

Building Blocks for the Molecular Expression of Quantum Cellular Automata. Isolation and Characterization of a Covalently Bonded Square Array of Two Ferrocenium and Two Ferrocene Complexes

Jieying Jiao,[†] Gary J. Long,^{*,‡} Fernande Grandjean,[§] Alicia M. Beatty,[†] and Thomas P. Fehlner^{*,†}

Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556-5670, Department of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65409-0010, and Department of Physics, B5, University of Liège, B-4000 Sart-Tilman, Belgium

Received March 10, 2003; E-mail: fehlner.1@nd.edu

The utilization of molecules as components of electronic circuits has caught the imagination of many.¹ The temptation to look for molecular mimics of existing electronic components is strong; however, molecules are exceedingly poor charge conductors and resistive heating rules out high device densities—the primary justification of the approach. On the other hand, molecules are excellent charge containers and a novel paradigm, quantum cellular automata (QCA), which is based on field-coupled charge containers, has been proven theoretically as well as operationally at low temperature using 50 nm quantum dots.^{2–4} Systems based on 2 nm dots are expected to operate at room temperature, hence, our interest in developing molecular expressions of the QCA paradigm.⁵

The smallest building block of QCA wires consists of two dots containing a single mobile electron. At the molecular level this building block is a mixed-valence complex about which much is known.^{6–8} A more versatile building block for constructing QCA circuits is a square of four electronically coupled dots containing two mobile electrons. Although molecular squares containing redox active metal centers have been described^{9–14} and mixed-valence complexes up to nuclearity three have been thoroughly analyzed,^{8,15} there is no example of an isolated four-metal, mixed-valence complex containing two mobile electrons in a square geometry. The independent existence and compatible electronic properties of such a species are of fundamental importance to the realization of the QCA paradigm. Here we report the full characterization of a symmetrical square containing two ferrocene and two ferrocenium moieties possessing measured properties that make it suitable for use as a component for charge-coupled QCA circuits.

The basic requirements to be met by a molecular QCA cell are dots consisting of metal complexes possessing two stable redox states, a planar array of four such complexes with 4-fold symmetry, sufficient through-bond or through-space interaction so that the 2-electron, 2-hole mixed-valence state is stable with respect to disproportionation to lower and higher oxidation states, type II or type III mixed-valence behavior appropriate for switching,¹⁶ and capability of isolation as a pure compound in useable yields from readily available starting materials. These design restrictions led to several failures and caused us to focus efforts on a square of four ferrocene complexes already described in the literature, i.e., $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)$, **1**.^{17,18} Although the reported electrochemistry was discouraging (a wave at 0.29 V with the “remaining 3 redox waves blend(ed) into a broad wave centered at ... 0.4 V”),¹⁸ visible and near-IR band positions were published for the 1+, 2+, and 3+ ions generated by bulk electrolysis. None

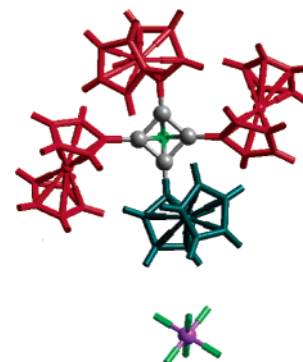


Figure 1. Molecular structure of **[1][PF₆]**. Fe–Fe edge distance 5.980 Å. The $\eta^5\text{-C}_5\text{H}_5$ ring bound to the Co atom (green) is not shown for clarity.

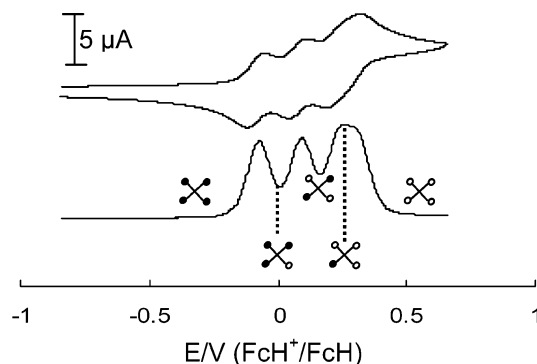


Figure 2. Cyclic and square wave voltammetry of **1** at 100 mv/s on a Pt electrode in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ mixed solvent, $\text{TBA}[\text{PF}_6]$ electrolyte, and Pt wire reference electrode ($E_{1/2}(\text{FcH}^+/\text{FcH}) = 0.344$ V). The solid and open dots in the diagrams represent Fe(II) and Fe(III), respectively.

of these ions were isolated. On the other hand, these spectroscopic data provided sufficient impetus to revisit the system.

The synthesis of **1** was carried out as described previously, and analytically pure material was isolated.^{17,18} Single crystals permitted a solid-state structure, which provides the dimensions of the square array of ferrocene moieties. The structure is similar to that of **[1][PF₆]** shown in Figure 1. Other spectroscopic properties are shown in Figures 3 and 4 and in the Supporting Information. Cyclic and square wave voltammetry (Figure 2) reveals four waves sufficiently separated to suggest isolation of the 1+ and 2+ cations is feasible. Note that choice of solvent is critical to prevent precipitation of the cations on the electrode, thereby leading to complex behavior.¹⁹

The analytically pure 1+ ion, **[1][PF₆]**, was prepared by oxidation of **1** with $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}][\text{PF}_6]$. It too was characterized in the solid state by X-ray diffraction (Figure 1). In contrast to **1**, **[1][PF₆]** exhibits a near-IR band (Figure 3) which is solvent dependent (Type II), an axial EPR spectrum at 4 K similar to that of ferrocenium

[†] University of Notre Dame.

