

Multiple-Electron Transfer in a Single Step. Design and Synthesis of Highly Charged Cation-Radical Salts

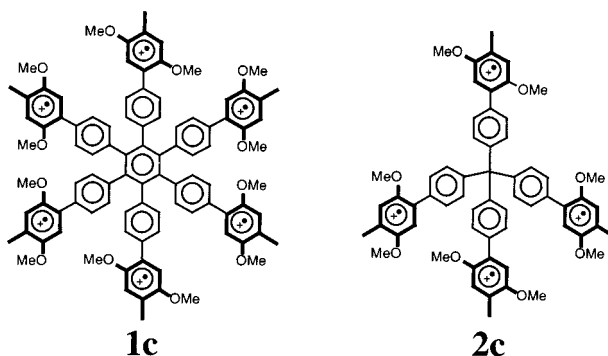
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ABSTRACT



Macromolecules **1c** and **2c** bearing multiple redox-active sites are synthesized by an efficient palladium-catalyzed coupling of 2,5-dimethoxytolylmagnesium bromide with readily available hexakis(4-bromophenyl)benzene and tetrakis(4-bromophenyl)methane. These macromolecular electron donors undergo reversible oxidation at a constant potential of 1.15 V vs SCE to yield robust, multiply charged cation radicals that are isolated in pure form using SbCl_5 as an oxidant. These nanometer-size cation-radical salts are shown to act as efficient “electron sponges” toward a variety of electron donors.

Design and synthesis of nanometer-size macromolecules is receiving considerable attention owing to their importance as materials that can be used as molecular devices such as sensors, switches, molecular wires, ferromagnets, and other electronic and optoelectronic devices.^{1–3} Thus, construction of organic molecules containing multiple redox-active chromophores are of particular interest owing to their importance not only for the preparation of materials with novel properties but also as multielectron redox catalysts.^{4–6} Accordingly, we now report the utilization of readily available hexaphenylbenzene⁷ and tetraphenylmethane⁸ as platforms for the

preparation of multicentered electron donors that are bearing six and four redox-active centers, respectively. Moreover, these novel macromolecular electron donors undergo multiple

(1) (a) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (b) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26. (c) Reichert, V. R.; Mathias, L. J. *Macromolecules* **1994**, *27*, 7015.

(2) (a) Pollak, K. W.; Leon, J. W.; Frechet, J. M. J.; Maskus, M.; Abruna, H. D. *Chem. Mater.* **1998**, *10*, 30. (b) Gorman, C. B. *Adv. Mater.* **1997**, *9*, 1107. (c) Wilson, L. M.; Griffin, A. C. *J. Mater. Chem.* **1993**, *3*, 991.

(3) Keegstra, M. A.; Feyter, S. D.; Schryver, F. C. D.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 774. (b) Oldham, W. J., Jr.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 2987. (c) Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *24*, 5695 and references therein.

(4) (a) Fillaut, J.-L.; Linares, J.; Astruc, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460. (b) Lambert, C.; Noll, G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2107.

(5) (a) Blackstock, S. C.; Selby, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 12155. (b) Bonvoisin, J.; Launay, J.-P.; Auweraer, M. V.d.; Schryver, F. C. D. *J. Phys. Chem.* **1994**, *98*, 5052 and references therein.

(6) (a) Bauld, N. L.; Bellville, D. J. *Tetrahedron Lett.* **1982**, *23*, 825. (b) Heo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621. (c) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602 and references therein.

