Synthesis of Bis(semiquinone)s and Their Electrochemical and Electron Paramagnetic Resonance Spectral Characterization[†]

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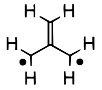
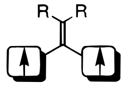
The syntheses of three new bis(semiquinone)s (**2**$^{\bullet\bullet 2-}$, **3**$^{\bullet\bullet 2-}$, and **5**$^{\bullet\bullet 2-}$) linked through carbon−carbon double bonds in a geminal fashion (**2**$^{\bullet\bullet 2-}$ and **3**$^{\bullet\bullet 2-}$), and through an sp^3 carbon (**5**$^{\bullet\bullet 2-}$), are presented, as well as the results of variable-temperature EPR (VT-EPR) spectroscopy on these biradicals and two previously reported bis(semiquinone)s, **1**$^{\bullet\bullet 2-}$ and **4**$^{\bullet\bullet 2-}$. We suggest that the potential difference in redox couples associated with a biradical is useful for qualitatively assessing changes in the exchange parameter within an isostructural series. The zero-field-splitting parameters for **1**$^{\bullet\bullet 2-}$−**5**$^{\bullet\bullet 2-}$ are consistent with their electronic structures: biradicals **1**$^{\bullet\bullet 2-}$−**3**$^{\bullet\bullet 2-}$ which have conjugating groups attached to the semiquinone rings have *D*-values less than **5**$^{\bullet\bullet 2-}$, a bis(semiquinone) that lacks such a conjugating group. Also, the *D*-value of **3**$^{\bullet\bullet 2-}$ is significantly less than those of **1**$^{\bullet\bullet 2-}$ and **2**$^{\bullet\bullet 2-}$, in agreement with larger interelectron separation in **3**$^{\bullet\bullet 2-}$, a biradical with quinone-methide π-system delocalization. Changes in counterion Lewis acidity are not manifested in the *D*-values of the biradical dianion **4**$^{\bullet\bullet 2-}$. The EPR spectrum of biradical **5**$^{\bullet\bullet 2-}$ is consistent with the existence of at least two rotamers having different zero-field-splitting parameters. Biradicals **1**$^{\bullet\bullet 2-}$−**4**$^{\bullet\bullet 2-}$ gave linear Curie plots, consistent with $J > 0$ (ferromagnetic coupling) or $J = 0$. The temperature-dependent intensity of EPR signals of **5**$^{\bullet\bullet 2-}$ are characteristic of antiferromagnetic coupling. Best fit results give $J = -114 \pm 6$ cal/mol for the $|D/hc| = 0.01309$ cm^{-1} rotamer of **5**$^{\bullet\bullet 2-}$, and $J = -76 \pm 3$ cal/mol for the $|D/hc| = 0.01026$ cm^{-1} rotamer of **5**$^{\bullet\bullet 2-}$.

The preparation of paramagnetic ligands for the construction of molecule-based magnets is an active area of research.[1] Several groups have synthesized novel nitroxide-type bi- and triradicals,[2] and we recently reported the synthesis and characterization of a mixed nitroxide−semiquinone biradical,[3] as well as the preparation of *m*-phenylene-linked and trimethylenemethane (TMM)-type bis(semiquinone)s.[4,5] The EPR spectroscopic features of the two bis(semiquinone)s were consistent with the proposed electronic structures. Herein, we report the synthesis of three new bis(semiquinone)s (**2**$^{\bullet\bullet 2-}$, **3**$^{\bullet\bullet 2-}$, and **5**$^{\bullet\bullet 2-}$) linked through carbon−carbon double bonds in a geminal fashion (**2**$^{\bullet\bullet 2-}$ and **3**$^{\bullet\bullet 2-}$) and through an sp^3 carbon (**5**$^{\bullet\bullet 2-}$), as well as the results of variable-temperature EPR (VT-EPR) spectroscopy of all five compounds (Chart 1).

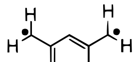
The design criteria for high-spin ligands is identical to those for design of organic biradicals, a topic that has been discussed in some detail.[6] Generally, the common approach is to attach "spin-containing groups" to a linker fragment known to couple unpaired electrons in a high-spin or ferromagnetic fashion.[7] Two common, successful linkers are those in nondisjoint[8] biradicals trimethylenemethane (TMM) and *m*-xylylene, known triplet ground-state molecules.[9,10]



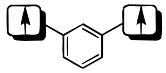
TMM



Generalized TMM-type Biradical

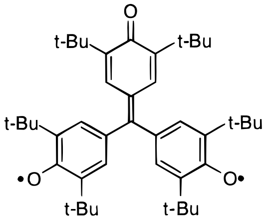


***meta*-Xylylene**



Generalized *meta*-Xylylene-typ Biradical

Biradicals **1**$^{\bullet\bullet 2-}$−**4**$^{\bullet\bullet 2-}$ were synthesized to test the viability of the TMM- and *m*-phenylene-type strategies for preparing high-spin bis(semiquinone)s. TMM-type bis(semiquinone)s **1**$^{\bullet\bullet 2-}$ and **2**$^{\bullet\bullet 2-}$ have adamantane and norbornane ring systems that "cap" the exocyclic C=C and provide steric protection of any spin density delocalized into the exocyclic C=C. Ultimately, we will use ligands **1**$^{\bullet\bullet 2-}$ and **2**$^{\bullet\bullet 2-}$ to extend our study of the effects of bond torsions on exchange coupling in TMM-type biradicals.[11,12] Bis(semiquinone) **3**$^{\bullet\bullet 2-}$ is an analogue of Yang's biradical,[13−16] and the semiquinone spins should delocalize into the quinone-methide group.



Yang's Biradical

Finally, biradical **5**$^{\bullet\bullet 2-}$ was examined to determine if the C=C groups of **1**$^{\bullet\bullet 2-}$−**3**$^{\bullet\bullet 2-}$ played a part in exchange coupling beyond holding the semiquinone groups close together in space.

Synthesis

Bis(orthoquinone)s **1** and **4** were prepared as described previously.[4,5] Compounds **2**, **3**, and **5** were prepared as

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[†] Taken from the M.S. Thesis of A.K.B.

