Conducting Materials

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Stepwise Sequential Redox Potential Modulation Possible on a Single Platform**

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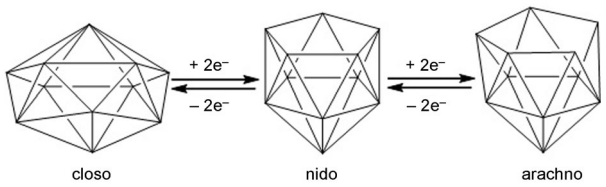
In memory of Heribert Barrera i Costa

Electron transfer is fundamental to many processes of life, including oxygen binding, photosynthesis, and respiration.[1] All organisms obtain energy by transferring electrons from an electron donor to an electron acceptor.[2] For example, the electron-transport chain in photosynthesis is remarkable.[3] In this work we show the first case of an artificial energetically favorable (downhill) sequence having well-defined, characterized, and structurally similar individual electron donors and acceptors made from a common frame. This example was made possible by using a metallacarborane cluster. There has been interest in producing systems with similar characteristics in highly predominant electroactive frameworks such as ferrocene (Fc), C_{60}, or perylene diimide.[4] The results have been, however, very limited.[5]

In the early 1970s, it was realized that the geometry of boron clusters is related to the number of electron pairs available for bonding.[6] The electronic and structural relationship between boron clusters having a common number of atoms in the cluster is shown in Scheme 1 for the case in which there are 11 vertices. These relationships suggest that the reversible transition from one cluster to its neighbor in Scheme 1 could be done through a redox process. This scenario, however, is seldom the case as there are frequently chemical reactions coupled to the redox process to make them irreversible.



Scheme 1. Electronic and structural relationship for borane clusters having 11 vertices.

Ferrocene, C_{60}, and perylene diimide are the most predominant electroactive frameworks. C_{60} can be structurally compared with 1,2-, 1,7-, or 1,12-$C_2B_{10}H_{12}$ *closo*-carboranes because all are neutral icosahedral molecules. However, C_{60} requires much less energy to incorporate $2e^-$ than the carboranes, that is, −0.98 V for C_{60}^- and −1.37 V for C_{60}^{2-} (Fc^+/Fc)[7] versus −2.5 V (SCE)[8] (corresponding to −2.91 V (Fc^+/Fc)). Also, there is no appreciable change in the C_{60} structure after the incorporation of $4e^-$,[7] whereas the carboranes alter their shape dramatically.[6] The low reduction potential of C_{60} has made it very attractive as an electron acceptor in devices,[9] whereas carboranes have not found a parallel application. In contrast, C_{60} appeared as an excellent platform to generate a large sequential set of electron acceptors; this proposal, however, seems to be hardly attainable.[10] Therefore carboranes could not compete with C_{60} as electron acceptors. However, the B–X bond (X = halogen) in boron clusters is much more stable to reduction than the C–X bond in sp^2 carbon atoms and this could be used as an advantage for the redox tuning of boron clusters.[11]

If carboranes are geometrically analogous to C_{60}, metallacarboranes such as $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$, $[\mathbf{1}]^-$, are analogous to Fc. Therefore, to bypass the inevitable relationship between the structure and the number of electron pairs in boron clusters, and to benefit from the strength of the B–X bond, we focused our attention on the less severe electron regulated metallacarboranes, and in particular on $[\mathbf{1}]^-$.[12] Compound $[\mathbf{1}]^-$ shows three quasireversible waves in cyclic voltammetry at +1.18, −1.80, and −2.75 V (Fc^+/Fc) assigned to Co^{IV}/Co^{III}, Co^{III}/Co^{II}, and Co^{II}/Co^{I}, respectively.[13] The cathodic peaks indicate that high energy is required to introduce one and two electrons into the system, but this energy could be lowered given that B–X bonds can be produced and that their presence in the cluster could really make the cathodic peaks more positive. This assumption was supported by the $E_{1/2}(Co^{III}/Co^{II})$ values of $[\mathbf{1}]^-$ in acetonitrile: −1.80 V for $[\mathbf{1}]^-$, and −1.48 V (Fc^+/Fc) for $[3,3'\text{-Co}(8\text{-Cl-}1,2\text{-}C_2B_9H_{10})_2]^-$. These two anions can be made with good purity and their $E_{1/2}(Co^{III}/Co^{II})$ values calculated.[13] The large number of boron atoms in the cluster offer the possibility of multiple B–X substitutions that could gradually and systematically decrease the $E_{1/2}(Co^{III}/Co^{II})$ value. However, no other chlorinated derivative of $[\mathbf{1}]^-$ is available in the pure form. The commonly described $[\text{Co}(8,9,10\text{-}Cl_3\text{-}1,2\text{-}C_2B_9H_8)_2]^-$, ($Cl_6$-$[\mathbf{1}]^-$) is indeed a mixture of penta-, hexa-, and heptachlorinated $[\mathbf{1}]^-$ derivatives.[14] No higher chlorinated derivatives of

