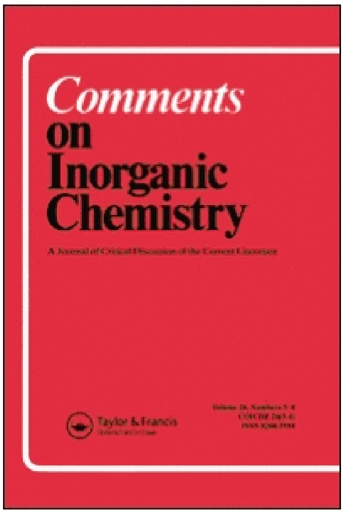

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Publication details, including instructions for authors and subscription information:
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# Structure-Property Relationships in New Semiquinone-Type Ligands: Past, Present, and Future Research Efforts

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**To cite this Article** Shultz, David A.(2002) 'Structure-Property Relationships in New Semiquinone-Type Ligands: Past, Present, and Future Research Efforts', Comments on Inorganic Chemistry, 23: 1, 1 — 21

**To link to this Article: DOI:** 10.1080/02603590214375

**URL:** http://dx.doi.org/10.1080/02603590214375

# Structure-Property Relationships in New Semiquinone-Type Ligands: Past, Present, and Future Research Efforts

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(Received October 24, 2000; Revised January 08, 2001; In final form January 12, 2001)

The utility of cross-conjugated, redox-active semiquinone ligands and their complexes for exploration and elucidation of various molecular structure-property relationships is discussed.

Keywords: *biradical; catechol; conformational exchange modulation; cross-conjugation; dioxolene; exchange coupling; high-spin; mixed valence; molecular magnetism; semiquinone; substituent effects*

## INTRODUCTION

### Why paramagnetic ligands?

Molecular magnetism has produced some of the most fascinating molecule-based materials known.[1–5] One of the most productive subfields

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*Comments Inorg. Chem.*
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has been preparation and study of Prussian blue analogs.[6–8] This class of coordination polymers derives interesting and novel properties from metal-metal interactions mediated by cyanide. Properties such as high-temperature magnetic ordering ($T > 300$ K), photomagnetism,[9] and electromagnetism[10] have been discovered and studied.

However, coordination polymers comprised of diamagnetic ligands only slightly larger than cyanide (*e.g.*, oxalate and azide[11]) do not magnetically order at temperatures above *ca*. 40 K.[12,13] This is due to the far weaker metal-metal exchange interactions that are attenuated by larger diamagnetic ligands, and due to low lattice dimensionality.

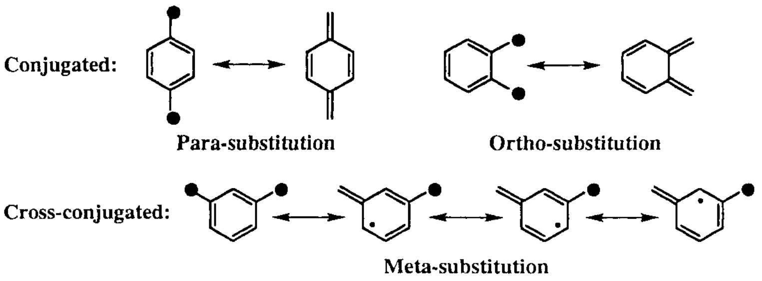
Thus, since higher ordering temperatures are desired, a successful approach is to use paramagnetic ligands and replace weak metal-metal interactions with stronger metal-ligand exchange.[14–18] Application of this approach has resulted in magnetically-ordered systems, althougth the highest ordering temperature to date is 46 K.[16] The reason that higher temperature ordering has not been reported is most likely due to the limited number of magnetic nearest neighbor contacts in the coordination polymer. With this in mind, the search for new materials based on paramagnetic ligands continues.

Another attractive feature common to many classes of paramagnetic ligands is electroactivity: many undergo reversible redox reactions. This feature is responsible for the phenomenon of valence tautomerism.[19–22]

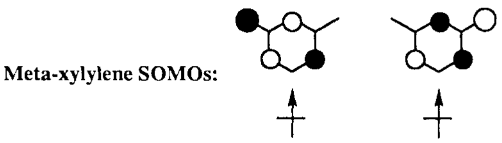
The search for three-dimensional materials with high ordering temperatures requires at least dinuclear ligands in which each metal ion is coordinated to a paramagnetic atom. That design element is easily achieved using ligands with more than one radical site. Herein, we will call ligands with more than one radical site that are directly exchange coupled, **high-spin** ligands.[23]

## High-spin ligands

About twenty years ago, chemists began to synthesize organic molecules with more than one unpaired electron with the goal of providing direct magnetostructural correlations. The marriage of computational chemistry, with a quantum mechanical basis for molecular design led to successful design principles for preparation of molecules with high-spin ground states. The design elements for triplet ground-state biradicals are illustrated below: cross-conjugated[24] connectivities preclude annihilation of unpaired electrons by π-bond formation, and form the basis for lower triplet-state energies. Thus, the conjugated structures *para-* and *ortho*-xylylene are closed-shell singlet ground-states, while *meta*-xylylene is an open-shell biradical. In fact, not only is *meta*-xylylene an open-shell biradical, it is a triplet-ground state biradical.