[‡] University of Missouri—Rolla.

[§] University of Liège.

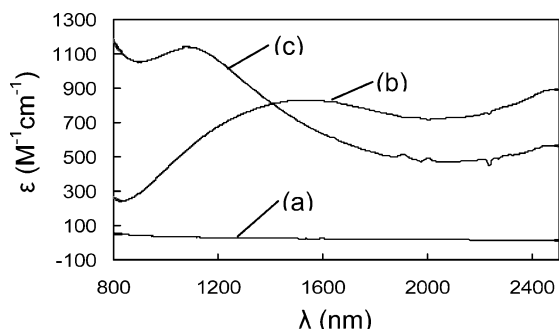


Figure 3. Near-infrared spectra of (a) **1** in CDCl_3 and (b) $[\mathbf{1}][\text{PF}_6]$ and (c) $[\mathbf{1}][\text{PF}_6]_2$ in $(\text{CD}_3)_2\text{CO}$.

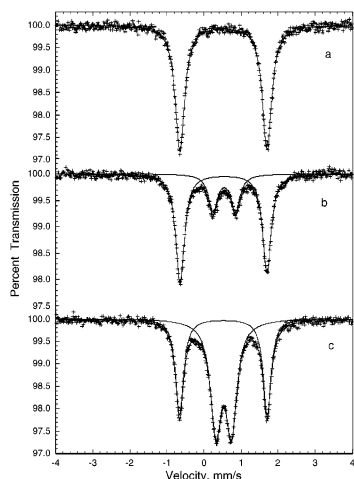


Figure 4. Mössbauer spectra of (a) **1**, (b) $[\mathbf{1}][\text{PF}_6]$, and (c) $[\mathbf{1}][\text{PF}_6]_2$ at 95 K relative to room-temperature α -iron foil.

ion (based on an observed $\Delta g = 1.26$, the electron is localized on the EPR time scale²⁰), a Mössbauer spectrum (Figure 4) consisting of two doublets with an area ratio of ~ 3 to 1 and ΔE_Q values of 2.34 and 0.60 mm/s characteristic of Fe(II) and Fe(III) sites, respectively,²¹ and two ring deformation bands in the IR characteristic of ferrocenium (851 cm^{-1}) and ferrocene (821 cm^{-1}) in $\approx 1:3$ intensity ratio (BF_4^- salt).²² In addition, the magnetic susceptibility as a function of temperature follows Curie–Weiss behavior down to 5 K with a magnetic moment of $2.27\ \mu_B$ consistent with the spin of one electron.²³

The $2+$ ion, $[\mathbf{1}][\text{PF}_6]_2$, proved to be a more formidable challenge. With the guidance of the Connelly/Geiger review,²⁴ several oxidizing agents were tried. Acyl-substituted ferrocenium proved satisfactory for oxidizing **1** (2 equiv) or $[\mathbf{1}][\text{PF}_6]$ (1equiv) quantitatively to the $2+$ ion. In this manner, $[\mathbf{1}][\text{X}]_2$, $\text{X} = \text{PF}_6$, BF_4 , and triflate, were prepared and isolated. All yielded powders which slowly decomposed on attempted crystallization. However, satisfactory elemental analysis of $[\mathbf{1}][\text{PF}_6]_2$ confirmed charge state and purity of the material. Relative to $[\mathbf{1}][\text{PF}_6]$, the intervalence charge-transfer band is shifted to higher energy (solvent independent, Type II–III);⁸ the EPR spectrum is nearly the same down to 4 K (the energy of the spin–spin interaction is small); the Mössbauer spectrum (Figure 4) consists of two doublets with an area ratio of ~ 1 to 1 and ΔE_Q values of 2.36 and 0.42 mm/s for the Fe(II) and Fe(III) sites, respectively; and the two ring deformations in the IR characteristic of ferrocenium and ferrocene are in $\approx 1:1$ intensity

ratio (BF_4^- salt). The magnetic susceptibility follows Curie–Weiss behavior to 5 K with a magnetic moment = $3.36\ \mu_B$, consistent with the spin of two uncoupled electrons.

The observed properties of the $2+$ ion, the 2-electron, 2-hole mixed-valence state, are appropriate for utilization in molecular QCA. The $2+$ ion can be isolated as a pure material from readily available starting materials albeit as a product of a nontrivial synthetic route. The $2+$ ion has trapped valence states on the IR time scale, a finding corroborated by the EPR and Mössbauer experiments at somewhat slower time scales. However, the presence of an intervalence charge-transfer band in the near-IR implies an electron hopping frequency ($\approx 10^{7.5}\text{ s}^{-1}$) appropriately fast for the QCA application. Spin–spin interaction is small and does not distort the energies of the pair of degenerate states required for signal transmission. The electrostatically favored trans-geometry of the ferrocenium units in the dication, the effects of conformational variations on switching, and the role of the counterions remain to be established. These points will be addressed in future work.

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Supporting Information Available: Preparation, characterization, and spectroscopic parameters for **1**, $[\mathbf{1}][\text{PF}_6]$, and $[\mathbf{1}][\text{PF}_6]_2$ and X-ray data for **1** and $[\mathbf{1}][\text{PF}_6]$ (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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