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$[\mathbf{1}]^-$ had been described until recently when the whole series from mono to dodecachlorinated $[\mathbf{1}]^-$ derivatives was reported.[14]

Each new dehydrochlorination step of $[\mathbf{1}]^-$ brought about a decrease of the $E_{1/2}(Co^{III}/Co^{II})$ value near 0.1 V. Thus for ten Cl substitutions, $[Co(C_2B_9H_6Cl_5)_2]^-$ (Cl_{10}-$[\mathbf{1}]^-$), an $E_{1/2}(Co^{III}/Co^{II})$ near −0.8 V (Fc^+/Fc) was expected, and this was confirmed by experiment.[14] The described $E_{1/2}$ tunability makes $[\mathbf{1}]^-$ a unique platform for achieving the targeted $E_{1/2}$ values. This valuable finding, however, faces a problem: it is impossible to get pure samples of each independent chlorinated species in practical quantities. Each sample was made of four to five components.[14] This problem precluded their use in devices, and also generated some controversy as the $E_{1/2}(Co^{III}/Co^{II})$ values of the different compounds could not be measured independently. To progress on the stepwise redox potential diminution we moved to the iodinated species of $[\mathbf{1}]^-$. The synthesis of $[3,3'\text{-}Co(8\text{-}I\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (I-$[\mathbf{1}]^-$),[15] $[3,3'\text{-}Co(8\text{-}I\text{-}C_2B_9H_{10})_2]^-$ (I_2-$[\mathbf{1}]^-$),[16] and $[3,3'\text{-}Co(8,9,10\text{-}I_3\text{-}1,2\text{-}C_2B_9H_8)_2]^-$ (I_6-$[\mathbf{1}]^-$)[13c] in pure form and in practical quantities had been described. Also their $E_{1/2}(Co^{III}/Co^{II})$ values had been measured,[13,15,17] but no relationship between them had been highlighted. To prove the $E_{1/2}(Co^{III}/Co^{II})$ dependence upon the number of iodine substituents in the platform, $[3,3'\text{-}Co(9,10\text{-}I_2\text{-}1,2\text{-}C_2B_9H_9)_2]^-$ (I_4-$[\mathbf{1}]^-$) and $[3,3'\text{-}Co(8,9,10,12\text{-}I_4\text{-}1,2\text{-}C_2B_9H_7)_2]^-$ (I_8-$[\mathbf{1}]^-$) needed to be prepared. Considering the stepwise lowering of the $E_{1/2}(Co^{III}/Co^{II})$ value with added chlorine substituents on $[\mathbf{1}]^-$, and the $E_{1/2}(Co^{III}/Co^{II})$ values for I-$[\mathbf{1}]^-$, I_2-$[\mathbf{1}]^-$, and I_6-$[\mathbf{1}]^-$, it was expected that with I_8-$[\mathbf{1}]^-$ it would be possible to reach $E_{1/2}(Co^{III}/Co^{II})$ values in the −0.6 to −0.8 V (Fc^+/Fc) range. Indeed this was the case. The synthesis of I_8-$[\mathbf{1}]^-$ was possible by using the steps and reaction conditions indicated in Scheme 2.