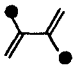
From an MO perspective, the singly-occupied MOs (SOMOs) of the biradical *meta*-xylylene, shown below, are said to be nondisjoint,[23,25,26] that is that they share a common electronic volume element. This SOMO co-extensivity gives rise to a non-negligible exchange integral that stabilizes the triplet state relative to the singlet state since the singlet-triplet gap is proportional to the exchange integral.



$$E_{singlet} - E_{triplet} \approx 2k \text{ (k = the exchange integral)}$$

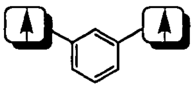
Another nondisjoint organic biradical with a triplet ground-state is trimethylenemethane (**TMM**), shown below.[27] Tetramethyleneethane (**TME**), on the other hand, is a singlet ground-state biradical.[28] Using the same MO argument as above, the SOMOs of **TME** are said to be disjoint, and the negligible exchange integral allows the singlet to become the ground-state. Note that **TME** is neither conjugated nor cross-conjugated.

**TMM: triplet ground-state**

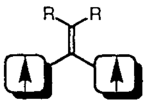


**TME: singlet ground-state**

This design principle (cross-conjugation → nondisjoint SOMOs → triplet ground-state) has been shown to be general. Thus, attaching atoms of positive spin density meta on a benzene ring, or geminal on a double bond results in triplet ground-state biradicals. Extension of this design to even higher-spin structures has been demonstrated.[23]



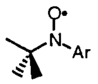
**Generalized**
***meta*-Phenylene-type**
**Biradical**



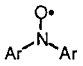
**Generalized**
**TMM-type**
**Biradical**

However, steric factors that attenuate delocalization into the benzene ring, or double bond also attenuate exchange coupling and can lead to low-spin ground-states.[29]

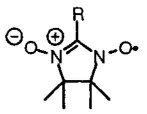
The search for more stable high-spin molecules naturally led to species incorporating nitroxide-type functionalities, the most common of which are depicted below. In addition to nitroxides, tetracyanoethylene radical anion,[30–34] and verdazyl radicals[35–37] are are now well-established building blocks for molecule-based magnetic materials.



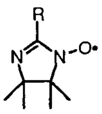
**Aryl-t-butylnitroxides**



**Diarylnitroxides**



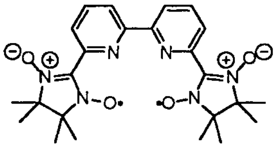
**Nitronylnitroxides**



**Iminonitroxides**

S > 1/2 ligands not based on high-spin design elements

The Rey and Zeissel groups have prepared fascinating ligands bearing more than one unpaired electron.[38,39] One particularly interesting example is shown below. These nitronylnitroxide groups are very weakly exchange coupled, since there is no direct *delocalization* of spin density from the nitronylnitroxide groups into the 2,2′-bipyridine π-system – the coupling takes place solely due to spin polarization. The very weak radical-radical coupling is manifested in the Curie law behavior of the ligand. Nevertheless, metal complexes with $Cu^{II}$ and $Ni^{II}$ have doublet and quintet ground states, respectively. Thus, high-spin *complexes* can be prepared from biradical ligands that are characterized by *negligible* radical-radical exchange coupling.



## New semiquinone-type ligands

Our research group has undertaken the design, synthesis, and characterization of dinuclear, paramagnetic ligands to be used to prepare novel molecule-based magnetic materials with magnetic, optical, and electronic properties of current interest. Our design is schematized below and features cross-conjugated,[24] electroactive molecules. Recently, we have focused on quinone-containing species,[40–49] although we have reported porphyrin-containing molecules.[50–54]

The Electroactive Groups (**EG**) can be either oxidized or reduced by one or more electrons to produce paramagnetic functionalities. Each **EG** is conjugated with the π-system of the **Linker**, but the two **EG** are not conjugated with each other.[24] This cross-conjugation is an important feature that allows the creation of nondisjoint, high-spin species[23,25,26] since **EG-Linker-EG** connectivity precludes annihilation of unpaired electrons by π-bond formation, as discussed above.

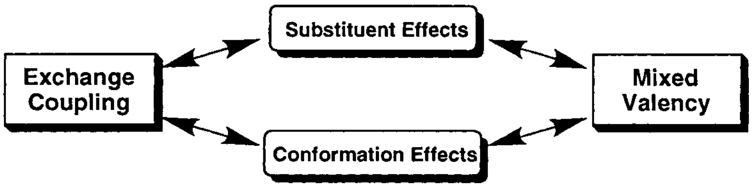
If the oxidation states of the two **EG** are different, then a mixed-valent ligand results, and the degree of delocalization can be controlled by structural features of the **Linker**. This control can be realized (1) by polar substituents on the **Linker**, (2) by substituents on the **Linker** that affect conformation, and (3) by the **Linker** $\pi$-system.