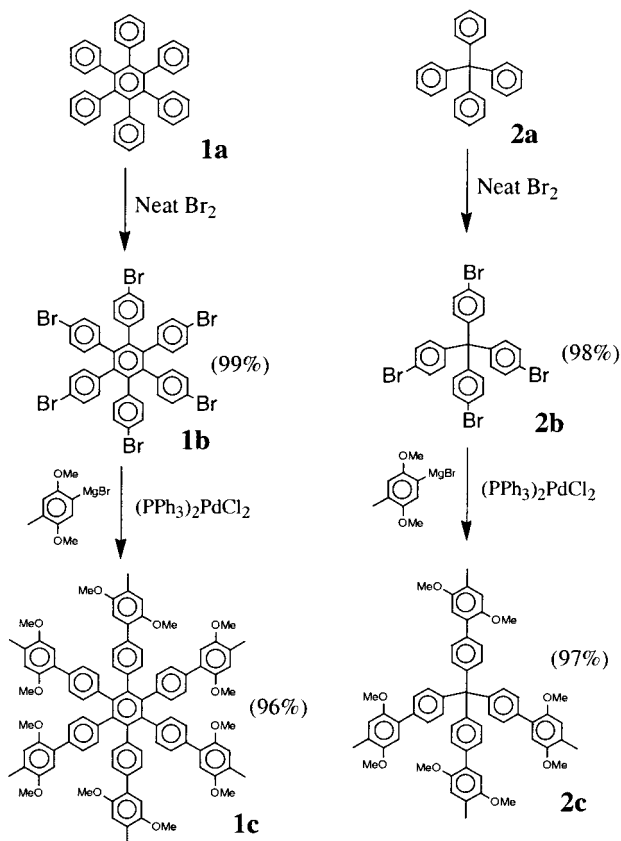
(7) Fieser, L. F. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 605.

(8) Wassmundt, F. W.; Kiesman, W. F. *J. Org. Chem.* **1995**, *6*, 1713.

electron loss in a single step (at a constant potential) to afford highly charged cation-radical salts that are remarkably robust and can be isolated in pure form.

The hydroquinone ether moiety, 2,5-dimethoxy-4-methylbenzene, was chosen as the redox-active unit to be linked to hexakis(4-bromophenyl)benzene (**1b**) and tetrakis(4-bromophenyl)methane (**2b**) platforms owing to its ability to generate a stable cation-radical salt upon a one-electron oxidation.⁹ As shown in Scheme 1, these molecular platforms

Scheme 1. Synthesis of Redox-Active Donors **1c** and **2c**



were readily prepared from hexaphenylbenzene (**1a**) and tetraphenylmethane (**2a**) by bromination using neat bromine.¹⁰ Thus, a coupling of a slight excess (5%) of 2,5-dimethoxy-4-methylphenyl Grignard reagent (derived from 4-bromo-2,5-dimethoxytoluene¹¹ and Mg in anhydrous tetrahydrofuran) with **1b** (or **2b**) in the presence of a palladium catalyst¹² afforded the macromolecule **1c** (or **2c**) in essentially quantitative yield (see Scheme 1). The structures of these highly symmetrical macromolecular donors **1c** and **2c** were readily established by ¹H/¹³C NMR spectroscopy and correct elemental analysis.¹³

(9) Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847 and references therein.

(10) Thus, a treatment of 5 g of **1a** (or **2a**) with excess Br₂ (3–5 mL) afforded **1b** (or **2b**) in quantitative yields by a simple trituration with chilled (–25 °C) ethanol.

(11) McHale, D.; Mamalis, P.; Green, J.; Marcinkiewicz, S. *J. Chem. Soc.* **1958**, 1600.

The electron donor strengths of **1c** and **2c** in comparison with the model compound (4,4'-dimethyl-2,5-dimethoxybiphenyl **3**¹⁴) were evaluated by electrochemical oxidation at a platinum electrode as a 2 × 10^{–3} M solution in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. The highly reversible cyclic voltammograms (see Figure 1) of various

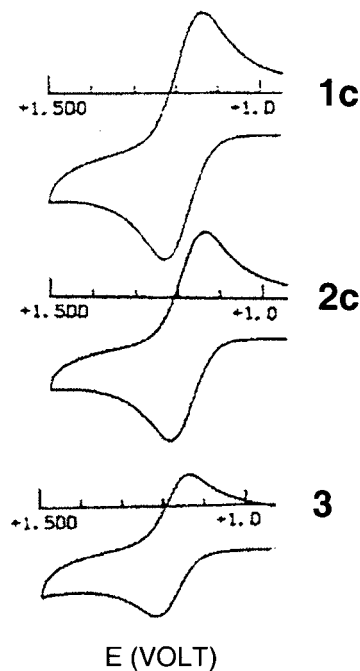


Figure 1. Cyclic voltammograms of 2 mM **1c** and **2c** and 5 mM model compound **3** (as indicated) in dichloromethane at a scan rate of $\nu = 200 \text{ mV s}^{-1}$ (25 °C).