I_8-$[\mathbf{1}]^-$ is the highest iodinated derivative of $[\mathbf{1}]^-$ reported so far and can be made in useful quantities as the NMe_4^+ salt for its possible applications. Its ^{11}B and ^1H NMR spectroscopy, MALDI-TOF and EA data (see the Supporting Information) confirmed its structure, along with the structure from the X-ray analysis that is presented in Figure 1.[18]

The X-ray crystal structure of the intermediate $[HNMe_3][1,5,6,10\text{-}I_4\text{-}7,8\text{-}C_2B_9H_8]$ shown in Figure 2,[18] was also solved. In a similar way the missing $[NMe_4][4,5\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}]$ and $[NMe_4][3,3'\text{-}Co(9,10\text{-}I_2\text{-}1,2\text{-}C_2B_9H_9)_2]$ have also been synthesized. See reaction conditions and steps needed in Scheme 3 (R = H). The $E_{1/2}(Co^{III}/Co^{II})$ values for $[\mathbf{1}]^-$,I-$[\mathbf{1}]^-$, I_2-$[\mathbf{1}]^-$, I_4-$[\mathbf{1}]^-$, I_6-$[\mathbf{1}]^-$, and I_8-$[\mathbf{1}]^-$ were experimentally determined by

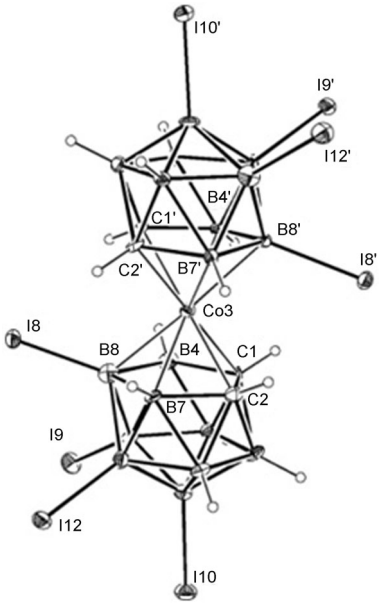


Figure 1. Ortep plot of $[3,3'\text{-}Co(8,9,10,12\text{-}I_4\text{-}1,2\text{-}C_2B_9H_7)_2]^-$ anion (I_8-$[\mathbf{1}]^-$). Thermal ellipsoids are shown at 30% probability. Selected bond lengths [Å] and angles [°]: C1–C2 1.64(2), C1′–C2′ 1.68(2), Co–C from 2.00(1) to 2.05(1), Co–B from 2.09(1) to 2.17(1), I–B from 2.15(2) to 2.23(2), C1-Co3-C2′ 179.0(5), C1′-Co3-C2 179.5(5) C1-Co3-C1′ 132.1(4) and C2–Co3–C2′ 131.4(5).

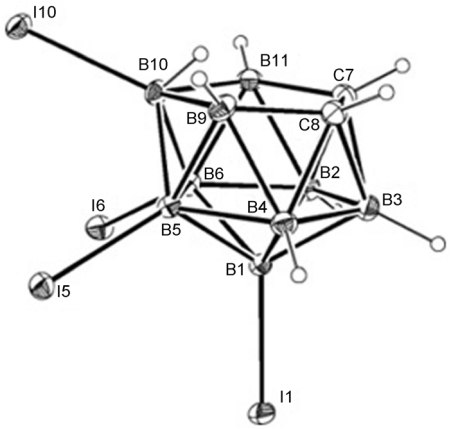
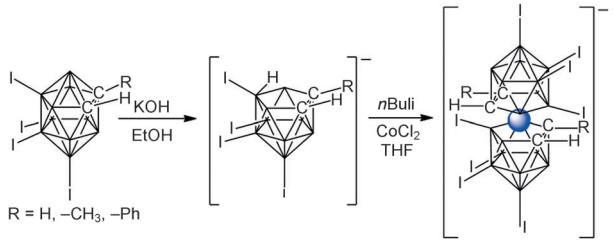
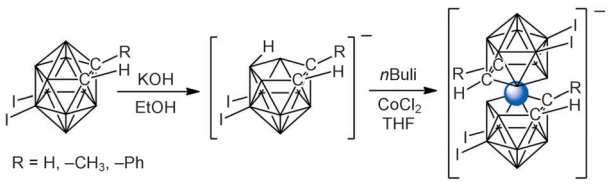