Magnetic and electronic properties of mixed-valent organic ligands and their metal complexes are practically unknown, and we are positioned to study a variety of such compounds and coordination polymers composed of such ligands.

If the oxidation states of the two **EG** are the same, and if they both carry an unpaired electron, then a biradical ligand results, and the degree of exchange coupling can be controlled by structural features of the **Linker**. As before, this control can be realized (1) by polar substituents on the **Linker**, (2) by substituents on the **Linker** that affect conformation, and (3) by the **Linker** $\pi$-system.

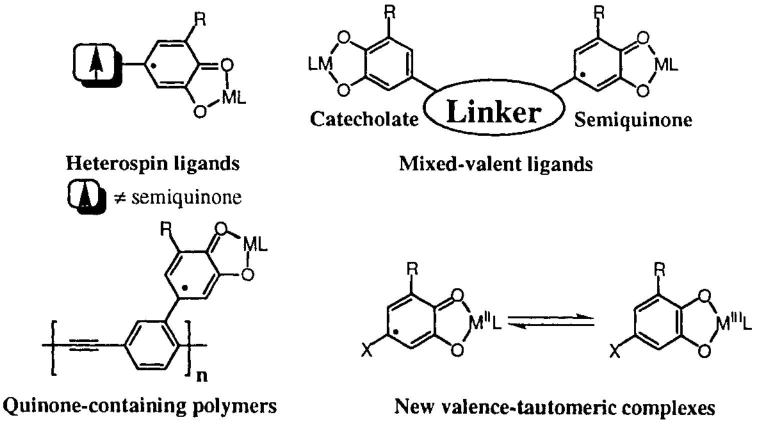
Magnetic properties of paramagnetic organic ligand coordination polymers have been well-studied, but few are bis-bidentate.[15,17,18,55] This increased coordination could result in higher ordering temperatures for such materials.

Thus, one major thrust of our research involves understanding the relationship between delocalization in mixed-valent organic ligands, and exchange coupling in the corresponding isovalent biradical ligands.



A second major thrust is the preparation of new high-spin molecules. In particular, we are interested in (1) new heterospin ligand complexes, (2) new mixed-valent, paramagnetic ligand complexes, (3) conjugated polymers bearing pendant semiquinone complexes, and (4) new valence tautomeric complexes.

To date, our studies make include the species shown below. Bis(semiquinone)s **1** – **5**[40–49] will be used to test how conformation affects the **Linker's** ability to exchange couple two semiquinones. Likewise, one-electron reduction of metal complexes of **1** – **5** will yield



Heterospin ligands

Mixed-valent ligands

Quinone-containing polymers

New valence-tautomeric complexes

mixed-valent semiquinone-**Linker**-catecholate complexes, and we can test how conformation modulates delocalization.[46]

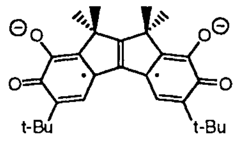
We have shown that the molecular conformation is affected by the functional groups that cap the **Linker**:[56] clearly, the π-systems of the **EG** and **Linker** in **1** are mutually coplanar, while in **2** and **3** moderate torsion is induced by the norbornyl and quinone groups, respectively. Bis(semiquinone) **4** has even greater torsions, and **5** is a model compound that allows assessment of the C=C as **Linker**.

Polymers **6** and **7** have been prepared by electrochemical reduction of the corresponding orthoquinone polymers.[48] These macromolecules could be used to prepare new, very high spin structures.

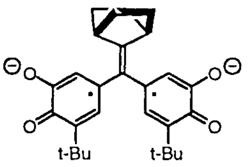
Heterospin biradicals **8**[42] and **9**[57] can be used to prepare a variety of novel complexes and coordination polymers.

Bis(semiquinone) complexes **10** – **12** have been prepared to determine if an inductive substituent effect can be used to control exchange coupling in the isovalent biradicals, and delocalization in mixed-valent semiquinone-**Linker**-catecholate complexes.[58]

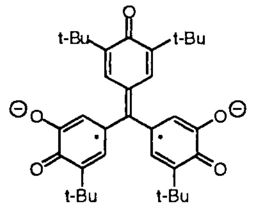
More recently in collaboration, we prepared and characterized $Cr^{III}$, $Ni^{II}$, and $Cu^{II}$ complexes of ligand **11**.[49] These complexes are characterized by $S = 2$ ($M = Cr^{III}$), $S = 3$ ($M = Ni^{II}$), and $S = 2$ ($M = Cu^{II}$) ground-states. High-spin complexes of semiquinone-type ligands with