donors were consistently obtained at a scan rate of 25–200 mV s^{–1}, and they all showed anodic/cathodic peak current ratios of $i_a/i_c = 1.0$ (theoretical) at ambient temperatures. It

(12) **General Procedure.** A 200-mL flask equipped with reflux condenser and a dropping funnel was charged with magnesium turnings (1.06 mg, 44 mmol) and THF (10 mL) under an argon atmosphere. A small crystal of iodine was added, and the mixture refluxed. A solution of 4-bromo-2,5-dimethoxytoluene (3.5 g, 22 mmol) in THF (40 mL) was added dropwise. After the addition was complete, the reaction mixture was refluxed for another 2 h and cooled to 22 °C. The Grignard solution was transferred via a cannula to a Schlenk flask containing **1b** (3.04 g, 3 mmol) and (PPh₃)₂PdCl₂ (70 mg, 0.1 mmol), under a flow of argon. The resulting pale yellow reaction mixture was refluxed for 12 h and cooled to room temperature. A standard aqueous workup and recrystallization of the crude solid from a dichloromethane/ethanol mixture afforded pure **1c** in 96% yield. Compare: Kumada, K. *Pure Appl. Chem.* **1980**, *52*, 669.

(13) Hexakis(4-methyl-3,6-dimethoxybiphenyl)benzene (**1c**): mp > 350 °C; ¹H NMR (CDCl₃) δ 2.18 (s, 18H), 3.39 (s, 18H), 3.681 (s, 18H), 6.61 (s, 6H), 6.70 (s, 6H), 7.12 (d, $J = 8.1 \text{ Hz}$, 12H), 6.98 (d, $J = 8.4 \text{ Hz}$, 12H); ¹³C NMR (CDCl₃) δ 16.02, 55.91, 57.47, 112.73, 117.50, 126.21, 127.49, 129.30, 131.26, 135.25, 139.36, 140.42, 150.50, 152.31. Anal. Calcd for C₉₆H₉₀O₁₂: C, 80.31; H, 6.32; O, 13.37. Found: C, 80.26; H, 6.35. Tetrakis(4-methyl-3,6-dimethoxybiphenyl)methane (**2c**): mp > 320 °C; ¹H NMR (CDCl₃) δ 2.29 (s, 12H), 3.79 (s, 12H), 3.84 (s, 12H), 6.83 (s, 4H), 6.89 (s, 4H), 7.12 (d, $J = 8.1 \text{ Hz}$, 12H), 6.98 (d, $J = 8.4 \text{ Hz}$, 12H); ¹³C NMR (CDCl₃) δ 16.79, 57.03, 57.91, 64.90, 113.68, 115.62, 126.78, 128.40, 129.00, 131.87, 136.61, 146.05, 150.87, 152.52. Anal. Calcd for C₆₁H₆₀O₈: C, 79.54; H, 6.57; O, 13.90. Found: C, 79.44; H, 6.48. These structures were further confirmed by high-resolution mass spectra.

is interesting to note that irrespective of the number of the electroactive aryl (2,5-dimethoxytolyl) groups (i.e., 6 aryls in **1c**, 4 aryls in **2c**), these electron donors showed only a single reversible (CV) wave at a potential of 1.15 ± 0.01 V vs. SCE, similar to that obtained with the model compound **3**. A quantitative evaluation of the CV peaks with added ferrocene (as an internal standard, $E_{\text{ox}} = 0.45$ V vs SCE) revealed that the reversible cyclic voltammograms in Figure 1 correspond to the production of a monocation of **3**, tetracation of **2c**, and hexacation of **1c** by transfer of one, four, and six electrons, respectively.¹⁵

