

Electronic Tuning of Nickel-Based Bis(dicarbollide) Redox Shuttles in Dye-Sensitized Solar Cells**

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Dye-sensitized solar cells (DSCs) are potential next-generation solar electricity sources since they are inexpensive, easy to fabricate, and can be relatively efficient.^[1] Because of this promise, there has been extensive research aimed at understanding and optimizing the performance of these devices by systematically altering many of their key components.^[2] Indeed, these studies have involved the design of new molecular dyes to increase light absorption,^[3] evaluation of alternative semiconducting photoanodes to improve charge collection,^[4] and use of protective layers at the semiconductor/redox electrolyte interface to suppress dark currents arising from electron interception.^[5] However, less attention has been devoted towards the influence of the DSC redox shuttle and how the chemical and physical properties of such shuttles affect overall device performance. Despite identifying shuttles with redox potentials comparable to the commonly used anionic I^-/I_3^- redox couple, researchers have been unable to identify ones with other advantages to the I^-/I_3^- system.^[6] However, the strongly corrosive nature of I^-/I_3^- is a fundamental limitation to the further optimization of DSC architectures, and significantly restricts the choice of dye and electrode materials.^[7]

Herein, we report a promising new class of noncorrosive B(9)/(B12)-modified Ni^{III}/Ni^{IV} bis(dicarbollide) complexes derived from the systematic functionalization of the Ni^{III}/Ni^{IV} bis(dicarbollide) framework with electron-donating and electron-withdrawing groups. Importantly, the parent $Ni^{III}/$

Ni^{IV} bis(dicarbollide) was previously shown to be a fast redox shuttle.^[8] With this new class of complexes, the redox shuttle potential can be tuned over a 200 mV range, overlapping the I^-/I_3^- redox couple. Therefore, the properties of these complexes can be studied in the context of next-generation DSCs.

In addition to a noncorrosive nature, the Ni^{III}/Ni^{IV} bis(dicarbollide) system also has many favorable properties versus other metallocene systems, including fast mass-transport, fast dye regeneration, and attractive electron transfer kinetics.^[8] Notably, the system is stable with respect to the electrode metals (Ag, Au, and Cu) that are commonly used in commercial DSC modules. To efficiently use the Ni^{III}/Ni^{IV} bis(dicarbollide) system as a DSC shuttle, new chemistry for modifying the bis(dicarbollide) cage is required. Hawthorne and co-workers pioneered the chemistry of icosahedral-based dicarbollide molecules and developed several important derivatization routes through the metallacarborane CH vertices and the B(8) positions (for numbering see Figure S2 in the Supporting Information).^[9] However, these strategies lead to equatorially functionalized bis(dicarbollide) structures (defined by the two C and three B atoms occupying one plane),^[10] which are sterically encumbered and undergo irreversible redox processes.^[10c]

There are now a variety of synthetic strategies for preparing functionalized carborane molecules and materials.^[11] In an effort to reduce steric encumbrance and to create Ni bis(dicarbollides) with programmable redox properties, we developed a new synthetic strategy for constructing bis(dicarbollide) species from the B(9)-functionalized derivatives of the parent carborane. The approach allows realization of targets originally recognized as important by Hawthorne,^[11f] and involves five high-yield steps, starting from commercially available *o*-carborane **1** (Scheme 1). Following known literature methods,^[12a] the B(9) position of *o*-carborane **1** can be iodinated in 95 % yield to afford 9-I-carborane **2**, which can be subsequently arylated following the procedure of Zakharin and co-workers to afford **3a–f** in good yields (see pp. S2–S4 in the Supporting Information).^[12b] Compounds **3a–f** undergo deboronation in ethanolic solution overnight, quantitatively yielding *nido*-carborane derivatives, isolated as $N[Me_3H]^+$ salts **4a–f**. These compounds were characterized by 1H , ^{11}B , $^{13}C\{^1H\}$ NMR spectroscopies, elemental analysis (**4a–f**), high-resolution ESI-MS (**4a–f**), and single-crystal X-ray analysis (**3a–f**),^[13] all of which confirm their structural formulations (see pp. S5–S12 in the Supporting Information). Reaction of **4a–f** with aqueous excess of $NiCl_2 \cdot 6H_2O$ in concentrated NaOH solution (40 %) results in transient Ni^{II}