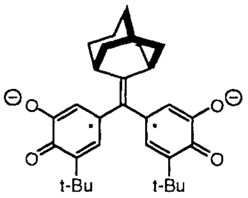
**1**



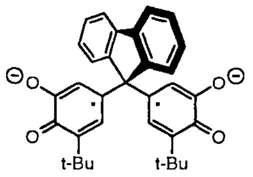
**2**



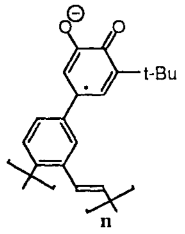
**3**



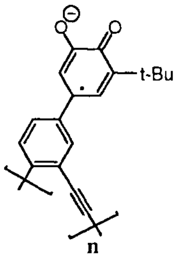
**4**



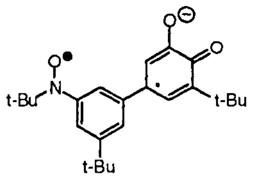
**5**



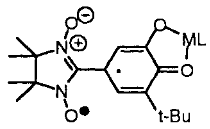
**6**



**7**

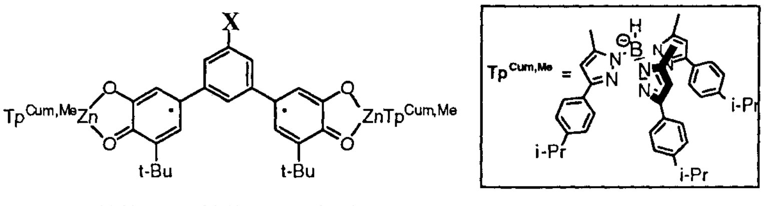


**8**



**9**

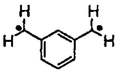
metal ions having large, negative zero-field splitting might give rise to a new class of single-molecule magnets.[59,60]



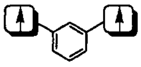
X = $NO_2$ (**10**), t-Bu (**11**), $NMe_2$ (**12**)

## CONFORMATION AND EXCHANGE COUPLING

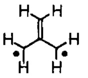
As mentioned in the Introduction, nondisjoint biradicals are often triplet ground-states due to the existence of a sizeable exchange integral that results from delocalization from the paramagnetic functional groups (**PFG**) into the **Linker** $\pi$-system.[23,25,26] Thus, disruption of **Linker-PFG** conjugation by steric interactions attenuates the exchange integral and diminishes the singlet-triplet gap. In certain cases, the singlet can be lower than the triplet. This conformational modulation of exchange coupling has been well-documented in biradicals with *meta*-phenylene **Linkers**.[29]



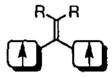
***meta*-Xylylene**



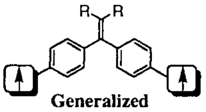
**Generalized *meta*-Phenylene-type Biradical**



**TMM**



**Generalized TMM-type Biradical**

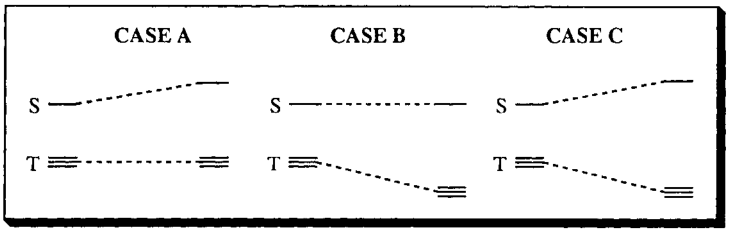


**Generalized Diphenyl-TMM-type Biradical**

However, relatively little is known about conformational exchange modulation in TMM-type biradicals.[29] To study this important structure-property relationship, we prepared a series of dinitroxide biradicals[56] and bis(semiquinone) ligands **1** – **5**. X-ray crystallographic analysis and magnetometry are nearly complete on the dinitroxide series of molecules and will be reported soon. Metal complexes of the bis(semiquinone) ligands are currently being prepared.

Understanding spin-spin interactions in S ≥ 1 (high-spin) organic molecules is a fundamental aspect of physical organic chemistry and plays a central role in molecule-based magnetic materials.[1–5,17,23,61–63] Major accomplishments in the field of organic biradicals include: (1) explaining and measuring the preference for a triplet ground-state in biradicals trimethylenemethane (TMM) and *meta*-xylylene (prototypical biradicals);[27,64] (2) the successful design and synthesis of high-spin organic molecules based on structural elements of TMM and *meta*-xylylene (*i.e.*, generalized *meta*-phenylene-type and TMM-type biradicals);[23,26,61–63,65] (3) the use of steric interactions to modulate the energy gap between triplet and singlet states.[29]

However, to date there exists no mechanism for enhancing the singlet-triplet gap of a cross-conjugated biradical in favor of the triplet state, other than removing debilitating steric interactions. We hypothesize that exchange coupling can be augmented by substituent effects. In general, a larger singlet-triplet gap could arise in one of three different ways as shown below.