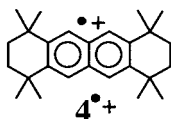
The highly reversible oxidation of **1c** and **2c** prompted the isolation of their multiply charged paramagnetic cation-radical salts. Thus, treatment of a solution of **1c** with antimony pentachloride (SbCl_5) in anhydrous dichloromethane at -78 °C immediately resulted in a bright green solution (vide infra) from which the microcrystalline salt $[\mathbf{1c}^{6+}(\text{SbCl}_6^-)_6]$ could be isolated, by precipitation using hexane, in nearly quantitative yield according to the stoichiometry shown:¹⁶



In a similar vein, tetracationic $[\mathbf{2c}^{4+}(\text{SbCl}_6^-)_4]$ was prepared in 96% yield from **2c**. These highly colored cation-radical salts are extremely robust and can be recrystallized readily from a dichloromethane solution by a slow diffusion of *n*-hexane at -30 °C. The purity of the crystalline hexacationic **1c**⁶⁺ and the tetracationic **2c**⁴⁺ was determined by iodometric titrations¹⁷ and was further confirmed by a spectroscopic titration method (vide infra).

To confirm these multiple electron-transfer processes for the formation of the hexacation and tetracation from **1c** and **2c** using SbCl_5 , we carried out their oxidation (in dichloromethane) using a stable hindered naphthalene cation radical (**4**⁺)¹⁸ as an aromatic one-electron oxidant ($E_{\text{red}} = 1.34$ V vs. SCE).

An Efficient Aromatic Oxidant

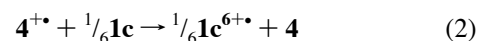


When a dark blue solution of **4**⁺ ($\lambda_{\text{max}} = 672, 616, 503,$ and 396 nm; $\epsilon_{672} = 9300$ M⁻¹ cm⁻¹) was mixed with 1/6

(14) 4,4'-Dimethyl-3,6-dimethoxybiphenyl (**3**): mp $162-163$ °C; ¹H NMR (CDCl_3) δ 2.44 (s, 3H), 2.55 (s, 3H), 3.89 (s, 3H), 3.96 (s, 3H), 6.89 (s, 1H), 6.98 (s, 1H), 7.35 (d, 2H), 7.55 (d, 2H); ¹³C NMR (CDCl_3) δ 16.79, 21.76, 56.73, 57.52, 113.92, 115.88, 127.04, 127.82, 129.49, 130.02, 136.71, 137.18, 150.93, 152.63; GC-MS *m/z* 242 (M^+), 242 calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 79.31; H, 7.49; O, 13.21. Found: C, 79.22; H, 7.58.

(15) The reduced current response for equimolar **1c** (or **2c**) as compared to the ferrocene as an added internal standard can be readily attributed to the difference in the diffusion coefficient of **1c** (or **2c**) due to difference in the size and the shape; see: Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248. However, a preliminary cyclic voltammetric study, which will be published elsewhere, showed a current ratio of 1 with an equimolar solution of **1c** and hexakis(4-ferrocenylphenyl)-benzene as an internal standard: Rathore, R.; Burns, C. L., unpublished results.

equiv of neutral **1c** in dichloromethane at 22 °C, a dramatic color change to bright green ($\lambda_{\text{max}} = 415, 550,$ and 1105 nm, $\epsilon_{1105} = 1400$ M⁻¹ cm⁻¹) occurred immediately:



(It is noteworthy that the absorption spectrum of hexacationic **1c**⁶⁺ obtained above was identical to that obtained by an oxidation of **1c** using either SbCl_5 or by an electrochemical method.¹⁹)

The UV-vis spectral analysis established the simultaneous oxidation of **1c** and reduction of **4**⁺ in quantitative yields (eq 2), and the uncluttered character of the electron transfer was established by the presence of well-defined isosbestic points at $\lambda_{\text{max}} = 388, 520,$ and 714 nm when a solution of **4**⁺ was treated with incremental amounts of **1c** (see Figure 2A). Furthermore, a plot of the depletion of **4**⁺ (i.e., decrease of the absorbance at 672 nm) and formation of **1c**⁶⁺ (i.e., increase in the absorbance at 1105 nm) against the increments of added **1c** in Figure 2B established that **4**⁺ was completely consumed after the addition of 1/6 equiv of **1c**; the resulting absorption spectrum of **1c**⁶⁺ remained unchanged upon further addition of neutral **1c** (i.e., eq 2).

