mono-tetraphenylethylene analogue **8** was prepared similarly from **7**, which in turn was synthesized by a Diels−Alder reaction of 4-benzoyltolan with tetraphenylcyclopentadienone in refluxing diphenyl ether (see Supporting Information for experimental details). The structures of these highly symmetrical macromolecular donors **5** and **8** were readily established by $^1H/^{13}C$ NMR spectroscopy as well as by correct elemental analysis and FAB mass spectrometry.

The electronic absorption spectra of the parent **TPE**, model donor **8**, and the hexaethylenic donor **5** obtained as dichloromethane solutions are compared in Figure S1 (see Supporting Information). The UV−vis absorption spectra of **5** and **8** are highly characteristic to that of the parent **TPE** with

(4) Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Lett.* **2001**, *3*, 2887.
(5) Lambert, C.; Noll, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 2107 and references therein.
(6) (a) Salem, L. *Science* **1976**, *191*, 822. (b) Salem, L.; Bruckmann, P. *Nature* **1975**, *258*, 526. (c) Wolf, M. O.; Fox, H. H.; Fox, M. A. *J. Org. Chem.* **1996**, *61*, 287.

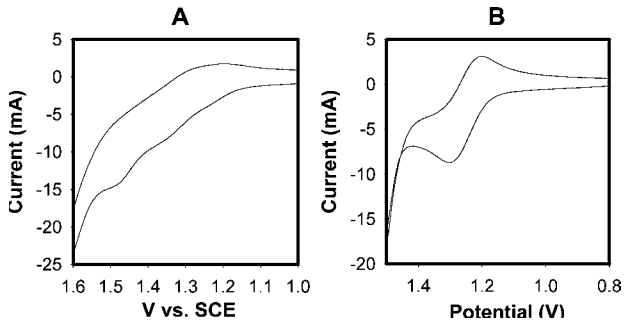


Figure 2. Cyclic voltammograms of 2 mM *hexakis*(4-tetraphenylethylene)benzene **5** (A) and model donor **8** (B) in CH_2Cl_2 containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate at a scan rate of 200 mV s^{-1} and at 22 °C.

the slight red shift of the absorption maxima in the spectrum of **5** as compared to model compound **8** and parent **TPE**. Moreover, the measured extinction coefficient at the maximum of **5** (λ_{max} = 324 nm, ϵ_{max} = 103 200 M^{-1} cm^{-1}) is found to be slightly higher than the expected 6-fold increase in comparison to the model **8** (λ_{max} = 319 nm, ϵ_{max} = 16 300 M^{-1} cm^{-1}) and parent tetraphenylethylene (λ_{max} = 306 nm, ϵ_{max} = 14 100 M^{-1} cm^{-1}). These observations suggest a weak electronic coupling among the tetraphenylethylene moieties in ground state of **5** through the hexaphenylbenzene propeller.

The electron donor strength of **5** in comparison with its model compound **8** was evaluated by electrochemical oxidation at a platinum electrode as a 2 × 10^{-3} M solution in dichloromethane containing 0.2 M *n*-Bu_4NPF_6 as the supporting electrolyte. The cyclic voltammogram of **5** in Figure 2A showed three overlapped oxidation waves at potentials of 1.22, 1.34, and 1.47 V vs SCE, whereas the model donor **8** showed only one reversible wave at a potential of 1.28 V vs SCE (Figure 2B). [Note that due to the extensive overlap of the oxidation waves in the CV of **5**, its three oxidation potentials were further confirmed by square wave voltammetry, as shown in Figure S2 in Supporting Information.] The presence of multiple oxidation waves in the CV of **5** (in contrast to the single six-electron oxidation wave previously observed for **1**)[4] suggests that the removal of the first electron from **5** affects the removal of further electrons and thus bears the earmarks that various tetraphenylethylene (**D**) moieties in **5** are electronically coupled via the propeller formed by six phenyl rings. A quantitative evaluation of the CV peak currents of various waves in **5** (with ferrocene as an internal standard) was hampered due to the overlapping of the waves in its cyclic voltammogram (see Figure 2A and S2).