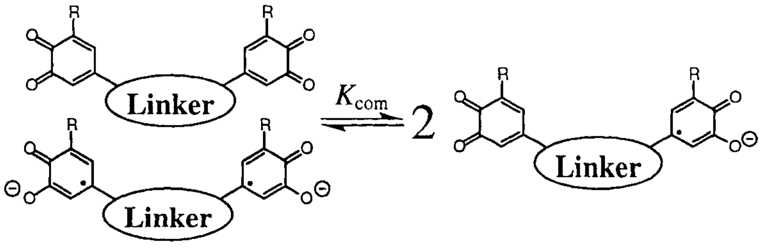


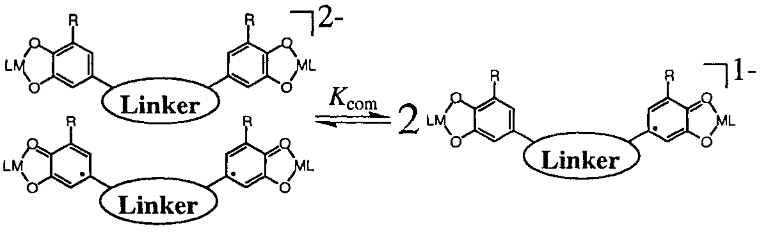
For Case A, the singlet is increased in energy relative to the triplet, while in Case B the triplet is lowered relative to the singlet, and in Case C the singlet is raised while the triplet is lowered. Cases B and C require that the substituent(s) alter the spin distribution in the molecule, and therefore that the substituent be in conjugation with the spin carrier. For biradical complexes like **10** – **12**, substituents in *conjugation* with the semiquinone groups (*i.e.*, ortho- or para- to them) would cause undesired severe torsions between the semiquinone groups and the *meta*-phenylene **Linker**. Our initial studies therefore include **10** – **12** in which the substituents are meta to the semiquinone groups and only an inductive effect on exchange coupling can be assessed.

Preliminary studies in our laboratories indicate that the singlet-triplet gap in **11** is nearly *twice* that of **10** suggesting that electron-donating meta substituents increase the singlet-triplet gap in bis(semiquinone) complexes. Since the substituents are meta, and conjugation with the semiquinone groups is impossible, this trend probably represents Case A modulation of a singlet-triplet gap. Further studies are ongoing in our laboratories.

## CONFORMATION AND MIXED VALENCY

The stabilization of a mixed-valent semiquinone-type species relative to the isovalent forms can be determined by measuring the comproportionation equilibria:





A convenient method for evaluating interactions between redox centers in mixed-valent compounds is by electrochemistry: the greater the separation of first and second redox events, the greater the interaction between the two redox centers. For no interaction, statistics demands that $K_{com} = 4$.[66]

Figure 1 shows the cyclic voltammograms for cross-conjugated bis(quinone)s that give bis(semiquinone)s **1** –**5** and **11** upon two-electron reduction. Pertinent data are collected in Table I for TMM-type bis(semiquinone)s **1** – **5**. The bis(quinone)s corresponding to biradicals **1** - **5** show increased redox splitting as semiquinone torsion *decreases*. The calculated values of $K_{\mathrm{com}}$ indicate that this series spans the Class II/III regime of mixed-valent compounds.[67]

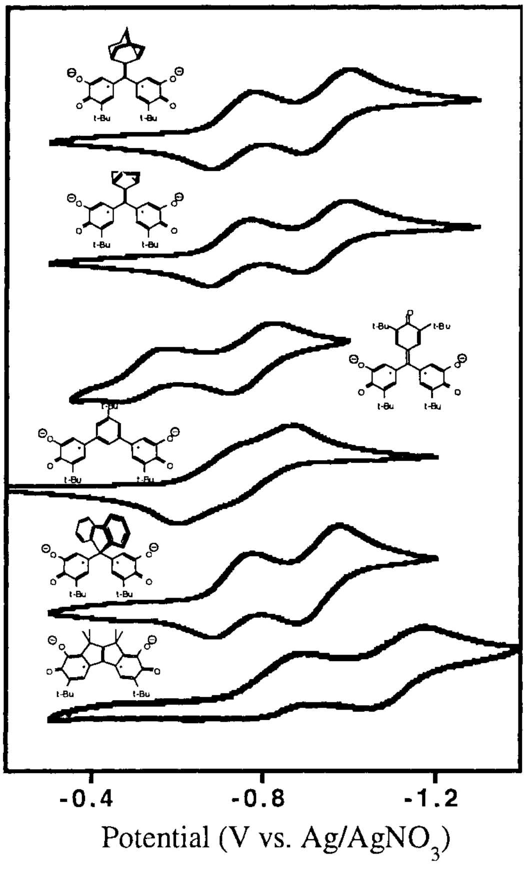


FIGURE 1 Cyclic voltammograms for bis(quinone)s **1** – **5** as 1 mM solutions in THF with 100 mM $n$-$Bu_4PF_6$ electrolyte. Voltammograms are for the bis(quinone) / bis(semiquinone) couple