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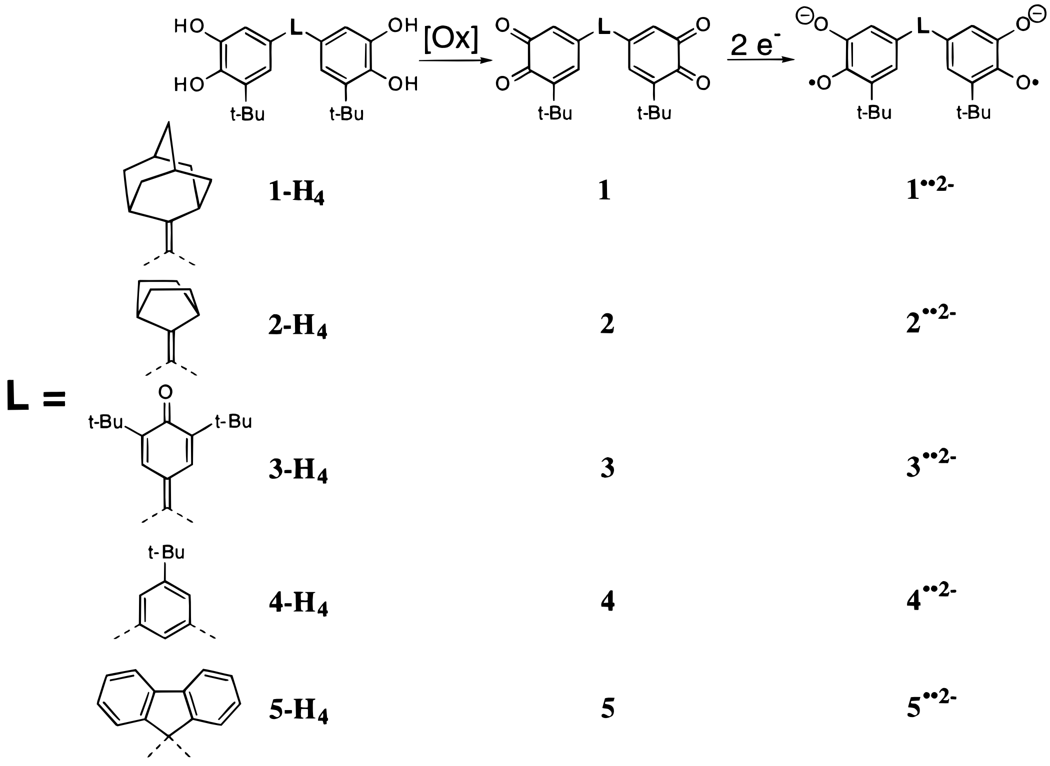
Chart 1



shown below. Methyl norbornane-7-carboxylate was prepared using a modified procedure of Kwart:[17] metalation of 7-bromonorbornane with lithium 4,4′-di-*tert*-butylbiphenylide (LiDBB),[18] followed by reaction of the alkyllithium with CO_2, and Fischer esterification gave ester **7** in excellent yield. Ester **7** was reacted with 2 equiv of 3-*tert*-butyl-5-lithiocatechol dimethyl ether,[5] followed by *p*-toluenesulfonic acid-promoted dehydration, and demethylation to give bis(catechol), **2-H$_4$**. Oxidation of **2-H$_4$** with Fétizon's reagent[19] gave bis(quinone) **2**.

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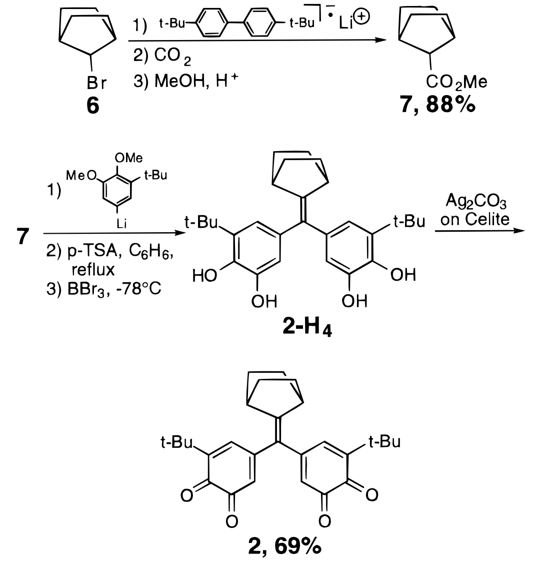
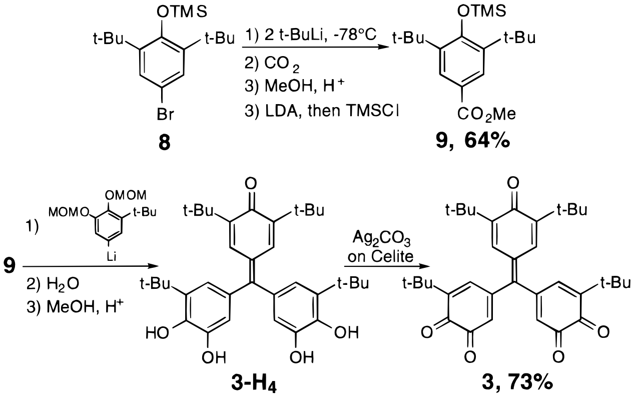
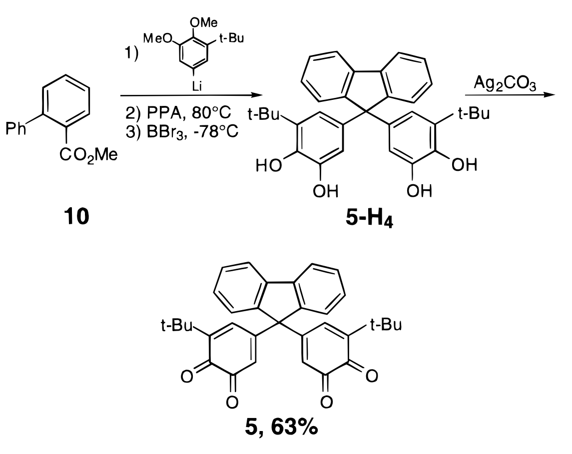


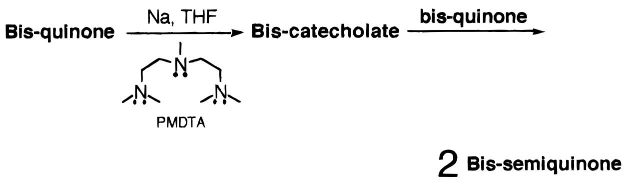
Bis(quinone) **3** was prepared in a similar fashion, by reaction of 3-*tert*-butyl-5-lithiocatechol bis(methoxymethyl) ether[5] with ester **9** followed by removal of the TMS group, elimination, deprotection, and oxidation of bis(catechol) **3-H₄**. Ester **9** was prepared by carboxylation of the lithium reagent formed from **8**,[20] followed by esterification and reprotection of the phenol group.



Condensation of 3-*tert*-butyl-5-lithiocatechol dimethyl ether with ester **10**[21] provided a carbinol that underwent electrophilic aromatic substitution upon exposure to polyphosphoric acid to form, after demethylation, fluorene derivative **5-H₄**. Oxidation provided bis(quinone) **5** in good yield.



Three methods were used to prepare bis(semiquinone)s. The first method is that reported by Müller:[22] reduction of quinone to catecholate, followed by comproportionation with an equimolar portion of quinone, eq 1. This method worked for bis(quinone)s **4** and **5**, suggesting C=C reduction or related reactivity in **1**–**3**. Alternatively, anthrasemiquinone (**AQ**$^{-\bullet}$) was used as a one-electron reducing agent,[23] eqs 2 and 3. Anthrasemiquinone reduction was the only method used that gave reproducible, positive results for **3**. Reductions of the bis(quinone)s that gave alkali metal salts were carried out in the presence of excess pentamethyldiethyltriamine (PMDTA), which we found to effectively inhibit formation of semiquinone aggregates.[24] Finally, controlled-potential-coulometry (CPC) was used for **1** and **2** because neither Na-metal reduction nor reduction with **AQ**$^{-\bullet}$ reproducibly gave biradicals. CPC was carried out on THF solutions of bis(quinone)s using tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte, eq 4. Neither EPR spectra nor the results of variable-temperature studies were a function of the method (or the semiquinone counterions) used for production of the biradicals.[25]



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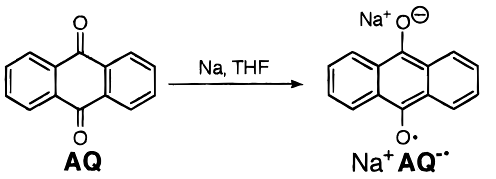