To determine how many electrons were involved in the various CV peaks of **5** as well as the spectral characteristics of various oxidized species, we carried out chemical coulometry using a hindered naphthalene cation radical salt[4] (**9**$^{+\bullet}$) as a stable one-electron aromatic oxidant (E_{red} = 1.34 V vs SCE) in dichloromethane as follows. [It is noteworthy that species with redox potential greater than ~1.35 V cannot be oxidized to any appreciable amounts using **9**$^{+\bullet}$.] Thus, treatment of a blue solution of **9**$^{+\bullet}$ (λ_{max} = 672 nm, log ϵ_{672} = 3.97 M^{-1} cm^{-1}, see green spectrum in Figure 3A) with incremental amounts of **5** showed that naphthalene cation radical **9**$^{+\bullet}$ was completely consumed after the addition of 1/3 equiv of **5** as judged by the presence of well-defined isosbestic points at 704 and 420 nm (see Figure 3A, red spectra). Moreover, reverse addition of a solution of **9**$^{+\bullet}$ (0.3 mmol, 0.01 M) to a solution containing 1/3 equiv of **5** (0.1 mmol, 0.1 M) in dichloromethane completely consumed the naphthalene cation radical, as shown by UV−vis spectroscopy (see Figure 3A). Moreover, both modes of mixing oxidant **9**$^{+\bullet}$ and **5** produced an identical red-colored species with characteristic twin absorption bands[7] at 490 and 965 nm (together with a very weak band at 1240 nm). Interestingly, reduction of the red-colored solution obtained above with zinc dust afforded the neutral **5** in quantitative yield as shown by NMR spectroscopy and by comparison with an authentic sample. Thus, a clean spectral coulometry in Figure 3A as well as quantitative regeneration of **5** from the oxidized solution (i.e., by reduction with zinc dust) suggests that the

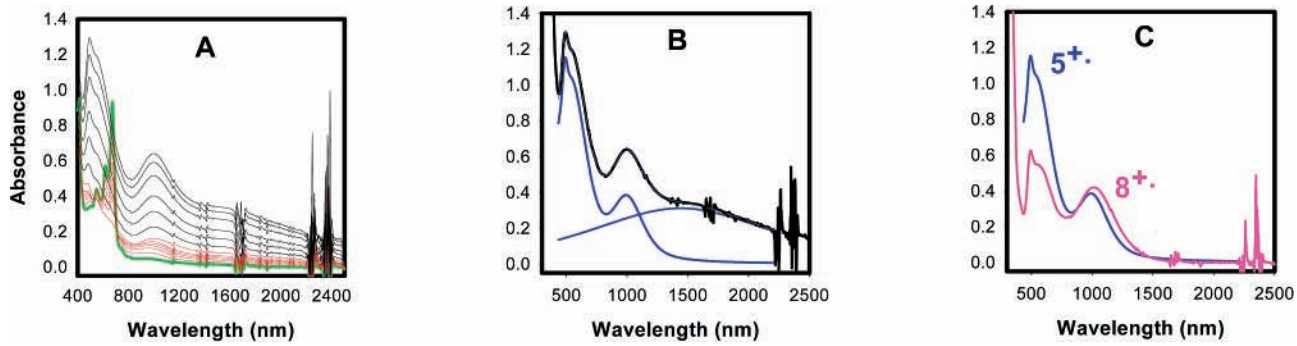
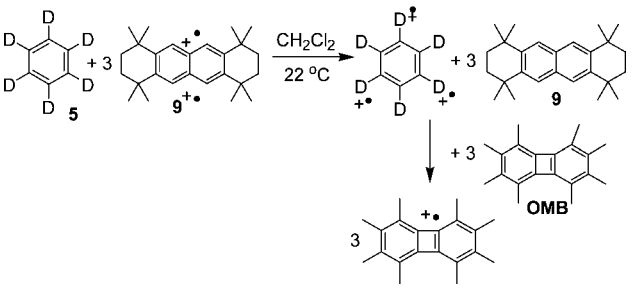


Figure 3. A. Spectral changes upon the reduction of 1.1 × 10^{-4} M **9**$^{+\bullet}$ (green) in dichloromethane at 22 °C by incremental addition of 4.7 × 10^{-3} M **5** to give first **5**$^{3+\bullet}$ (red) and then **5**$^{+\bullet}$ (black) upon further additions of neutral **5**. B. Plot of deconvoluted spectra of **5**$^{+\bullet}$. C. Similarity in the UV−vis region of the spectrum of the cation radical **5**$^{+\bullet}$ (blue, partial spectrum obtained by deconvolution) with that of the model **8**$^{+\bullet}$ (magenta).

oxidation of **5** to its trication radical $\mathbf{5}^{3+\bullet}$ indeed occurs according to the stoichiometry in Scheme 2.

Scheme 2 Redox Titration of **5** with Naphthalene Cation Radical $\mathbf{9}^{+\bullet}$



The exact nature of the $\mathbf{5}^{3+\bullet}$ in Scheme 2 cannot be delineated with confidence at this point; however, a treatment of the red-colored solution obtained in Scheme 2 with 3 equiv of octamethylbiphenylene[4] (**OMB**, an electron donor with $E_{ox} = 0.80$ V vs SCE) produced 3 equiv of highly robust $\mathbf{OMB}^{+\bullet}$ ($\lambda_{max} = 600$ nm, log $\epsilon_{672} = 3.97$ M^{-1} cm^{-1}),[4] as confirmed by UV−vis spectroscopy.