TABLE I Redox splitting[a] and comproportionation equilibrium constants[b] for **1** – **5**

| *Biradical* | $\Delta E$ / $mV^c$ | $K_{com}$ | $\lvert D/hc \rvert$ / $cm^{-1}$ | *Reference* |
|---|---|---|---|---|
| **1** | 280 | 53951 | 0.007 9 | [46] |
| **2** | 220 | 5224 | 0.009 1 | [43] |
| **3** | 250 | 16788 | 0.008 6 | [43] |
| **4** | 210 | 3540 | 0.009 5 | [43] |
| **5** | 200 | 2399 | ≈ 0.011 5 | [43] |

a. Determined by cyclic voltammetry.

b. Calculated from: $\log K_{com} = 16.9 \cdot \Delta E$.

c. ΔE is for the bis(quinone)/quinone-semiquinone/bis(semiquinone) couples.

Frozen solution EPR spectra for bis(semiquinone)s **1** – **4** and **11** produced electrochemically are shown in Figure 2, and zero-field splitting parameters are shown in Table I.

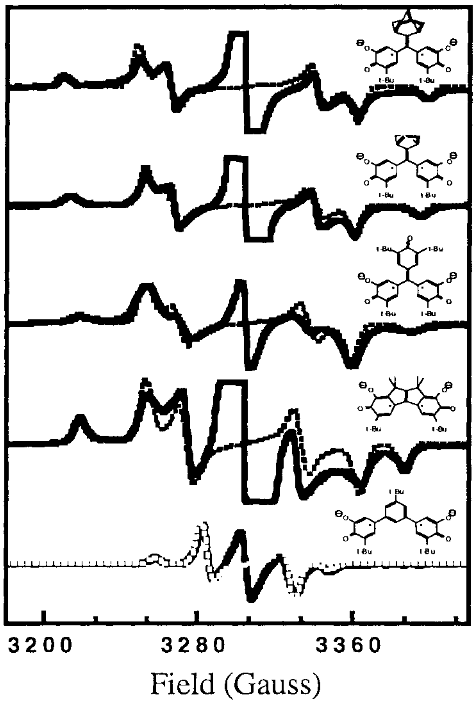


FIGURE 2 X-band EPR spectra for bis(semiquinone)s **1** – **4** and **11** as in THF at 77K. Biradicals were produced electrochemically with $n$-$Bu_4NPF_6$ as electrolyte

As can be seen in the Figure 3, redox splitting increases, as the |D/hc| values for the *S* =1 bis(semiquinone)s *decrease*. Since the *D*-values are due solely to dipole-dipole interactions and therefore depend only on interelectronic distance, we maintain that increased ΔE values are due to stabilization of mixed-valent forms relative to isovalent forms. Thus, bond torsions modulate mixed valency. Clearly, additional studies are required to correlated conformational exchange modulation with conformational mixed-valency modulation.

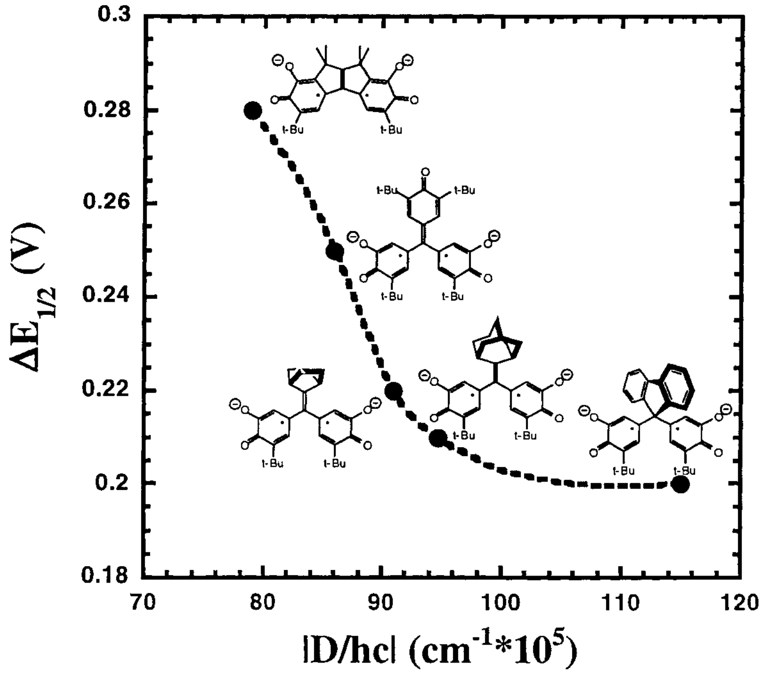


FIGURE 3 Redox splitting for the bis(quinone) / bis(semiquinone) couples plotted vs. zero-field splitting parameter |D/hc| for bis(semiquinone)s **1** –**5**. Biradicals were produced electrochemically with *n*-$Bu_4NPF_6$ as electrolyte

## SUBSTITUENT EFFECTS AND MIXED VALENCY

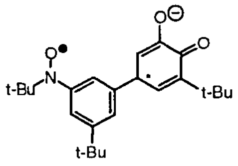
To date, we reported substituent effects on mixed valency within a series of cross-conjugated bis(porphyrin) molecules.[52,53] Bis(semiquinone)s

**10** – **12** present an additional opportunity for studying substituent effects, however an inductive effect might not manifest itself in redox splitting. In this case, other methods will be needed to evaluate mixed valency in derivatives of **10** – **12**.