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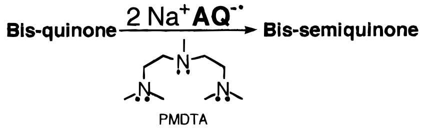

(3)

$$\text{Bis-quinone} \xrightarrow[\text{THF, } n\text{-Bu}_4\text{NPF}_6]{\text{CPC}} \text{Bis-semiquinone} \qquad (4)$$

Electrochemistry

Figure 1 shows the cyclic voltammograms of **1**–**5** as solutions in THF, and pertinent data are collected in Table 1. All bis(quinone)s examined showed separate waves for the first and second redox couples which correspond to bis(quinone) to (quinone–semiquinone) and (quinone–semiquinone) to bis(semiquinone) couples, respectively. Bis(quinone)s **1**, **2**, and **5** exhibited nearly identical CV waveforms with redox couples at ca. −0.73 and ca. −0.94 V vs Ag/AgNO$_3$, and splittings of the redox

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(25) Reduction of **4** by eqs 1, 3, or 4 gave the same results.

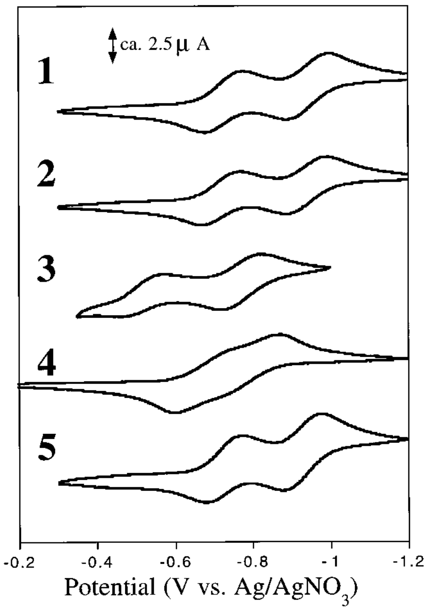

Figure 1. Cyclic voltammograms for bis(quinone)s **1**−**5** as 1 mM solutions in THF. Supporting electrolyte is tetra-*n*-butylammonium hexafluorophosphate (100 mM). Scan rate = 200 mV/s.

Table 1. Cyclic Voltammetric Data for Bis(quinone)s 1−5[a]

bis(quinone)	$E_{1/2}(1)^b$	$E_{1/2}(2)^c$	$\Delta E_{1/2}{}^d$
1	−0.73	−0.94	−0.21
2	−0.72	−0.94	−0.22
3	−0.52	−0.77	−0.25
4	−0.67	−0.79	−0.12
5	−0.73	−0.93	−0.20

[a] 0.5 mM bis(quinone) in THF, 100 mM *n*-Bu$_4$NPF$_6$ electrolyte; potentials in volts vs Ag/AgNO$_3$; scan rate = 200 mV/s. [b] Redox potential for bis(quinone) ↔ (quinone−semiquinone) couple; $E_{1/2} = (E_{p,c} - E_{p,a})/2$. [c] Redox potential for (quinone−semiquinone) ↔ bis(semiquinone) couple; $E_{1/2} = (E_{p,c} - E_{p,a})/2$. [d] $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$.

couples of ca. −0.21 V. Any effect of the exocyclic double bonds of **1** and **2** are not manifested in the CVs since the redox potentials are nearly identical to those of **5**—a molecule that has the quinone groups attached geminal on an sp^3 carbon atom and delocalization beyond the semiquinone rings is impossible.

Bis(quinone) **3**, like **1** and **2**, has two quinone groups attached geminal on a C=C, but the double bond of **3** is part of a quinone-methide π-system. This larger π-system permits greater delocalization of charge and spin after reduction than possible in reduced forms of **1** and **2**. Increased delocalization is clearly apparent in the more positive $E_{1/2}(1)$ and $E_{1/2}(2)$ values for **3** compared to **1**, **2**, or **5**. It is important to note that $\Delta E_{1/2}$ for **3** is slightly larger than in **1**, **2**, and **5**. We interpret the larger $\Delta E_{1/2}$ as additional evidence of greater delocalization in **3** than in **1** and **2**. Greater delocalization of the semiquinone charge should result in greater Coulombic repulsion upon addition of the second electron to form the bis(semiquinone), hence the larger $\Delta E_{1/2}$. Bis(quinone) **4** has quinone rings positioned about twice as far apart as in **1**−**3** and **5**. The greater quinone-ring spatial separation, in combination with the six-atom *m*-phenylene coupler, has an overall effect of decreasing $\Delta E_{1/2}$ by nearly 2-fold.

It would be useful if $\Delta E_{1/2}$ were an electrochemical “handle” on exchange coupling (J) for *isostructural*, nondisjoint, biradicals, like $\mathbf{1}^{\bullet\bullet 2-}$−$\mathbf{3}^{\bullet\bullet 2-}$ and perhaps $\mathbf{5}^{\bullet\bullet 2-}$.[26] A relationship between $\Delta E_{1/2}$ and J is reasonable since charge and spin are delocalized over the same atoms, i.e., electrostatic repulsion between electrons in the SOMOs—a major contributor to $\Delta E_{1/2}$—should scale with the exchange energy for the same pair of electrons. The ferromagnetic component of J is the exchange integral ($\boldsymbol{k}_{a,b}$) whose magnitude is directly proportional to coextensivity (the sharing of common atoms) of biradical SOMOs,[27] and $\boldsymbol{k}_{a,b}$ should therefore be *proportional* to the electron−electron repulsion responsible for $\Delta E_{1/2}$. Finally, localizing spin in a region of space where overlap can occur with the other radical moiety (as in $\mathbf{1}^{\bullet\bullet 2-}$−$\mathbf{3}^{\bullet\bullet 2-}$ and $\mathbf{5}^{\bullet\bullet 2-}$) creating weak bonding interactions should increase the antiferromagnetic component of J.[27] Thus, an observed increase in electron−electron repulsion in a series of isostructural dianion biradicals should correlate with J in the series. Based on values of $\Delta E_{1/2}$, $|J|(\mathbf{3}^{\bullet\bullet 2-}) > |J|(\mathbf{2}^{\bullet\bullet 2-}) \approx |J|(\mathbf{1}^{\bullet\bullet 2-})$. Since $\Delta E_{1/2}$ for **5** is nearly identical to $\Delta E_{1/2}$ for both **1** and **2**, and **5** lacks the π-topology required for ferromagnetic coupling, J is expected to be more negative (i.e., more antiferromagnetic) for $\mathbf{5}^{\bullet\bullet 2-}$ than for $\mathbf{2}^{\bullet\bullet 2-}$ or $\mathbf{1}^{\bullet\bullet 2-}$.