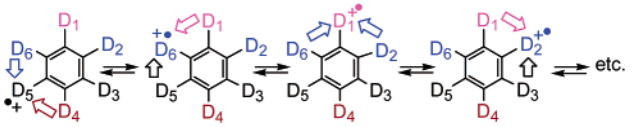
Interestingly, a further incremental addition of hexaethylenic donor **5** (∼2 equiv) to the above solution of $\mathbf{5}^{3+\bullet}$ showed a steady increase in the absorbance at 490 and ∼1000 nm as well as an appearance of a new (broad) overlapped absorption band extending in the near-IR region (Figure 3A, black spectra). Furthermore, the final spectrum in Figure 3A remained unchanged upon addition of a large excess of **5** and was thus assigned to the monocation radical $\mathbf{5}^{+\bullet}$. The spectral identity of $\mathbf{5}^{+\bullet}$ was further confirmed by its generation using different oxidants[4] (such as DDQ/CF_3COOH, $SbCl_5$, $NOSbCl_6$, etc.) in the presence of an excess of **5**, as well as by complete recovery of the neutral **5** by the reduction of the above solutions using zinc dust and octamethylbiphenylene (compare Scheme 2).

A careful deconvolution of the spectrum of $\mathbf{5}^{+\bullet}$ in Figure 3B (using a standard software) revealed that it consisted of the characteristic twin absorption bands ($\lambda_{max} = 496$, 568 (sh), and 1010 nm) due to the cationic tetraphenyl-ethylenic moiety ($\mathbf{D}^{+\bullet}$),[7] as confirmed by a spectral comparison with the model $\mathbf{8}^{+\bullet}$ ($\lambda_{max} = 495$, 570(sh), and 1000 nm; magenta spectrum) in Figure 3C, as well as an additional broad absorption band at 1450 nm (WAHM = 5608 cm^{-1}), see Figure 3B. It is important to note that the position and intensity of the near-IR band in $\mathbf{5}^{+\bullet}$ remained unchanged upon changing the solvent polarity, i.e., from dichloromethane to acetonitrile.

The new NIR transition, which is largely absent in the trication radical $\mathbf{5}^{3+\bullet}$ and the model cation radical $\mathbf{8}^{+\bullet}$, is believed to arise due to the rapid hopping of a single hole over six tetraphenylethylene (**TPE**) moieties in $\mathbf{5}^{+\bullet}$ via the hexaphenylbenzene propeller by utilizing adjacent **TPE** donor (D_1−D_6) moieties, as pictorially shown below.

The thesis that the hole hops over all six **TPE** donor (D) moieties in $\mathbf{5}^{+\bullet}$ is based on ample literature precedence.[3,8] For example, the cofacial orientation of phenylene moieties, even at 120°, in various ethanoanthracene derivatives allows extensive electronic coupling, as established by the observation of intense charge-resonance bands in the NIR region.[3] It is also important to mention here that the hole in $\mathbf{5}^{+\bullet}$ cannot hop on various **TPE** moieties via the central benzene ring because they lie perpendicular to each other.[8] Moreover, the symmetrical nature of the molecule suggests that the hole can hop via electron transfer from one of the two adjacent donor moieties with equal probability, and occurrence of enough rapid repetitions of this electron-transfer process in $\mathbf{5}^{+\bullet}$ ensures that the hole migrates on all **TPE** moieties (see the structures above in Scheme 3).

Scheme 3. Schematic Representation of the Hole Hopping in $\mathbf{5}^{+\bullet}$



In summary, we have synthesized a novel (circular) dendritic structure in which the observation of an intense charge-resonance transition (1450 nm) is suggestive of the fact that a single hole is mobilized via electron transfer over six identical redox-active centers arranged cofacially in a circular array.[10] Such an observation, coupled with ready preparation of these structures, should spur theoretical exploration of this new class of intervalence materials in which a hole can hop over multiple redox centers. We are currently exploring the potential applications of these materials and a variety of other hexaarylbenzene derivatives for the preparation of photonic devices.

Acknowledgment. We are grateful to Professor F. A. Khan (State University of West Georgia at Carrolton) for the mass spectral data of **5** and **8** and the donors of the Petroleum Research Fund (AC12345), administered by the American Chemical Society, and National Science Foundation (Career Award) for financial support; C.L.B. thanks the Department of Education for a GAANN fellowship.

Supporting Information Available: Synthetic details and $^1H/^{13}C$ NMR data for **5** and **8** and Figure S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) For tetraphenylethylene cation radical, see: Barbosa, F.; Peron, V.; Gescheidt, G.; Fürstner, A. *J. Org. Chem.* **1998**, *63*, 8806.

(8) See: Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581.

(9) Also note that the stability of C_6I_6 dication is attributed to a similar electronic coupling between six iodo groups in C_6I_6; see: Sagl, D. J.; Martin, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 5827.

(10) Photophysical characteristics of **5** will be reported separately.