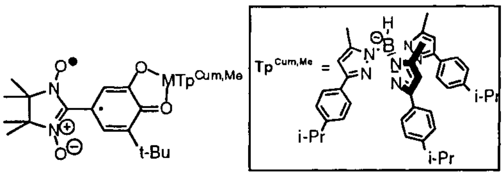
## NEW HIGH-SPIN LIGANDS

### Heterospin ligand complexes

To date, we have prepared the heterospin ligands and complexes shown below.



**8**

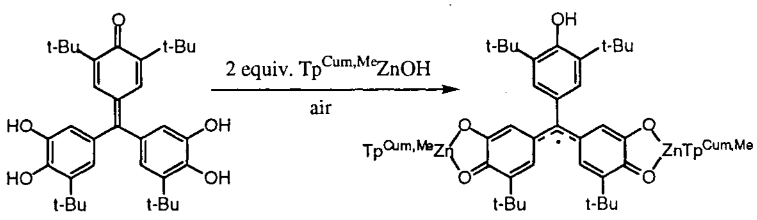


**9a-e** (M = $Mn^{II}$, $Co^{II}$, $Ni^{II}$, $Cu^{II}$, $Zn^{II}$)

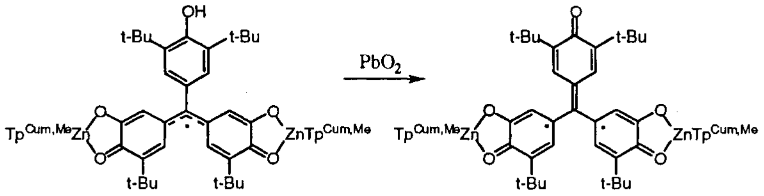
The ligand-based unpaired electrons of 9 are strongly ferromagnetically coupled. In fact, the $Zn^{II}$ complex shows $\chi_{para}\bullet T = 1$ between 2 and 300 K indicating that only the triplet state is populated, even at room temperature.[57] The $Mn^{II}$, $Co^{II}$, $Ni^{II}$ complexes **9a-e** show moderate antiferromagnetic metal-semiquinone exchange couplings (ca. –40 to –70 $cm^{-1}$),[58] while the $Cu^{II}$ derivative exhibits ferromagnetic exchange coupling, ($J = +75$ $cm^{-1}$).[57] The signs of the exchange parameters can be traced to the magnetic orbital symmetries.[68] We envision using these ligands to prepare novel coordination polymers.

### Mixed-valent, paramagnetic ligand complexes

All of the bis(semiquinone) complexes prepared can be transformed into mixed-valent species. Our first report of such molecules originated from studies on metal complexes of **3**. We reported that bis(catechol) **13** reacted with $Tp^{Cum,Me}ZnOH$ to give S = 1/2 complex **14**, rather than the expected **15**.[47] However, oxidation of **14** gave **15**.[45,47]

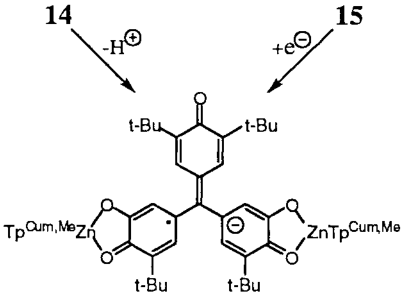


**13** **14**



**14** **15**

Complexes **14** and **15** are quite interesting since each is a source of the mixed-valent complex **16**. As shown below, **16** can be prepared from **14** by deprotonation, and from **15** by reduction.[45]

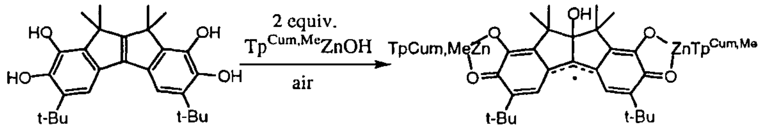


**16**

Future efforts will use these mixed-valent, paramagnetic ligands to prepare metal complexes of paramagnetic metal ions with interesting, new magnetic properties.