Figure 2. Ortep plot of $[1,5,6,10\text{-}I_4\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$ anion. Thermal ellipsoids are shown at 30% probability. Selected bond lengths [Å] and angles [°]: C7-C8 1.533(9), I–B from 2.183(6) to 2.197(6), C7-C8-B9 113.3(5), C8–C7 B11-114.8(5) and B9-B10-B11 102.1(5).



Scheme 2. Synthesis of I_8-$[\mathbf{1}]^-$ and its $C_{clusters}$ derivatives (R = H, Me, Ph). THF = tetrahydrofuran.



Scheme 3. Synthesis of I_4-$[\mathbf{1}]^-$ and its $C_{clusters}$ derivatives (R = H, Me, Ph).

cyclic voltammetry and their values versus Fc^+/Fc are tabulated in Table 1.

A plot of the $E_{1/2}(Co^{III}/Co^{II})$ values against the number of iodine substituents on the platform is given in the Supporting Information. Each new iodine averages a shift of +0.133 V, thus the not yet produced $[Co(C_2B_9H_6I_5)_2]^-$ would have an $E_{1/2}(Co^{III}/Co^{II})$ value near −0.48 V (Fc^+/Fc). Therefore just by the addition of ten iodine substituents on boron in $[\mathbf{1}]^-$ the $E_{1/2}(Co^{III}/Co^{II})$ value drops from −1.80 V to −0.48 V (Fc^+/Fc).

Table 1: $E_{1/2}$ data for I_n-$[\mathbf{1}]^-$ (n = 0, 1, 2, 4, 6, 8) and $C_{clusters}$ derivatives.[a]

Compound	$E_{1/2}$ vs. Fc^+/Fc [V]	Compound	$E_{1/2}$ vs. Fc^+/Fc [V]
$[\mathbf{1}]^-$	−1.80	Me_2I_4-$[\mathbf{1}]^-$	−1.00
I-$[\mathbf{1}]^-$	−1.50	I_6-$[\mathbf{1}]^-$	−0.82
I_2-$[\mathbf{1}]^-$	−1.32	I_8-$[\mathbf{1}]^-$	−0.68
I_4-$[\mathbf{1}]^-$	−1.15	Ph_2I_8-$[\mathbf{1}]^-$	−0.61
Ph_2I_4-$[\mathbf{1}]^-$	−1.03	Me_2I_8-$[\mathbf{1}]^-$	−0.54

[a] Cyclic voltammogram responses were recorded at the glassy carbon electrode in MeCN $5x10^{-3}$ I_n-$[\mathbf{1}]^-$ using $[NBu_4][PF_6]$ (0.1 M) as the supporting electrolyte. The electrochemical cell contained $Ag/AgCl/KCl_{sat}$ as the reference electrode and a platinum wire as the auxiliary electrode. All experiments were performed at room temperature. The potential values have been referenced to the Fc^+/Fc couple [$E_{1/2}(Fc^+/Fc)$ = 0.64 V versus a standard hydrogen electrode (SHE)].