EPR Spectroscopy

Figure 2 shows the EPR spectra of $\mathbf{1}^{\bullet\bullet 2-}$−$\mathbf{5}^{\bullet\bullet 2-}$ recorded at 77 K in THF. All spectra are consistent with randomly oriented triplet species[28] along with doublet monoradical impurities. The zero-field-splitting parameters for the biradicals, obtained by simulation,[29] are given in Table 2. The spectral shapes of $\mathbf{1}^{\bullet\bullet 2-}$−$\mathbf{4}^{\bullet\bullet 2-}$ are invariant with temperature changes, suggesting the lack of rotomers.[11]

The zero-field splitting parameters for $\mathbf{1}^{\bullet\bullet 2-}$−$\mathbf{5}^{\bullet\bullet 2-}$ are consistent with their electronic structures: biradicals $\mathbf{1}^{\bullet\bullet 2-}$−$\mathbf{3}^{\bullet\bullet 2-}$ which have conjugating groups attached to the semiquinone rings have D-values less than either rotamer of $\mathbf{5}^{\bullet\bullet 2-}$. Also, the D-value of $\mathbf{3}^{\bullet\bullet 2-}$ is significantly less than those of $\mathbf{1}^{\bullet\bullet 2-}$ and $\mathbf{2}^{\bullet\bullet 2-}$, in agreement with larger interelectron separation in $\mathbf{3}^{\bullet\bullet 2-}$, a biradical with quinone-methide π-system delocalization.

Rotello’s group has shown differential response of spin and charge density to hydrogen bonding interactions,[30] so it is reasonable to expect a change in zero-field splitting parameters—particularly $|D/hc|$—when counterions of differing Lewis acidity are associated with the semiquinone groups. However, the zero-field splitting parameters of Na$_2\mathbf{4}^{\bullet\bullet 2-}$(PMDTA)$_n$, Table 2, are nearly identical to those of $(n\text{-Bu}_4\text{N})_2\mathbf{4}^{\bullet\bullet}$,[2−4] indicating that any changes in counterion Lewis acidity are not well-manifested in the D-value.[31] It is interesting to note that the D-value for $\mathbf{3}^{\bullet\bullet 2-}$ is nearly 2.7-times greater than that of Yang’s biradical (ca. 0.0028 cm^{-1}).[32] The greater

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[26] For an interesting and relevant discussion of the differences in $\Delta E_{1/2}$ for disjoint and coextensive biradical dications, see: Bushby, R. J.; McGill, D. R.; Ng, K. M.; Taylor, N. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1405.

[27] Kollmar, C.; Kahn, O. *Acc. Chem. Res.* **1993**, *26*, 259.

[28] Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

[29] Powder EPR spectra were simulated using: WINEPR SimFonia, Shareware Version 1.25, Bruker Analytische Messtechnik GmbH, Copyright ©1994−1996.

[30] Niemz, A.; Rotello, V. M. *J. Am. Chem. Soc.* **1997**, *119*, 6833.

[31] Li, Na, K, Rb, and Cs salts of $\mathbf{4}^{\bullet\bullet 2-}$ all have nearly identical ***D***-values; see Supporting Information for EPR spectra.

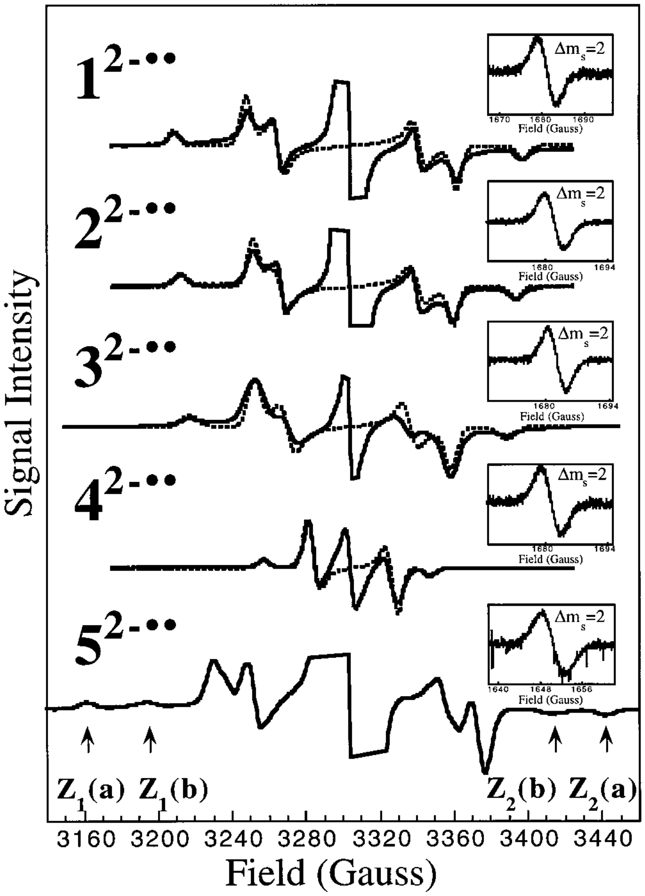
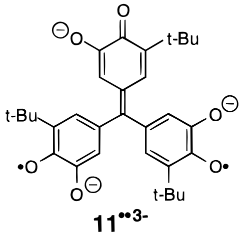


Figure 2. X-band EPR spectra of biradicals $\mathbf{1}^{\bullet\bullet 2-}$–$\mathbf{5}^{\bullet\bullet 2-}$ as frozen solutions in THF at 77 K. Dashed lines are simulated spectra. Signals at $g = 2$ are due to monoradicals. Insets: $\Delta m_s = 2$ transitions. Counterions for $\mathbf{3}^{\bullet\bullet 2-}$ and $\mathbf{4}^{\bullet\bullet 2-}$: Na$^+$; counterions for $\mathbf{1}^{\bullet\bullet 2-}$, $\mathbf{2}^{\bullet\bullet 2-}$, and $\mathbf{5}^{\bullet\bullet 2-}$: n-Bu$_4N^+$. ***D*-values** for rotamers of $\mathbf{5}^{\bullet\bullet 2-}$ were estimated as [(Z$_2$(a) − Z$_1$(a)]/2 and [(Z$_2$(b) − Z$_1$(b)]/2; see text.

D-value of $\mathbf{3}^{\bullet\bullet 2-}$ is most likely due to its lower symmetry which results in less delocalization of spin-density into the quinone-methide π-system than might be expected. If this supposition is correct, the C_3-symmetric biradical $\mathbf{11}^{3-\bullet\bullet}$[33] should have a *D*-value smaller than that of $\mathbf{3}^{\bullet\bullet 2-}$ and nearly equal to that of Yang's biradical.



$\mathbf{11}^{\bullet\bullet 3-}$

As shown in Figure 3, the EPR spectrum of biradical $\mathbf{5}^{\bullet\bullet 2-}$ is consistent with the existence of at least two rotamers having different zero-field splitting parameters. We propose structures $\mathbf{5a}^{\bullet\bullet 2-}$–$\mathbf{5c}^{\bullet\bullet 2-}$ shown below as possible rotomers. Calculated *D*-values[34] for $\mathbf{5a}^{\bullet\bullet 2-}$–$\mathbf{5c}^{\bullet\bullet 2-}$ are 0.0088 cm^{-1}, 0.0078 cm^{-1}, 0.0075 cm^{-1}, respectively, in reasonable agreement with the two observed *D*-values.