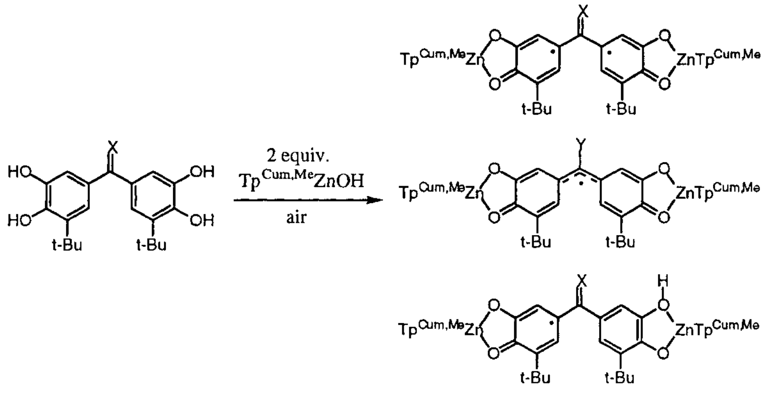
## Quinone-Methide Semiquinones

Complex **14** is the first example of a structurally-characterized Quinone-Methide-Semiquinone (QMSQ) complex.[45] The only other ligand of this type was reported by Dei *et al.*[69] Preliminary studies of metal complexation of **16** indicate that another QMSQ complex, **17**, is formed as part of the reaction mixture as shown below.[58] This structure will be reported in a full paper that discusses the metal complexation of 1,1-di-(t-butylcatechol)ethylene derivatives.



**16** **17**

Depending on the nature of the × group in the bis(catechol) below, product complexes can be bis(semiquinone)s (top), QMSQs (middle), or molecules with both semiquinone and protonated catecholate ligands.[58] This chemistry also occurs for metal ions other than $Zn^{II}$.[58]

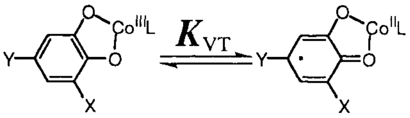


## Conjugated polymers bearing pendant semiquinone complexes

We recently reported the synthesis, electrochemistry, and EPR spectra of polymers **6** and **7** as *n*-$Bu_4N^+$ salts produced by electrochemical reduction of the corresponding quinone polymers.[48] We are excited about preparing metal complexes of these conjugated polymers, and efforts along these lines are underway. We feel that these ligands can form the basis for new very high spin species.

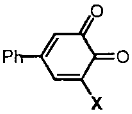
## New valence tautomeric complexes

We are interested in synthesizing mono-dioxolene complexes with monoanionic ancillary ligands, L, that undergo valence tautomeric equilibria:[19,20,22]



The novelty here would be that the catecholate tautomer (above left) would be diamagnetic. This can be accomplished two different ways: (1) design an ancillary ligand that can stabilize both the $Co^{II}$ and $Co^{III}$ forms; (2) add dioxolene substituents that can stabilize both the $Co^{II}$ and $Co^{III}$ forms. We feel that the second approach is more straightforward. Moreover, Pierpont has found that the $Tp^{Cum,Me}$ ligand stabilizes the $Co^{II}SQ$ tautomer, and no evidence exists for the $Co^{III}$ tautomer in the solid state. Solution studies of $Tp^{Cum,Me}Co(3,5\text{-}DBSQ)$ have not been reported.

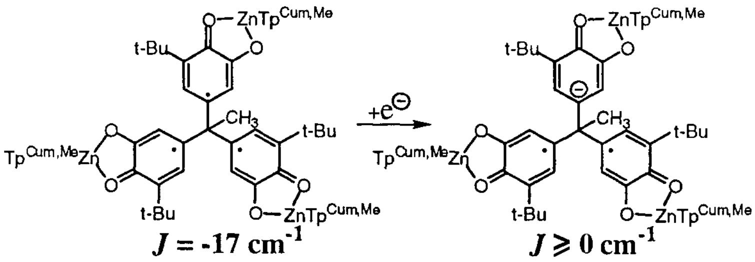
Along these lines, we have prepared quinones **18** – **20**.[58] Cyclic voltammetry shows that the reduction potential varies *ca.* 250 mV in this series. Cobalt complexes are being prepared.



**X** = t-Bu (**18**), Cl (**19**), F (**20**)

## Delocalization as a design element for high-spin ligands

We are interested in the effect of electron delocalization on ground-state spin multiplicity. In mixed-valent metal complexes, double exchange,[70,71] also known as spin-dependent delocalization[2] is known to stabilize that state of highest spin multiplicity. To date there is no organic ligand analog. We have prepared a tris(semiquinone) complex and determined by EPR methods that the three semiquinones are antiferromagnetically coupled. Reduction yields the mixed-valent biradical, and we are studying the magnetic properties of this mixed-valent species. Clearly, this molecule does not represent an example of double exchange, but delocalization should affect the spin-state preference.[72–74]



## SUMMARY

We have shown how cross-conjugated, redox-active semiquinone-type ligands are uniquely suited to studying structure-property relationships in open-shell molecules and metal complexes, and for preparing novel paramagnetic ligands.

### *Acknowledgements*

This work has been supported by the National Science Foundation, Research Corporation, the Camille and Henry Dreyfus Foundation, and the NC State Department of Chemistry.

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