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

Rajendra Rathore,* Carrie L. Burns, and Mihaela I. Deselniciu

Department of Chemistry, Marquette University, PO Box 1881, Milwaukee, Wisconsin 53201
rajendra.rathore@marquette.edu

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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 SbCl5 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 tetraphenylethane8 as platforms for the preparation of mult centered electron donors that are bearing six and four redox-active centers, respectively. Moreover, these novel macromolecular electron donors undergo multiple

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 tetraakis(4-bromophenyl)methane (2b) platforms owing to its ability to generate a stable cation-radical salt upon a one-electron oxidation. As shown in Scheme 1, these molecular platforms were readily prepared from hexaphenylbenzene (1a) and tetraphenylmethane (2a) by bromination using neat bromine. Thus, a coupling of a slight excess (5%) of 2,5-dimethoxy-4-methylphenyl Grignard reagent (derived from 4-bromo-2,5-dimethoxytoluene and Mg in anhydrous tetrahydrofuran) with 1b (or 2b) in the presence of a palladium catalyst 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 $^1$H/$^{13}$C NMR spectroscopy and correct elemental analysis.

The electron donor strengths of 1c and 2c in comparison with the model compound (4,4’-dimethyl-2,5-dimethoxybiphenyl) 3(9) were evaluated by electrochemical oxidation at a platinum electrode as a $2 \times 10^{-3}$ 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 donors were consistently obtained at a scan rate of 25–200 mV s$^{-1}$, and they all showed anodic/cathodic peak current ratios of $i_d/i_c = 1.0$ (theoretical) at ambient temperatures. It

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

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![Scheme 1](image-url)

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**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 $\nu = 200$ mV s$^{-1}$ (25 °C).

(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 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 cannula to a Schlenk flask containing 1b (3.04 g, 3 mmol) and PdCl$_2$(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; $^1$H NMR (CDCl$_3$) δ 2.18 (s, 18H), 3.39 (s, 18H), 3.681 (s, 18H), 6.61 (s, 6H), 6.70 (s, 6H), 7.12 (d, $J = 8.1$ Hz, 12H), 6.98 (d, $J = 8.4$ Hz, 12H); $^13$C NMR (CDCl$_3$) 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. Calc'd for C$_{22}$H$_{22}$O$_2$: C, 80.31; H, 6.32; O, 13.37. Found: C, 80.26, H, 6.35. Tetraakis(4-methyl-3,6-dimethoxybiphenyl)methane (2c): mp > 320 °C; $^1$H NMR (CDCl$_3$) δ 2.29 (s, 12H), 3.79 (s, 12H), 3.84 (s, 12H), 6.83 (s, 4H), 6.89 (s, 4H), 7.12 (d, $J = 8.1$ Hz, 12H), 6.98 (d, $J = 8.4$ Hz, 12H); $^13$C NMR (CDCl$_3$) 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. Calc'd for C$_{32}$H$_{26}$O$_2$: 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-dimethoxy) 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, $E_{\text{red}} = 0.45$ 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.\textsuperscript{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 [1c$^{4+}$SbCl$_6$]$_6$ could be isolated, by precipitation using hexane, in nearly quantitative yield according to the stoichiometry shown:\textsuperscript{16}

$$1c + 9SbCl_5 \rightarrow 1c^{6+}SbCl_6^- + 3SbCl_3$$

(1)

In a similar vein, tetracationic [2c$^{4+}$(SbCl$_6$)]$_6$ 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 titrations\textsuperscript{17} 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$^+$)\textsuperscript{18} as an aromatic one-electron oxidant ($E_{\text{red}} = 1.34$ V vs. SCE).

![An Efficient Aromatic Oxidant](image)

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 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:

$$4^{+} + \frac{1}{6}1c \rightarrow \frac{1}{6}1c^{6+} + 4$$

(2)

(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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{21}

It is interesting to note that the oxidizing strength of these multiple charged cation radicals 1c$^{4+}$ and 2c$^{4+}$ ($E_{\text{red}} = 1.15$ V vs. SCE) is similar to that of the extensively utilized tris-4-bromophenylammonium cation radical\textsuperscript{22} (magic blue, $E_{\text{red}} = 1.1$ V vs. SCE) as an aromatic oxidant in a variety of

\textsuperscript{16} For the stoichiometry of the oxidation of donors with SbCl$_5$, see: Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. Org. Chem. 1998, 63, 5847.

\textsuperscript{17} The purity of the isolated [1c$^{6+}$] and [2c$^{4+}$] 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.


\textsuperscript{19} The oxidation of 4$^+$ to its green cation radical can be carried out electrochemically at $E_{\text{onset}} = 1.2$ V vs SCE in dichloromethane containing 0.05 M n-Bu$_4$NPF$_6$ at 0 °C.

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

\textsuperscript{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-hexabenzocoronen framework will lead to extensive electronic communication amongst aryl groups. Compare: Ito, S.; Herwig, P. T.; Böhme, T.; Rabe, J. P.; Retig, W.; Müllen, K. J. Am. Chem. Soc. 2000, 122, 7698.
electron-transfer catalyzed (ETC) organic transformations. For example, the oxidation of a colorless solution of octamethylbiphenylene (5, $E_{\text{red}} = 0.8$ V vs. SCE) with 1/6 equiv of $[1c^{6+}(\text{SbCl}_5^-)_6]$ or 1/4 equiv of $[2c^{4+}(\text{SbCl}_5^-)_4]$ in dichloromethane immediately yielded a dark blue solution of $5^{+•}$ ($\lambda_{\text{max}} = 602$ nm) in quantitative yield as estimated by the UV–vis spectral analysis (eq 3).

In a similar vein, a variety of aromatic and olefinic donors (D) such as 2,5-dimethyl-1,4-dimethoxybenzene, perylene, octamethylanthracene, 1,2-dianisyl-1,2-ditoly-ethylene, tetraanisylethylene, and 2,3-dianisylbicyclo-[2.2.2]oct-2-ene were quantitatively oxidized to their brightly colored cation radicals using $[1c^{6+}(\text{SbCl}_5^-)_6]$ and $[2c^{4+}(\text{SbCl}_5^-)_4]$ 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.

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Figure 2. (A) Spectral changes attendant upon the reduction of $1.5 \times 10^{-4}$ M naphthalene cation radical $4^{+•} (- -)$ by incremental addition of $1.2 \times 10^{-3}$ M 1c to its hexacation radical $1e^{6+•} (- -)$ in dichloromethane at 22 °C. (B) A plot of depletion of absorbance (data from Figure 2A) of $4^{+•}$ (O, monitored at 672 nm) and an increase of the absorbance of $1e^{6+•}$ (●, monitored at 1100 nm) against the equivalent of added 1c showed a complete consumption of $4^{+•}$ after addition of 1/6 equiv of 1c. (C) UV–vis absorption spectra of cation radicals $1e^{6+•} (- -)$, $2c^{4+•} (- -)$, and $3^{+•} (\cdots)$ obtained by SbCl$_5$ oxidation in dichloromethane at 22 °C.

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\begin{align*}
6 \quad 5^{+•} + 1c^{6+} & \rightarrow 6 \quad 5^{+•} + 1c \quad (3)
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