The highly characteristic absorption spectra of the hexacationic **1c**⁶⁺ and tetracationic **2c**⁴⁺ are strikingly similar to that of the model cation radical **3**⁺ as shown in Figure 2C.²⁰ Moreover, the spectra of partially oxidized **1c** (or **2c**) were uniformly the same irrespective of the degree of oxidation, as confirmed by the reverse addition of a solution of naphthalene cation radical **4**⁺ to a solution of **1c** (or **2c**). As such, the strong similarity in the UV-vis absorption spectra of **1c**⁶⁺ and **2c**⁴⁺ with that of the model **3**⁺ suggests that there are minimal interactions between the donor moieties in **1c** and **2c** via the platform frameworks.²¹

It is interesting to note that the oxidizing strength of these multiply charged cation radicals **1c**⁶⁺ and **2c**⁴⁺ ($E_{\text{red}} = 1.15$ V vs. SCE) is similar to that of the extensively utilized tris-4-bromophenylamminium cation radical²² (magic blue, $E_{\text{red}} = 1.1$ V vs. SCE) as an aromatic oxidant in a variety of

(16) For the stoichiometry of the oxidation of donors with SbCl_5 , see: Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847.

(17) The purity of the isolated $[\mathbf{1c}^{6+}(\text{SbCl}_6^-)_6]$ and $[\mathbf{2c}^{4+}(\text{SbCl}_6^-)_4]$ was determined by iodometric titration and was found to be greater than 98%. For a general procedure for iodometric titrations of cation radicals, see: Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 4399 and also ref 9.

(18) Rathore, R.; Le Maguères, P.; Lindeman, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 809. Also see: Rathore, R.; Le Maguères, P.; Kochi, J. K. *J. Org. Chem.* **2000**, *65*, 6826.

(19) The oxidation of **1c** to its green cation radical can be carried out electrochemically at $E_{\text{ox}} = 1.2$ V vs SCE in dichloromethane containing 0.05 M *n*-Bu₄NPF₆ at 0 °C.

(20) UV-vis absorption data for various cation radicals in dichloromethane at 22 °C: $[\mathbf{1c}^{6+}(\text{SbCl}_6^-)_6]$ λ_{max} 415, 550, and 1105 nm, $\epsilon_{1105} = 1400$ M⁻¹ cm⁻¹; $[\mathbf{2c}^{4+}(\text{SbCl}_6^-)_4]$ λ_{max} 385, 570, and 1000 nm, $\epsilon_{1000} = 1700$ M⁻¹ cm⁻¹; $[\mathbf{3}^{+}\text{SbCl}_6^-]$ λ_{max} 420, 640, and 1115 nm, $\epsilon_{1115} = 3200$ M⁻¹ cm⁻¹.

(21) The lack of electronic communication amongst various aryl groups in **1c** can be attributed to the propeller shape of the hexaphenylbenzene framework. We believe that the synthesis of an analogue of **1c** (in progress) in which the six aryl groups are connected to planar hexa-*peri*-hexabenzocoronene framework will lead to extensive electronic communication amongst aryl groups. Compare: Ito, S.; Herwig, P. T.; Böhme, T.; Rabe, J. P.; Rettig, W.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7698.