Table 2. Zero-Field-Splitting Parameters and Results of VT-EPR Studies for Biradicals $\mathbf{1}^{\bullet\bullet 2-}$–$\mathbf{5}^{\bullet\bullet 2-}$ [a]

biradical	$\lvert D/hc\rvert/10^{-4}$ cm^{-1}	$\lvert E/hc\rvert/10^{-4}$ cm^{-1}	Curie plot[b]
$\mathbf{1}^{\bullet\bullet 2-}$ [c]	94.7	6.30	linear
$\mathbf{2}^{\bullet\bullet 2-}$ [c]	91.0	5.75	linear
$\mathbf{3}^{\bullet\bullet 2-}$ [e]	86.0	6.70	linear
$\mathbf{4}^{\bullet\bullet 2-}$ [d]	45.3	0	linear
$\mathbf{5}^{\bullet\bullet 2-}$ [c]	130.9	–	curved, $J = -114$ cal/mol
	102.6	–	curved, $J = -76$ cal/mol

[a] Zero-field-splitting parameters determined by simulation.[28] [b] Curved Curie plots fit with eq 5; see text. [c] Biradical prepared by CPC; n-Bu$_4$N$^+$ counterions. [d] Biradical prepared by sodium metal reduction in the presence of excess PMDTA. [e] Biradical prepared by sodium anthrasemiquinone reduction in the presence of excess PMDTA.

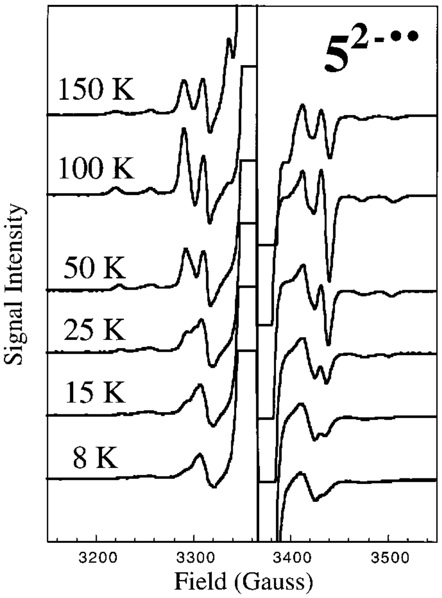
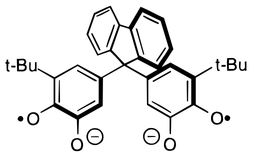
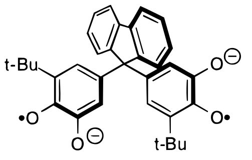


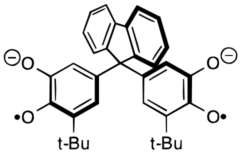
Figure 3. X-band EPR spectra of biradical $\mathbf{5}^{\bullet\bullet 2-}$ as a frozen solution in THF at 8, 15, 25, 50, 100, and 150 K. Signals at $g = 2$ are due to monoradicals.



$\mathbf{5a}^{\bullet\bullet 2-}$ (C_2)



$\mathbf{5b}^{\bullet\bullet 2-}$ (C_1)



$\mathbf{5c}^{\bullet\bullet 2-}$ (C_2)

Curie plots for the doubly integrated $\Delta m_s = 2$ signals of $\mathbf{1}^{\bullet\bullet 2-}$–$\mathbf{4}^{\bullet\bullet 2-}$ and doubly integrated $\Delta m_s = 1$ signals of $\mathbf{5}^{\bullet\bullet 2-}$ are shown in Figures 4 and 5, respectively, and are summarized in Table 2. Biradicals $\mathbf{1}^{\bullet\bullet 2-}$–$\mathbf{4}^{\bullet\bullet 2-}$ gave linear

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(32) Mukai, K.; Ishizu, K.; Nakahara, M.; Deguchi, Y. *Bull. Chem. Soc., Jpn.* **1980**, *53*, 3363.

(33) We recently prepared a trinuclear metal complex with biradical $\mathbf{11}^{3-\bullet\bullet}$ that exhibits $\boldsymbol{D} \approx 0.005$ cm^{-1}, less than the ***D***-value for $\mathbf{3}^{3-\bullet\bullet}$ in accord with our predictions; Shultz, D. A.; Lee, H.; Bodnar, S. H., manuscript in preparation.

(34) Sandberg, K. A.; Shultz, D. A. *J. Phys. Org. Chem.* **1998**, in press.

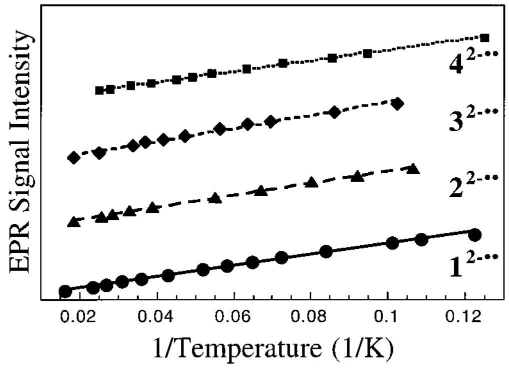
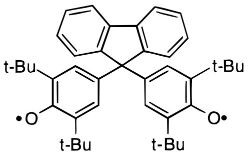


Figure 4. Curie plots for biradicals $\mathbf{1}^{\bullet\bullet 2-}$–$\mathbf{4}^{\bullet\bullet 2-}$. The data points were collected between 8 and 150 K and represent normalized signal intensities obtained by double integration of the $\Delta m_s = 2$ signals.

responses, consistent with $J > 0$ (ferromagnetic coupling) or $J = 0$.[35] The intensity of $\Delta m_s = 1$ signals of $\mathbf{5}^{\bullet\bullet 2-}$ decreased with decreasing temperature consistent with antiferromagnetic coupling. The data were fit to eq 5:[35,36]

$$I_{\mathrm{EPR}} = \frac{C}{T}\left[\frac{3\exp\left(\frac{-2J}{RT}\right)}{1 + 3\exp\left(\frac{-2J}{RT}\right)}\right] \qquad (5)$$

where C is a constant and J is the exchange parameter. Best fit results give $J = -114 \pm 6$ cal/mol for the $|D/\mathrm{hc}| = 0.01309\ \mathrm{cm}^{-1}$ rotamer, and $J = -76 \pm 3$ cal/mol for the $|D/\mathrm{hc}| = 0.01026\ \mathrm{cm}^{-1}$ rotamer. Both J-values are reasonably close to that of the related fluorenyl-bis(phenoxy) biradical, $\mathbf{12}^{\bullet\bullet}$ ($J = -65$ cal/mol).[37,38]



$\mathbf{12}^{\bullet\bullet}$

As expected, based on $\Delta E_{1/2}$ values and the lack of the requisite π-topology for ferromagnetic coupling, J for $\mathbf{5}^{\bullet\bullet 2-}$ is more negative than J-values for $\mathbf{1}^{\bullet\bullet 2-}$–$\mathbf{3}^{\bullet\bullet 2-}$. Thus, $\Delta E_{1/2}$ for biradical redox couples can be useful for qualitatively assessing J within a series of isostructural compounds.

Conclusions

A series of bis(semiquinone)s have been prepared. The difference between the first and second redox potentials has been shown to be useful for qualitatively assessing exchange coupling within a series of isostructural compounds. The biradicals have zero-field-splitting parameters in accord with their structures, and the results of VT-EPR studies indicate that coupling in $\mathbf{1}^{\bullet\bullet 2-}$–$\mathbf{4}^{\bullet\bullet 2-}$ is consistent with the π-topologies of their coupler groups. Fluorenyl-bis(semiquinone), $\mathbf{5}^{\bullet\bullet 2-}$, exists as at least two rotamers in frozen THF. Intensities of signals from two rotamers were recorded as a function of temperature. Fitting the temperature-dependent intensities to a Bleaney–Bowers-type equation gave $J = -76$ cal/mol and -114 cal/mol. Thus, the exocyclic C=C TMM-type couplers in $\mathbf{1}^{\bullet\bullet 2-}$–$\mathbf{3}^{\bullet\bullet 2-}$ are acting as spin couplers despite expected large torsion angles.