This is an unprecedented finding that allows the tuning of the redox potential of a platform with a minor change in its shape and dimensions so as to adjust its $E_{1/2}$ value to a specific purpose. To compare the $E_{1/2}(Co^{III}/Co^{II})$ value after substitution on C or on B anions $[3,3'\text{-}Co(1\text{-}Ph\text{-}9,10\text{-}I_2\text{-}1,2\text{-}C_2B_9H_8)_2]^-$ (Ph_2I_4-$[\mathbf{1}]^-$), $[3,3'\text{-}Co(1\text{-}Me\text{-}9,10\text{-}I_2\text{-}1,2\text{-}C_2B_9H_8)_2]^-$ (Me_2I_4-$[\mathbf{1}]^-$), $[3,3'\text{-}Co(1\text{-}Ph\text{-}8,9,10,12\text{-}I_4\text{-}1,2\text{-}C_2B_9H_6)_2]^-$ (Ph_2I_8-$[\mathbf{1}]^-$), and $[3,3'\text{-}Co(1\text{-}Me\text{-}8,9,10,12\text{-}I_4\text{-}1,2\text{-}C_2B_9H_6)_2]^-$ (Me_2I_8-$[\mathbf{1}]^-$) were synthesized using similar strategies as those used for I_4-$[\mathbf{1}]^-$ and I_8-$[\mathbf{1}]^-$. Their $E_{1/2}(Co^{III}/Co^{II})$ values are tabulated in Table 1. The first noticeable point is that the $C_{cluster}$ substitution produces an anodic shift as it does on B, but it is smaller; second, the effect of Me, near 0.07, is larger than the effect of Ph, in the range from +0.04 to +0.06.

Once it had been demonstrated that $[\mathbf{1}]^-$ allows a stepwise tunable redox potential system, it was our goal to observe if the latter tunable property transcended into a different observable one.

We chose the growth of polypyrrole (PPy) to explore this possibility. The motivation of this study was the potential use of conducting polymers for practical applications in active areas of research in fields as varied as rechargeable batteries, electrochromic displays, information memory, antistatic materials, anticorrosives, electrocatalysis, sensors, electromechanical devices, infrared polarizers, radars, and biomedical applications, among others.[19]

Besides, it was already known that $[\mathbf{1}]^-$ facilitated the electrochemical growth of PPy from pyrrole, thus producing an extraordinary overoxidation resistance to the material.[20] The electrochemical synthetic procedure we have used for PPy doped with the iodinated derivatives of $[\mathbf{1}]^-$ consists of applying a linear potential ramp versus time to a solution of pyrrole and the doping anion, up to a certain oxidizing voltage.[21] The current is measured between the working electrode and the reference electrode. Once the oxidizing potential target is reached, the polarity of the working electrode is reversed to a specified reducing voltage. This cycle is applied repeatedly and in each cycle a higher intensity is observed, thus indicating the growth of the material.

The synthetic procedure is similar to that of the cyclic voltammetry electrochemical method of a reversible system, and in favorable cases produces an oxidation peak that has a similar shape to the reduction peak. As can be seen in Figure 3 for PPy/$[I_n\text{-}\mathbf{1}]^-$, both the forward and reverse scans produce current peaks. The separation between the anodic and cathodic peaks is, however, much larger than the equivalent separation in an electrochemical reversible system.

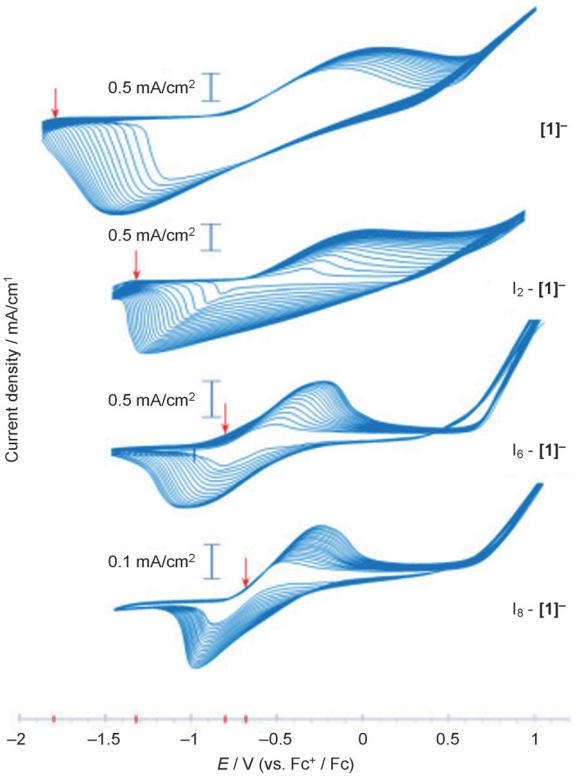


Figure 3. Growth curves of PPy doped with I_n-$[\mathbf{1}]^-$ (n = 0, 2, 6, 8). The red arrows correspond to the $E_{1/2}$ value for I_n-$[\mathbf{1}]^-$.