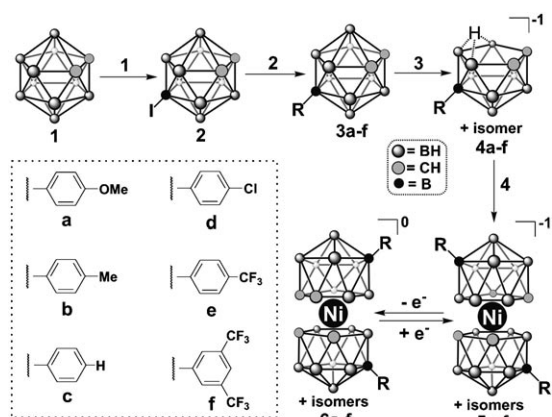
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Scheme 1. 1) I_2 , CH_2Cl_2 , 6 h, 95 %; 2) RMgBr , diethyl ether, 10 mol % $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, RT, 3 d, 67–75 %; 3) EtOK , EtOH , reflux, 12 h, 98 %; 4) 40 % aq. NaOH , aq. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, then air, 65–80 % (oxidation) in situ aq. FeCl_3 , 5 min (reduction) MeOH , NaBH_4 , 10 min, 95 %.

species, which immediately oxidize upon air exposure to form the corresponding Ni^{III} complexes **5a–f**.

Compounds **5a–f** are purified by oxidizing further to the Ni^{IV} analogues using aqueous FeCl_3 , and passing the resulting mixture through a silica gel plug, which affords pure **6a–f**. These Ni^{IV} compounds can be rapidly and quantitatively reduced back to the corresponding Ni^{III} complexes with NaBH_4 in methanol, and isolated as tetrabutylammonium (TBA^+) salts. Although compounds **5a–f** are paramagnetic, their ^1H and ^{13}C NMR spectra clearly show the presence of the aryl functional groups (see pp. S40–S43 in the Supporting Information). Furthermore, the least soluble **6a–f** isomers were characterized by single-crystal X-ray diffraction (see Figure 1 and pp. S23–S33 in the Supporting Information).^[9e,13]

In the case of complexes **6a**, **6b**, and **6e** in which each dicarbollide cage is functionalized at the B(9) position, the *meso* species readily crystallize, whereas in the case of **6c**, **6d**, and **6f**, *dd(II)* stereoisomers are obtained (dicarbollide cages functionalized at two isomeric boron vertices, B(9) and B(12)). In all cases, a cisoid geometry of the two dicarbollide cages is observed in the diffraction analyses, with dicarbollide carbons arranged in a staggered conformation. The carbon–carbon bond distances in **6a–f** show little variation (average C–C 1.63 ± 0.03 Å), regardless of the substituents. This is in contrast to dicarbollides with substituents directly on the equatorial C atoms, which exhibit relatively large variations in C–C distances.^[10g]

Although the Ni –bis(dicarbollide) complexes **6a–f** appear structurally similar, they differ markedly in color, suggesting significant electronic structure differences. In particular, a unique crystal packing arrangement is observed for **6f**, where the Ni^{IV} center does not interact with the phenyl moieties (Figure 1B). This observation may reflect electron density redistribution within the molecule induced by the highly polarizing CF_3 groups. Compound **6a** is dark blue while **6b** and **6c** are dark red, while compounds **6d** and **6e** are dark orange, and **6f** is light orange, similar to the unfunctionalized Ni^{IV} –bis(dicarbollide). The optical properties of **6a–f** in dichloroethane solution reflect the observed solid state

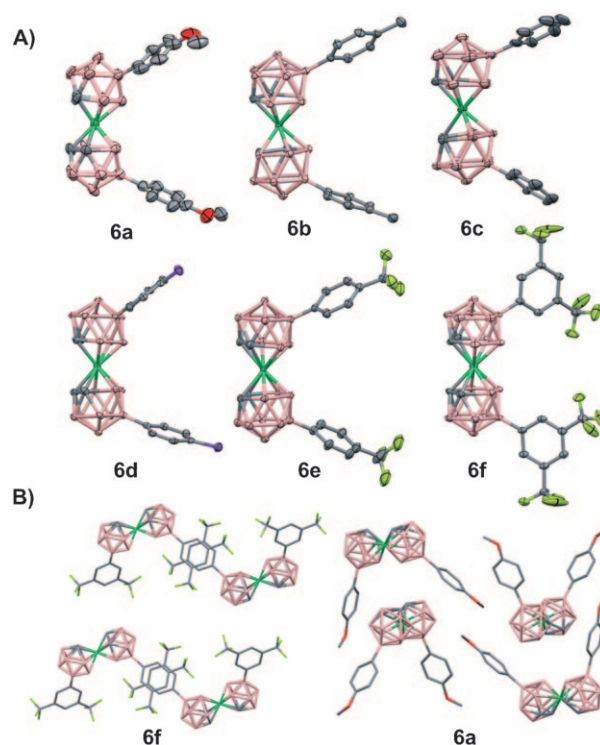


Figure 1. a) Diffraction-determined structures of **6a–f** with atoms drawn with 50 % thermal ellipsoid probabilities. Only one stereoisomer in the unit cell is shown. All solvents and hydrogen atoms are omitted for clarity. C gray, B beige, O red, F yellow, Cl purple, Ni green. b) Crystal lattice packing of **6f** (left) and **6a** (right).

trends. In all cases, an absorption band in the visible region of the spectrum is observed, which blue-shifts from **6a** to **6f** (Figure 2B). This band sensitivity is not observed in the case of the **5a–f** series, both in solid and solution (Figure 2A).