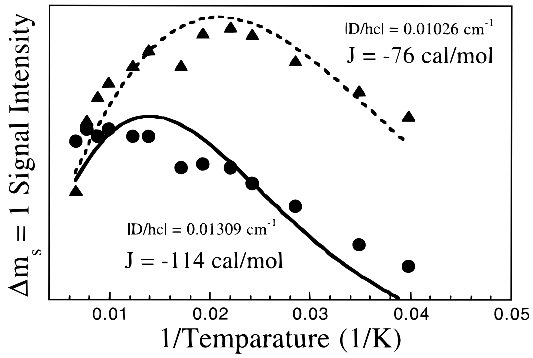


Figure 5. Curie plots for biradical $\mathbf{5}^{\bullet\bullet 2-}$. The data points were collected between 8 and 150 K and represent normalized signal intensities obtained by double integration of the $\Delta m_s = 1$ signals. The data points correspond to the signals marked Z_1(a) and Z_1(b) in Figure 2.

Experimental Section

General. Unless noted otherwise, reactions were carried out in oven-dried glassware under an argon atmosphere. THF was distilled under nitrogen from sodium benzophenone ketyl, toluene was distilled from sodium metal under nitrogen, and methylene chloride and acetonitrile were distilled from CaH_2 under nitrogen. Benzene, methanol, and p-toluenesulfonic acid hydrate were used as received from Fisher Scientific. *tert*-Butyllithium (1.5 M in pentane) was used as received from Acros Chemical. Other chemicals were purchased from Aldrich Chemical Co. Electrochemical experiments and X-Band EPR spectroscopy were performed as described previously.[3] NMR spectra were recorded at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Elemental analysis was performed by Atlantic Microlab, Inc, Norcross, GA. Mass Spectra were obtained at the NC State University Mass Spectrometry Facility.

Methyl Norbornane-7-carboxylate.[17] In a 250 mL Schlenk flask, 7-bromonorborane (3.7 g, 21.3 mmol) was dissolved in 10 mL of THF and cooled to −78 °C. To this was added a dark green solution of LiDBB, formed by stirring DBB (12.5 g, 47 mmol) over excess lithium metal in 50 mL of THF for 3 h.[18] During the addition of the LiDBB solution, the reaction solution was first colorless and then turned red and finally dark green. The resulting solution was stirred for 15 min at −78 °C, followed by cannulating over a large excess of freshly crushed CO_2. The resulting light yellow solution was allowed to warm to room temperature, and the THF was removed. Et_2O was added, and the organic layer extracted twice with 1 M aqueous NaOH. The combined aqueous extracts were acidified by the addition of concentrated HCl, followed by extraction in to Et_2O. The resulting organic fractions were combined, washed once with H_2O and once with saturated aqueous NaCl, and finally dried over Na_2SO_4. The crude acid was then esterified by refluxing overnight in acetone with K_2CO_3 (6 g, 42.7 mmol) and CH_3I (9.1 g, 64 mmol, 4 mL). Acetone was then removed, the mixture was dissolved in Et_2O and H_2O, and the resulting organic layer was washed once with 1 M aqueous NaOH, once with water, and finally with saturated aqueous NaCl, followed by drying over Na_2SO_4. Solvent removal and Kugelrohr distillation (100 °C, 200 mTorr) yielded the ester as a sweet-smelling oil (2.9 g, 88% yield).

Bis(5-*tert*-butyl-3,4-dimethoxyphenyl)norbornyl Carbinol. In a 50 mL Schlenk flask, 4-bromo-6-*tert*-butylcatechol dimethyl ether (820 mg, 2.99 mmol) was dissolved in 10 mL of THF and cooled to −78 °C. *tert*-Butyllithium (3.9 mL of a 1.5 M solution, 5.9 mmol) was added dropwise, and the light

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(35) *The Chemistry of Quinonoid Compounds, Vol. II*; Berson, J. A., Ed.; John Wiley & Sons: New York, 1988; pp 473–489.

(36) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.

(37) Chandross, E. A.; Kreilick, R. *J. Am. Chem. Soc.* **1964**, *86*, 1263.

(38) Kopf, P. W.; Kreilick, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 6569.

yellow, turbid solution was stirred for 1 h at −78 °C. A solution of methyl norbornane-7-carboxylate (210 mg, 1.5 mmol) in 5 mL of THF was then added, and the reaction was stirred overnight to give a faint yellow solution. The reaction was quenched with saturated aqueous NH_4Cl, transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was separated and dried over Na_2SO_4, and the solvent was removed to yield a thick yellow oil which was purified by radial chromatography (SiO_2, 5% Et_2O:petroleum ether) to give a thick, colorless oil (610 mg, 90% yield). ^{1}H NMR (C_6D_6, 300 MHz) δ (ppm): 7.40 (s, 2H), 7.11 (s, 2H), 3.78 (s, 6H), 3.32 (s, 6H), 2.63 (s, 1H), 2.17−2.21 (bm, 4H), 1.78 (s, 1H), 1.64 (d, J = 6.8 Hz, 2H), 1.51 (s, 18H), 1.23 (d, J = 7.2 Hz, 2H), 1.14 (d, J = 7.0 Hz, 2H). ^{13}C NMR (C_6D_6, 75 MHz) δ(ppm): 153.5, 147.9, 143.4, 142.1, 117.2, 110.2, 79.7, 60.1, 59.5, 55.5, 38.9, 35.5, 31.7, 31.0, 30.5. IR (film from CH_2Cl_2) ν (cm^{-1}): 3617, 3520. Anal. Calcd for $C_{32}H_{46}O_5$: C, 75.26; H, 9.08. Found: C, 75.34; H, 9.06.

Bis(5-*tert*-butyl-3,4-dimethoxyphenyl)methylenenorbornane. The alcohol from the previous step (500 mg, 0.98 mmol) and *p*-toluenesulfonic acid hydrate (35 mg, 0.2 mmol) were added to a 200 mL round-bottom flask with 100 mL of benzene. The flask was connected to a Dean−Stark trap and reflux condenser and refluxed with azeotropic removal of water for 3 h. The reaction was cooled, transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was collected and dried over Na_2SO_4, and the resulting solid was purified by radial chromatography (SiO_2, 10% Et_2O:petroleum ether) to give a white solid (460 mg, 95% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.75 (d, J = 2.0 Hz, 2H), 6.54 (d, J = 2.0 Hz, 2H), 3.88 (s, 6H), 3.75 (s, 6H), 2.74 (bm, 2H), 1.77 (d, J = 6.6 Hz, 4H), 1.44(d, J = 6.9 Hz, 4H), 1.36 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ(ppm): 152.4, 149.1, 147.0, 141.8, 137.4, 127.5, 120.9, 112.3, 60.4, 55.7, 38.4, 35.1, 30.7, 29.1. Anal. Calcd for $C_{32}H_{44}O_4$: C, 78.00; H, 9.00. Found: C, 77.87; H, 9.07.