One could argue that the obvious difference between the PPy/$[I_n\text{-}\mathbf{1}]^-$ growth traces is due to the different shape of the anions. This difference should not be the case as it has been demonstrated that the geometry and apparent size of the boron clusters with different numbers of like substituents is strongly influenced by the type of boron cluster framework. This influence is observed in the ease of the formation of solid solutions by different types of boron clusters. For instance, a mixture of 9-X-12-Y-3,4,5,6,7,8,10,11-Me_8-1,2-$C_2B_{10}H_2$, in which (X,Y) are (I,Cl), (I,H), (H,H), and (H,Cl) combines into a single crystal to produce an average formula of 9-$I_{0.707}H_{0.293}$-12-$Cl_{0.566}H_{0.434}$-3,4,5,6,7,8,-10,11-Me_8-1,2-$C_2B_{10}H_2$.[21] Other examples are found in $[PdBr_{1.133}Cl_{0.867}$-

$(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$ and $[PdBrCl_{0.541}Me_{0.459}\text{-}(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]\cdot CH_2Cl_2$, which were made from $[PdBr_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$, $[PdCl_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$, $[PdBrCl(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$, and $[PdBrMe(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})]$ mixtures.[22]

Therefore, it shall be assumed that any differences in the growth of PPy doped with derivatives of the platform $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ will depend little on the number of iodine substituents and largely on their $E_{1/2}$ redox potential. Figure 3 shows the growth of four PPy/I_n-$[\mathbf{1}]^-$ conducting organic polymers with $n=0$, 2, 6, and 8 and with the $E_{1/2}$ value for I_n-$[\mathbf{1}]^- = -1.80$ ($n=0$), $-1{,}32$ ($n=2$), -0.82 ($n=6$), and -0.68 ($n=8$) V (Fc^+/Fc). The $E_{1/2}$ potentials for I_n-$[\mathbf{1}]^-$ are more negative than the cathodic peak for PPy/$[\mathbf{1}]^-$ and PPy/I_2-$[\mathbf{1}]^-$, and in between the cathodic and anodic peaks for PPy/I_6-$[\mathbf{1}]^-$ and PPy/I_8-$[\mathbf{1}]^-$. The red arrows in Figure 3 indicate $E_{1/2}$ value for the doping of I_n-$[\mathbf{1}]^-$.

The traces for the couple PPy/$[\mathbf{1}]^-$ and PPy/I_2-$[\mathbf{1}]^-$, on one side and the couple PPy/I_6-$[\mathbf{1}]^-$, and PPy/I_8-$[\mathbf{1}]^-$, on the other are very different. Notably, PPy/I_6-$[\mathbf{1}]^-$ and PPy/I_8-$[\mathbf{1}]^-$ display: 1) a much smaller separation between the anodic and cathodic peaks, 2) more slender peaks, and 3) have a well-defined plateau between the anodic peak and the slope starting between 0.65 and 1 V. All these differences are related to how close the $E_{1/2}$ value for I_n-$[\mathbf{1}]^-$ is to the gravity center between the anodic and cathodic peaks, $(E_a - E_c)/2$. Remarkably, the gravity center for the anodic and cathodic peaks is $-0.63(2)$ V (Fc^+/Fc) for all four PPy/I_n-$[\mathbf{1}]^-$ materials ($n=0$, 2, 6, 8). As seen in Figure 3 the effect of the electroactive anion, all other conditions being equal, on the growth of the PPy/I_n-$[\mathbf{1}]^-$ material is clear.

What are the implications of a predictable and accessible $E_{1/2}$ tunable platform? Our opinion is that the possibilities are numerous, mainly in nanoscience and molecular materials. They offer a unique opportunity to combine different, but highly compatible materials with different electron-transfer characteristics. At this moment we are studying the generation of electron-transfer-cascade materials made of thin layers, each with distinct electron-transfer characteristics. The $[\mathbf{1}]^-$ platform, as a result of its high stability, availability, possibility for functionalization, and tunable electroactivity, offers a wide range of possibilities that are not encountered for other popular electroactive platforms.