DFT calculations on the optimized structures of **6a** and **6e** (both are *meso* isomers, providing a good comparative basis)

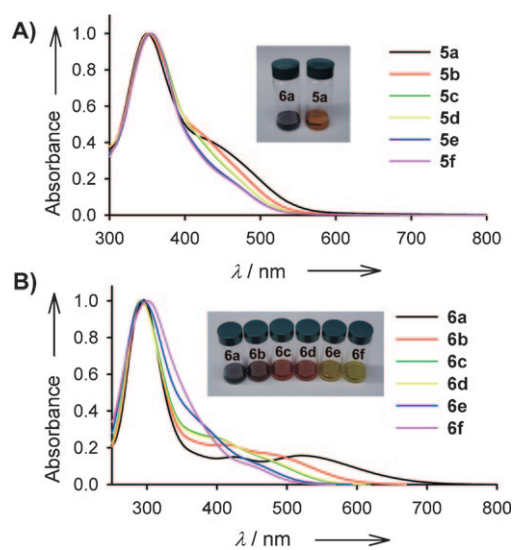


Figure 2. UV/Vis spectra of dicarbollide complexes: a) **5a–f** and b) **6a–f** and their corresponding solutions in dichloroethane.

suggest that the visible excitation arises from intramolecular electron transfer from the filled orbitals of the electron-rich aryl substituent to the lowest unoccupied orbital of the electron-poor bis(dicarbollide) cage (see pp. S12–S19 in the Supporting Information). These results imply that the bis(dicarbollide) π -system is conjugated with the aryl functional groups attached through the B atoms of **6a–f**, thereby providing a basis for tuning the redox potentials through the aryl substituent electron-donating and -withdrawing groups.

The electrochemistry of **6a–f** was studied by cyclic voltammetry, and similar to the unfunctionalized Ni–bis(dicarbollide), all derivatives undergo quasi-reversible one-electron processes. The $E_{1/2}$ values measured for each metal-lacarborane derivative correlate well with the electron-donating or -withdrawing nature of the aryl substituents (see pp. S20–S21 in the Supporting Information). Plotting these potentials versus the corresponding Hammett constants reveals a linear relationship,^[14] indicating that one can deliberately tune the electrochemical potential of these complexes through choice of substituents (Figure 3). This

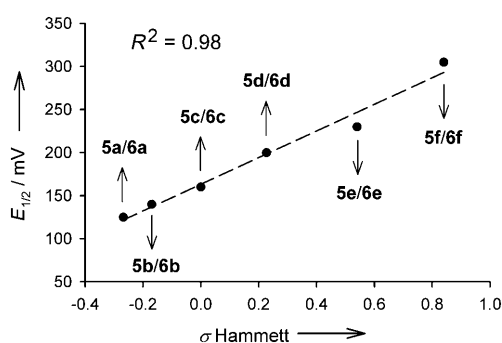


Figure 3. Redox potential of Ni^{III}/Ni^{IV} derivatives versus Hammett constants.

study is the first example of systematic electronic tuning of transition metal–bis(dicarbollides) using the type of novel B-arylation chemistry reported herein.

The electrochemical dependence of electrochemical properties on carborane functionalization was explored for Co^{II}/Co^{III}–bis(dicarbollides) through monosubstitution at the B(8) positions with alkyl and aryl groups by Teixidor and co-workers.^[15a] Most recently the same group reported redox tunability of cobalt-based clusters by sequential chlorination at multiple boron vertices.^[15b] More importantly, the control reported herein allows direct probing of the effect of varying Ni–bis(dicarbollide) redox potential on DSC response. As an example, modifying the aryl substituent with electron-withdrawing CF₃ groups raises $E_{1/2}$ of the bis(dicarbollide) to over 300 mV vs. SCE, affording an impressive DSC open-circuit voltage (V_{oc}) of 770 mV for the **5f/6f** couple under 1 sun illumination (see the Supporting Information for details of DSC fabrication). In contrast, ferrocene/ferrocenium based DSCs yield only V_{oc} = 200 mV under the same conditions.^[16] We attribute this significant V_{oc} enhancement to the large rotational barrier of the dicarbollide ligands required to interconvert **5** and **6**, thereby retarding electron interception

by **6**, and thus accounting for the significantly larger DSC V_{oc} values for the Ni–bis(dicarbollide) redox shuttle.^[8] Insulating barrier layers deposited at the semiconductor/electrolyte interface have also been used to enhance DSC photovoltaic performance by hindering electron interception by fast shuttles.^[5] As shown in Table 1, photovoltage enhancements

Table 1: DSC open-circuit voltages for various redox electrolytes with 0 and 1 ALD cycle of Al₂O₃ (1 cycle = 1.1 Å on average).