Bis(5-*tert*-butyl-3,4-benzoquinonyl)methylenenorbornane, 2. The alkene from the previous reaction (50 mg, 0.1 mmol) was dissolved in 5 mL of CH_2Cl_2 in a 50 mL round-bottom flask. The solution was cooled to −78 °C, BBr_3 (380 mg, 1.52 mmol, 0.15 mL) was added, and the solution immediately darkened to a deep purple color. The reaction was then stirred for 12 h, and the bath temperature was kept below −40 °C (allowing the reaction to warm to room-temperature resulted in ca. 15% of the desired product and a difficult to separate reaction mixture). The reaction mixture was poured onto ice, transferred to a separatory funnel, washed once with saturated aqueous NaCl (at which point the color dissipated), dried over Na_2SO_4, and evaporated to dryness. The resulting crude catechol, **2-H$_4$**, was dissolved in 10 mL of THF and stirred with Fétizon's reagent (300 mg, ca. 1.1 mmol Ag) overnight yielding a dark red-green solution which was filtered and evaporated. The dark red-green solid was purified by column chromatography (SiO_2, methylene chloride) to give **2** as a green solid (35 mg, 81% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.63 (d, J = 2.2 Hz, 2H), 6.21 (d, J = 2.0 Hz, 2H), 2.83 (s, 2H), 1.81 (d, J = 7.7 Hz, 4H), 1.62 (d, J = 7.0 Hz, 4H), 1.27 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 180.1, 179.3, 164.1, 151.2, 150.4, 135.5, 127.6, 123.3, 39.8, 35.7, 29.2, 28.2. IR (film from THF) ν (cm^{-1}): 1685, 1657, 1615, 1560. Anal. Calcd for $C_{28}H_{32}O_4$: C, 77.75; H, 7.46. Found: C, 77.63; H, 7.51.

Methyl 3,5-Di-*tert*-butyl-4-hydroxybenzoate. In a 100 mL Schlenk flask, 4-bromo-2,6-di-*tert*-butylphenol trimethylsilyl ether, **8** (2.5 g, 6.99 mmol), was dissolved in 25 mL of THF and cooled to −78 °C. *tert*-Butyllithium (9.4 mL of a 1.5 M solution, 14 mmol) was added dropwise, and the resulting light yellow solution was stirred for 1 h at −78 °C. This solution was cannulated onto a large excess of dry ice in a 500 mL two-neck round-bottom flask, and the reaction was allowed to be warmed to room temperature. The reaction was acidified with 10 mL of 1 M HCl, transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was separated, dried over Na_2SO_4, and the solvent was evaporated. This yielded the crude acid, which was then dissolved in 200 mL each of methanol and Et_2O with a catalytic amount of concentrated HCl (3 drops). This mixture was refluxed overnight under argon and cooled, and the methanol was removed at the rotovap. The crude product, a thick yellow oil, was dissolved in Et_2O, transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was separated, dried over Na_2SO_4, and the solvent removed in vacuo. This gave a yellow solid which was purified by column chromatography (SiO_2, 10% Et_2O:petroleum ether) to give a white solid (1.38 g, 75% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.90 (s, 2H), 5.67 (s, 1H), 3.88 (s, 3H), 1.46 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.6, 158.1, 135.8, 127.0, 121.2, 51.7, 34.3, 30.2. IR (film from CH_2Cl_2) ν (cm^{-1}): 3575, 1697. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.60; H, 9.20.

Methyl 3,5-Di-*tert*-butyl-4-(trimethylsilyloxy)benzoate, 9. A 100 mL Schlenk flask containing distilled diisopropylamine (0.44 mL, 3.10 mmol) and 10 mL of THF was cooled to −78 °C, and *n*-BuLi (1.0 mL of a 2.5M solution, 2.54 mmol) was added. This solution was stirred for 10 min, followed by the addition of the methyl ester from the previous reaction (740 mg, 2.8 mmol) as a solution in 15 mL of THF, followed by stirring while warming to room temperature. Trimethylsilyl chloride (1.42 mL, 11.2 mmol) was added and the mixture refluxed overnight. The reaction mixture was cooled and quenched with 1 mL of H_2O, transferred to a separatory funnel, and sequentially washed once with H_2O and saturated aqueous NaCl, followed with drying over Na_2SO_4. The organic layer was separated, and solvent removal gave the crude product which was purified by column chromatography (Et_3N-deactivated SiO_2, 10% Et_2O:petroleum ether) to give a white solid (0.800 g, 85% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.96 (s, 2H), 3.88 (s, 3H), 1.42 (s, 18H), 0.42 (9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.6, 157.7, 141.1, 127.7, 122.1, 51.8, 35.3, 31.3, 3.9. IR (film from CH_2Cl_2) ν (cm^{-1}): 1714. Anal. Calcd for $C_{19}H_{32}O_3Si$: C, 67.81; H, 9.58. Found: C, 67.92; H, 9.53.

Bis(5′-*tert*-butyl-3′,4′-bis(methoxymethyloxy)phenyl)-3,5-di-*tert*-butyl-4-oxophenylenemethane. In a 100 mL Schlenk flask, 4-bromo-6-*tert*-butylcatechol dimethoxymethyl ether (1.43 g, 3.75 mmol) was dissolved in 10 mL of THF and cooled to −78 °C. *tert*-Butyllithium (5.0 mL of a 1.5 M solution, 7.50 mmol) was added dropwise, and the colorless, turbid solution was stirred for 1 h at −78 °C. The TMS-protected phenol from the previous reaction (600 mg, 1.79 mmol) was then added as a solution in 10 mL of THF, and the reaction allowed to warm to room temperature and stir overnight. The next day, 5 mL of a deoxygenated 1 M aqueous NaOH solution was added, and the reaction mixture was allowed to stir another 48 h. The color slowly darkened from light yellow to a deep orange-red of the quinone methide. The reaction was transferred to a separatory funnel and washed once with saturated aqueous NH_4Cl and once with saturated aqueous NaCl, followed by drying over Na_2SO_4 and solvent removal. This gave an orange oil which was purified by radial chromatography (SiO_2, gradient elution; 100% petroleum ether → 20% Et_2O:petroleum ether) to give an orange solid (1.08 g, 84% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.20 (s, 2H), 6.89 (s, 4H), 5.31 (s, 4H), 5.11 (s, 4H), 3.67 (s, 6H), 3.46 (s, 6H), 1.40 (s, 18H), 1.27 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 186.2, 156.9, 149.4, 147.5, 146.8, 142.5, 135.3, 132.7, 129.2, 126.1, 118.8, 99.3, 95.4, 57.7, 56.5, 35.3, 30.6, 39.7. Anal. Calcd for $C_{43}H_{62}O_9$: C, 71.44; H, 8.65. Found: C, 71.17; H, 8.69.

Bis(5′-*tert*-butyl-3′,4′-benzoquinonyl)-3,5-di-*tert*-butyl-4-oxophenylenemethane, 3. The quinone-methide from above (75 mg, 0.1 mmol) was dissolved in 15 mL of methanol, and concentrated hydrochloric acid (∼1 drop) was added. The mixture was allowed to reflux overnight under argon, yielding a dark red solution. Methanol was removed at the rotovap, and the crude product was dissolved in Et_2O, transferred to a separatory funnel, washed once with saturated aqueous NaCl, followed by drying over Na_2SO_4 and solvent removal, to yield crude catechol, **3-H$_4$**. Oxidation was performed by dissolving the catechol in 10 mL of THF and stirring with Fétizon's reagent (400 mg, ca. 1.4 mmol Ag) overnight. The dark red solution was filtered and the THF removed. The red-orange solid was purified by column chromatography (SiO_2, CH_2Cl_2) to give the product, **3**, as a red, glassy solid (47 mg, 87% yield). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.11 (s, 2H), 6.73 (d, J = 2.2 Hz, 2H), 6.37 (d, J = 2.2 Hz, 2H), 1.29 (s, 36H). ^{13}C NMR ($CDCl_3$, 75 MHz). δ (ppm): 186.3, 179.5, 178.9, 152.1, 151.4, 149.4, 144.1, 135.8, 135.2, 130.8, 128.6, 36.23, 36.17, 29.75, 29.45. IR (film from THF) ν (cm^{-1}): 1661, 1614, 1565. HRMS (FAB) Calcd for $C_{35}H_{47}O_5(M^+ + 5H)$: 547.3423. Found: 547.3399.