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[1] R. E. Blankenship in *Molecular Mechanisms of Photosynthesis*, Blackwell Science, Oxford, **2002**, chap. 6–7.
[2] R. Cotterill, *Biophysics: An Introduction*, Wiley, Chichester, **2003**, chap. 9.
[3] a) A. Amunts, O. Drory, N. Nelson, *Nature* **2007**, *447*, 58–63; b) M. R. Wasielewski, *J. Org. Chem.* **2006**, *71*, 5051–5066; c) R. Lomoth, A. Magnuson, M. Sjödin, P. Huang, S. Styring, L. Hamarström, *Photosynth. Res.* **2006**, *87*, 25–40; d) J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, *Inorg. Chem.* **2005**, *44*, 6802–6827.
[4] a) Y. Araki, R. Chitta, A. S. D. Sandanayaka, K. Langewalter, S. Gadde, M. E. Zandler, O. Ito, F. D'Souza, *J. Phys. Chem. C* **2008**, *112*, 2222–2229; b) M. Morisue, D. Kalita, N. Haruta, Y. Kobuke, *Chem. Commun.* **2007**, 2348–2350; c) A. Sautter, B. K. Kaletaş, D. G. Schmid, R. Dobrawa, M. Zimine, G. Jung, I. H. M. van Stokkum, L. De Cola, R. M. Williams, F. Würthner, *J. Am. Chem. Soc.* **2005**, *127*, 6719–6729; d) T. Konishi, A. Ikeda, S. Shinkai, *Tetrahedron* **2005**, *61*, 4881–4899.
[5] a) A. Laiho, R. H. A. Ras, S. Valkama, J. Ruokolainen, R. Österbacka, O. Ikkala, *Macromolecules* **2006**, *39*, 7648–7653; b) Z. R. Hong, Z. H. Huang, X. T. Zeng, *Chem. Phys. Lett.* **2006**, *425*, 62–65; c) V. Shrotriya, J. Ouyang, R. J. Tseng, G. Li, Y. Yang, *Chem. Phys. Lett.* **2005**, *411*, 138–143; d) R. H. Xie, G. W. Bryant, G. Sun, T. Kar, Z. Chen, V. H. Smith, Jr., Y. Araki, N. Tagmatarchis, H. Shinohara, O. Ito, *Phys. Rev. B* **2004**, *69*, 201403.
[6] a) R. E. Williams, *Inorg. Chem.* **1971**, *10*, 210–214; b) K. Wade, *J. Chem. Soc. D* **1971**, 792–793; c) D. M. P. Mingos, *Nature Phys. Sci.* **1972**, *236*, 99–102; d) R. W. Rudolph, W. R. Pretzer, *Inorg. Chem.* **1972**, *11*, 1974–1978.
[7] L. Echegoyen, L. E. Echegoyen, *Acc. Chem. Res.* **1998**, *31*, 593–601.
[8] J. H. Morris, H. J. Gysling, D. Reed, *Chem. Rev.* **1985**, *85*, 51–76.
[9] a) T. C. Clarke, J. R. Durrant, *Chem. Rev.* **2010**, *110*, 6736–6767; b) S. Günes, H. Neugebauer, N. S. Saricifti, *Chem. Rev.* **2007**, *107*, 1324–1338; c) J. L. Segura, N. Martin, D. M. Guldi, *Chem. Soc. Rev.* **2005**, *34*, 31–47; d) J. Roncali, *Chem. Soc. Rev.* **2005**, *34*, 483–495; e) L. Sánchez, M. Sierra, N. Martín, A. J. Myles, T. J. Dale, J. Rebek, Jr., W. Seitz, D. M. Guldi, *Angew. Chem.* **2006**, *118*, 4753–4757; *Angew. Chem. Int. Ed.* **2006**, *45*, 4637–4641.