Shuttle	E_{redox} vs. SCE [mV]	0 Cycles ^[a,b] [mV]	1 Cycle ^[a,c] [mV]
5a/6a	125	690	760
5b/6b	140	710	710
5c/6c	160	640	720
5d/6d	200	710	790
5e/6e	230	740	810
5f/6f	305	770	850

[a] V_{oc} uncertainties are within 3 %, averaging over three different cells.

[b] DSC photovoltages with no ALD modification. [c] DSC photovoltages with 1 ALD cycle of Al₂O₃.

are observed following atomic layer deposition (ALD) of only ca. 1.1 Å of Al₂O₃ on the TiO₂ photoanode. Most impressively, **5f/6f** affords a DSC V_{oc} of 850 mV, significantly higher than that typically observed in liquid I[−]/I₃[−] solar cells.^[17]

A major attraction of the present redox shuttle system is the ability to tune the DSC photovoltage by derivatization of the carborane moiety. As the potential difference between the TiO₂ quasi-Fermi level and the redox shuttle potential is increased, the V_{oc} must necessarily increase. However, the complex interplay of various DSC kinetic processes such as dye regeneration, electron recombination, electron-transfer at the counterelectrode, and shuttle transport through the electrolyte and framework, make predicting overall photovoltaic performance non-straightforward.^[18] Nevertheless, Marcus normal-region behavior is observed here with the electron-withdrawing derivatives, where there is V_{oc} enhancement in going to more positive shuttle potentials (Table 1), where the concentration of **6** is held constant to minimize the varying effects of electron capture from the TiO₂ conduction band. Note, however, that with the electron-donating aryl substituents, V_{oc} is considerably greater than predicted. In fact, **5b/6b**-based DSCs exhibit extraordinary V_{oc} values of 710 mV, and even with TiO₂ photoanode ALD modification, no noticeable increase in photovoltage is observed. By monitoring the TiO₂ conduction band electrons at 980 nm^[19] with nanosecond transient-absorption spectroscopy (see p. S22 in the Supporting Information), it is noted that the fast ($t_{1/2}$ ≈ 5 μs) electron interception dynamics appear similar for all the dicarbollide derivatives, with no noticeable trends correlating with aryl Ni–bis(dicarbollide) chemical modification. Attempts to evaluate the longer timescale dynamics, by the open-circuit photovoltage decay method, are unfortunately inconclusive.

Differences in the electron-donating or -withdrawing substituents effect are apparent in the DSC J – V curves, where cells based on more electron-rich dicarbollides have fill

factors and power conversion efficiencies superior to the electron-poor dicarbollides (Figure SI5). This may be a consequence of more favorable electrolyte–dye interactions involving the electron-donating aryl methoxy and tolyl groups. In fact, the **5b/6b** couple has lower solubility and, in contrast to **5a/6a**, does not have potentially coordinating groups. In the cases of the **5a/6a** and **5b/6b** redox couples, DSC performance is optimized at only 1.8 mM of complex **6**. However, for **5c/6c**, **5d/6d**, **5e/6e**, and **5f/6f**, doubling the concentration of **6** increases fill factors and overall DSC performance. The polar electron-withdrawing groups may have a greater chemical interaction with the dye, resulting in a higher local shuttle concentration near the TiO₂ photoanode (due to slower diffusion). With backside-illumination through the platinum counterelectrode, fill factors and device efficiencies increase for the electrolytes having low molar absorptivities (see Figure S5 in the Supporting Information). In general, device power conversion efficiencies ranging from 0.7 to 2.0% (for *J–V* curves see Figure S5 in the Supporting Information) are achieved with the present Ni–bis(dicarbollide) shuttles. Future work will focus on optimizing electrolyte concentrations for these derivatives.

In conclusion, we have demonstrated that through chemical functionalization of the Ni–bis(dicarbollide) moiety in the B(9/12) positions, the Ni^{III}/Ni^{IV} redox pair potential can be systematically tuned, and these derivatives can be readily synthesized on multigram scales. To date, limited probing of the importance of the DSC redox shuttle chemical characteristics have been carried out, and to create useful DSC systems, major advances must be achieved in optimizing the electrolyte–dye interaction.^[20] The new Ni^{III}/Ni^{IV}–bis(dicarbollide) systems lay the groundwork for such optimization, and although the entire scope is not yet explored, the chemistry reported herein offers an avenue to create diverse DSC redox shuttles, which will yield valuable fundamental information concerning device function. Through functional groups that modulate redox shuttle polarity, solubility, and binding properties, it should now be possible to identify structures that maximize DSC kinetics and performance.

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