2′-Biphenylyl-bis(5″-*tert*-butyl-3″,4″-dimethoxyphenyl)carbinol. In a 50 mL Schlenk flask, 4-bromo-6-*tert*-butylcatechol dimethyl ether (1.22 g, 4.46 mmol) was dissolved in 15 mL of THF and cooled to −78 °C. *tert*-Butyllithium (5.8 mL of a 1.5 M solution in pentane, 8.8 mmol) was added dropwise, and the colorless suspension was stirred for 1 h at −78 °C. Methyl 2-phenylbenzoate, **10** (430 mg, 2.03 mmol), was added as a solution in 5 mL of THF, and the reaction mixture was warmed and stirred overnight at room temperature. The resulting light yellow turbid solution was quenched with 1 mL of saturated aqueous NH_4Cl and transferred to a separatory funnel, followed by washing once with saturated aqueous NaCl. The organic layer was separated, dried over Na_2SO_4, and evaportated to dryness. The resulting yellow oil was purified by radial chromatography (SiO_2, 10% Et_2O: petroleum ether) to give the product as a white solid (1.06 g, 93% yield). ^1H NMR (d_6-acetone, 300 MHz) δ (ppm): 7.31 (td, J = 7.4, 1.3 Hz, 1H), 7.24 (td, J = 7.5, 1.4 Hz, 1H), 7.00−7.13- (m, 5H), 6.84 (m, 4H), 6.71 (d, J = 2.0 Hz, 2H), 3.83 (s, 6H), 3.66 (s, 6H), 1.25 (s, 18H). ^{13}C NMR (d_6-acetone, 75 MHz) δ (ppm): 153.4, 148.0, 146.9, 143.8, 143.3, 142.7, 141.6, 133.2, 130.6, 130.1, 127.7, 127.0, 119.8, 111.8, 83.4, 60.5, 56.0, 35.7, 31.0. IR (film from CH_2Cl_2) ν (cm^{-1}): 3555. Anal. Calcd for $C_{37}H_{44}O_5$: C, 78.13; H, 7.79. Found: C, 78.20; H, 7.86.

9,9-Bis(5′-*tert*-butyl-3′,4′-dimethoxyphenyl)fluorene. To the alcohol from the previous step (300 mg, 0.53 mmol) in a 50 mL beaker was added approximately 10 g of polyphosphoric acid, giving a thick purple gel. The mixture was heated with stirring to about 90 °C on a hot plate. After 5 min, a white precipitate was observed, and heating was maintained another 15 min during which time the color changed from purple to brown with extensive precipatation. The suspension was cooled and quenched by the addition of 100 mL of ice−water. The brown suspension was transferred to a separatory funnel and extracted twice with Et_2O to give a yellow solution which was washed once with saturated aqueous NaCl, separated, dried over Na_2SO_4, and evaporated to dryness. The resulting yellow solid was purified by radial chromatography (SiO_2, 5% Et_2O: petroleum ether) to give the product as a white solid (250 mg, 86% yield). ^1H NMR (d_6-acetone, 300 MHz) δ (ppm): 7.89 (d, J = 7.4 Hz, 2H), 7.49 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 6.86 (d, J = 2 Hz, 2H), 6.61 (d, J = 2.1 Hz, 2H), 3.78 (s, 6H), 3.59 (s, 6H), 1.24 (s 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 152.5, 151.9, 147.1, 142.2, 140.1, 127.5, 127.4, 126.2, 120.1, 119.7, 110.8, 65.6, 60.3, 55.7, 35.2, 30.7. Anal. Calcd for $C_{37}H_{42}O_4$: C, 80.69; H, 7.68. Found: C, 80.58; H, 7.65.

9,9-Bis(5′-*tert*-butyl-3′,4′-benzoquinonyl)fluorene, 5. The cyclized product from above (200 mg, 0.36 mmol) was dissolved in 10 mL of CH_2Cl_2 in a 50 mL round-bottom flask and cooled to −78 °C. Boron tribromide (1.4 g, 0.52 mL, 5.5 mmol) was added in one portion, and the cooling bath was removed. The reaction was stirred overnight and quenched by pouring onto ice. The resulting solution was transferred to a separatory funnel, washed once with saturated aqueous NaCl, separated, and dried over Na_2SO_4. The resulting catechol, **5-H$_4$**, and Fétizon's reagent (1.2 mg, ca. 3 mmol Ag) were combined in a 50 mL round-bottom flask with 10 mL of THF, stirred overnight, and filtered to yield a dark red-brown solution. Solvent removal yielded a brown solid which was purified by column chromatography (SiO_2, CH_2Cl_2) to give **5** as an olive-green solid (130 mg, 79% yield). ^1H NMR (d_6-acetone, 300 MHz) δ (ppm): 8.10 (d, J = 7.5 Hz, 2H), 7.76 (d, J = 7.5 Hz, 2H), 7.64 (dt, J = 7.5, 2.1 Hz, 2H), 7.53 (dt, J = 7.6, 1.8 Hz, 2H), 6.84 (d, J = 2.2 Hz, 2H), 6.22 (d, J = 2.3 Hz, 2H), 1.17 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ(ppm): 180.3, 179.0, 154.2, 151.7, 142.8, 141.4, 133.6, 130.2, 128.9, 125.7, 125.2, 121.5, 65.3, 35.7, 29.2. IR (film from CH_2Cl_2) ν (cm^{-1}): 1664, 1626. HRMS (FAB) Calcd for $C_{33}H_{34}O_4$ (M^+ + 4H): 494.2457. Found: 494.2448.

Preparation of the Bis(semiquinone)s. Bis(semiquinone) $\mathbf{4}^{\bullet\bullet 2-}$ was prepared as described previously[24] by first stirring **4** over a freshly prepared sodium mirror in THF/PMDTA until the solution was colorless. This was then filtered into a THF/PMDTA solution containing an equimolar amount of the **4**, resulting in an immediate color change to dark green. Bis(semiquinone) $\mathbf{3}^{\bullet\bullet 2-}$ was prepared by reduction with freshly prepared sodium anthrasemiquinone, prepared according to the literature procedure.[23] The reduction was accomplished by addition of 2 equiv of $Na^+\mathbf{AQ}^{-\bullet}$ to THF/PMDTA to a THF solution of **3**, giving a dark purple solution. Both of these operations were carried out in the glovebox.

For CPC reductions, THF solutions of ca. 1−10 mM in bis(orthoquinone) and 100 mM in TBAH were reduced at −1.2 V vs $Ag/AgNO_3$. The resulting solutions, generally dark green in color, were transferred via syringe to a Schlenk flask (oven-dried and Ar-purged), subjected to three freeze−pump−thaw cycles, and transferred to the glovebox for EPR sample preparation.

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Supporting Information Available: Spectral data (25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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