[10] a) M. Zheng, F. F. Li, Z. J. Shi, X. Gao, K. M. Kadish, *J. Org. Chem.* **2007**, *72*, 2538–2542; b) M. Carano, M. Marcaccio, F. Paolucci, P. Birkett, *Photochem. Photobiol. Sci.* **2006**, *5*, 1132–1136; c) F. Zhou, G. J. Van Berkel, B. T. Donovan, *J. Am. Chem. Soc.* **1994**, *116*, 5485–5486; d) A. A. Popov, I. E. Kareev, N. B. Shustova, E. B. Stukalin, S. F. Lebedkin, K. Seppelt, S. H. Strauss, O. V. Boltalina, L. Dunsch, *J. Am. Chem. Soc.* **2007**, *129*, 11551–11568.
[11] U. Páramo-Garcío, M. Ávila-Rodríguez, M. G. García-Jiménez, S. Gutiérrez-Granados, J. G. Ibáñez-Cornejo, *Electroanalysis* **2006**, *18*, 904–910.
[12] a) I. B. Sivaev, V. I. Bregadze, *Collect. Czech. Chem. Commun.* **1999**, *64*, 783–805; b) D. A. Rudakov, V. L. Shirokii, V. A. Knizhnikov, A. V. Bazhanov, E. I. Vecher, N. A. Maier, V. I. Potkin, A. N. Ryabtsev, P. V. Petrovskii, I. B. Sivaev, V. I. Bregadze, I. L. Eremenko, *Russ. Chem. Bull. Int. Ed.* **2004**, *53*, 2554–2557.
[13] a) L. Matel, R. Cech, F. Macasek, S. Hermanek, J. Plesek, *Radiochem. Radioanal. Lett.* **1978**, *35*, 241–246; b) L. Mátel, F. Macášek, P. Rajec, S. Heřmánek, J. Plešek, *Polyhedron* **1982**, *1*, 511–519; c) M. D. Mortimer, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1996**, *35*, 5750–5751.
[14] P. Gonzalez-Cardoso, A. I. Stoica, P. Farràs, A. Pepiol, C. Viñas, F. Teixidor, *Chem. Eur. J.* **2010**, *16*, 6660–6665.
[15] I. Rojo, F. Teixidor, C. Viñas, R. Kivekäs, R. Sillanpää, *Chem. Eur. J.* **2003**, *9*, 4311–4323.
[16] I. Rojo, F. Teixidor, C. Viñas, R. Kivekäs, R. Sillanpää, *Organometallics* **2003**, *22*, 4642–4646.
[17] M. Corsini, F. Fabrizi de Biani, P. Zanello, *Coord. Chem. Rev.* **2006**, *250*, 1351–1372.
[18] See the Supporting Information for details for the X-ray structure analyses. CCDC 837895 ($[HNMe_3][1,5,6,10\text{-}I_4\text{-}7,8\text{-}C_2B_9H_8]$) and 837896 ($[NMe_4][3,3'\text{-}Co(8,9,10,12\text{-}I_4\text{-}1,2\text{-}C_2B_9H_7)_2]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] a) D. D. Ateh, H. A. Navsaria, P. Vadgama, *J. R. Soc. Interface* **2006**, *3*, 741 – 752; b) S. F. Michael, B. A. Deore in *Self-Doped Conducting Polymers* (Eds.: Wiley-*Blackwell)*, Blackwell Science, Oxford, **2007**, p. 338.

[20] a) C. Masalles, J. Llop, C. Viñas, F. Teixidor, *Adv. Mater.* **2002**, *14*, 826 – 829; b) C. Masalles, S. Borrós, C. Viñas, F. Teixidor, *Adv. Mater.* **2002**, *14*, 449 – 452.

[21] F. Teixidor, G. Barberà, A. Vaca, R. Kivekäs, R. Sillanpää, J. Oliva, C. Viñas, *J. Am. Chem. Soc.* **2005**, *127*, 10158 – 10159.

[22] S. Paavola, F. Teixidor, C. Viñas, R. Kivekäs, *J. Organomet. Chem.* **2002**, *657*, 187 – 193.