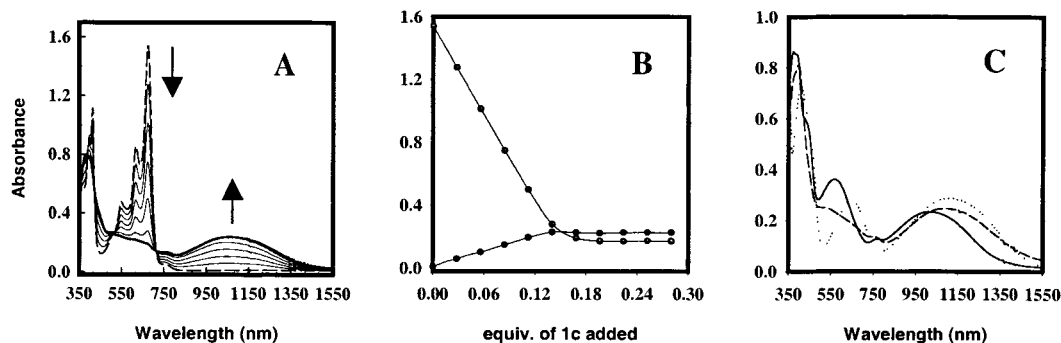
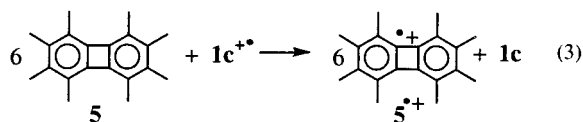


Figure 2. (A) Spectral changes attendant upon the reduction of 1.5×10^{-4} M naphthalene cation radical $4^{+\bullet}$ (---) by incremental addition of 1.2×10^{-3} M **1c** to its hexacation radical $1c^{6+\bullet}$ (—) in dichloromethane at 22 °C. (B) A plot of depletion of absorbance (data from Figure 2A) of $4^{+\bullet}$ (○, monitored at 672 nm) and an increase of the absorbance of $1c^{6+\bullet}$ (●, monitored at 1100 nm) against the equivalent of added **1c** showed a complete consumption of $4^{+\bullet}$ after addition of 1/6 equiv of **1c**. (C) UV-vis absorption spectra of cation radicals $1c^{6+\bullet}$ (---), $2c^{4+\bullet}$ (—), and $3^{+\bullet}$ (···) obtained by $SbCl_5$ oxidation in dichloromethane at 22 °C.

electron-transfer catalyzed (ETC) organic transformations.²³ For example, the oxidation of a colorless solution of octamethylbiphenylene²⁴ (**5**, $E_{red} = 0.8$ V vs. SCE) with 1/6 equiv of $[1c^{6+\bullet}(SbCl_6^-)_6]$ or 1/4 equiv of $[2c^{4+\bullet}(SbCl_6^-)_4]$ in dichloromethane immediately yielded a dark blue solution of $5^{+\bullet}$ ($\lambda_{max} = 602$ nm)²⁴ in quantitative yield as estimated by the UV-vis spectral analysis (eq 3).



In a similar vein, a variety of aromatic and olefinic donors²⁵ (**D**) such as 2,5-dimethyl-1,4-dimethoxybenzene, perylene, octamethylantracene, 1,2-dianisyl-1,2-ditolylethylene, tetraanisylethylene, and 2,3-dianisylbicyclo[2.2.2]oct-2-ene were quantitatively oxidized to their brightly colored cation radicals²⁵ using $[1c^{6+\bullet}(SbCl_6^-)_6]$ and $[2c^{4+\bullet}(SbCl_6^-)_4]$ according to the stoichiometry in eq 3.

Presently, we are actively pursuing the usage of these highly robust cation-radical salts as electron-transfer catalysts

in various organic and organometallic transformations and the isolation of their single crystals for X-ray crystallography and the study of solid-state properties.

Acknowledgment. We are grateful to Professor F. A. Khan (State University of West Georgia at Carrollton) for the mass spectral data of macromolecular donors **1c** and **2c**.

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(22) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719. Also see: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, 96, 877 and references therein.

(23) (a) Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, R. A., Jr.; Reynolds, D. W.; Wirth, D. D.; Chiou, H. S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, 20, 371. (c) Mirafzal, G. A.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, 115, 6072. (d) Chanon, M. *Bull. Soc. Chim. Fr.* **1985**, 209. (e) Rathore, R.; Kochi, J. K. *Acta Chem. Scand.* **1998**, 52, 114 and references therein.

(24) Rathore, R.; Le Maguères, P.; Kochi, J. K. *J. Org. Chem.* **2000**, 65, 6826.

(25) Cation radicals of various donors mentioned here have been characterized previously; see: (a) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, 120, 6931. (b) Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, 63, 5847 and references therein.