

Partially oxidized ferrocenyl complexes for nonlinear optics

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Second-order nonlinearity ($\chi^{(2)}$) in a series of partially oxidized bisferrocenes linked through conducting -C=N- linkages has been measured and found to vary linearly with the redox potential difference between the ferrocene moiety and the oxidant.

DESIGNING organic molecules having large optical nonlinearities has been the topic of much current research^{1,2}. Organometallic complexes prepared along these lines have been found to exhibit large second-order nonlinearities³⁻⁵. Indeed, they offer a variety of tunable parameters unmatched in the realm of organic chemistry such as low energy electronic transitions, variable oxidation states of the metal atom, and electronic and steric properties of the ligand for optimizing molecular hyperpolarizabilities. The recent discovery of large second-order nonlinearity ($\chi^{(2)}$) in certain mixed valence compounds⁶ with a tunable intervalence charge transfer transition suggests that there may be considerable potential for the discovery of large optical nonlinearities in

mixed valent organometallic molecules. The largest second harmonic generation efficiency (220 x U) to date for an organometallic compound came from a series of ferrocene-based conjugated salts⁷. But their microscopic nonlinearities have not been measured. Here we report first hyperpolarizability ($\chi^{(2)}$) in a series of oxidized bisferrocenes linked through various conducting organic spacers, measured by the recently developed hyper-Rayleigh scattering technique (HRS)⁸⁻¹⁰.

Ferrocene carboxaldehyde has been linked to aromatic amines and diamines to generate mononuclear functionalized ferrocenes and the corresponding bisferrocenes. These molecules are then oxidized using I₂, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 7,7',8,8'-tetracyanoquinodimethane (TCNQ) to give the products indicated in Figure 1. Compounds 1a-3d have been characterized" by various spectroscopic and analytical techniques and their $\chi^{(2)}$ values measured in acetonitrile with 1064 nm radiation at low solute concentrations (10⁻⁵-10⁻⁶ M) by the HRS technique (Table 1). Since these molecules are ionic in nature, the HRS technique is specially suited for $\chi^{(2)}$ measurements on them. The error on these hyperpolarizabilities is $\pm 8\%$. The wavelength of peak absorption in these molecules in the visible region is also shown in Table 1. For compounds absorbing appreciably in the green (~ 532 nm) corrections were made as suggested by Laidlaw *et al.*⁶ and corrected values of $\chi^{(2)}$ are listed.

The nonzero and small P value of ferrocene (1a) is probably due to octupolar contributions from the non-centrosymmetric eclipsed form which exists along with the staggered D_{5d} conformation in solution. However, the size of the π system along which the electrons are delocalized is small and results in a low P value. Attaching a pendant acceptor to ferrocene results in a donor-acceptor motif (2a) and P increases moderately as expected. What is surprising is that P increases further by a factor of *ca* 1.5 when another ferrocene is attached to the benzene ring through a similar Schiffbase linkage resulting in a donor-acceptor-donor D-A-D motif (3a). Considering that the $-C=N-$ linkage acts as an acceptor¹², 2a is in fact, a D-A-D and 3a, a donor-acceptor-donor-acceptor-donor (D-A-D-A-D) system. Alternating the D-A motif appears to be suitable for nonlinear optics (NLO) in the neutral molecules, unlike alternating pendant donors and acceptors on the π framework.

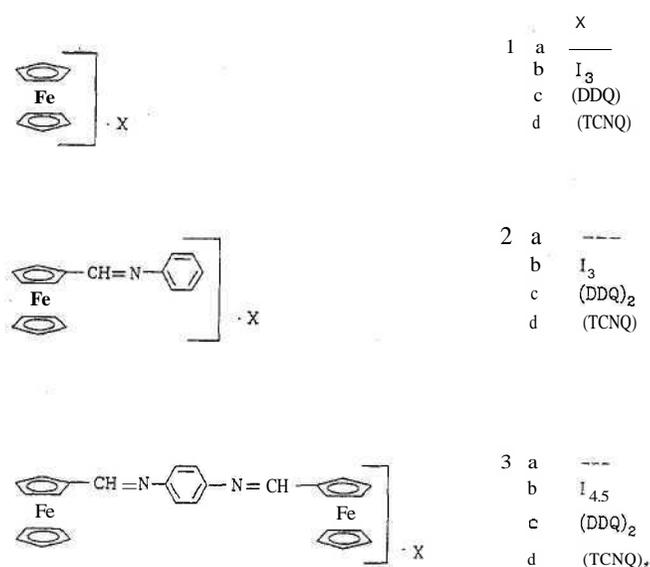


Figure 1. Structures of the neutral and oxidized ferrocene.

Table 1. The second-order nonlinearity ($\times 10^{-30}$ esu), relative redox potential, $\Delta E_{1/2}$ (V), the absorption maximum λ_{max} (nm), and absorbance at 532 nm ϵ_{532} ($\times 10^3 M^{-1} cm^{-1}$) of compounds 1a-3d

Compound	P	$\Delta E_{1/2}$	λ_{max}	ϵ_{532}
1a	0.8	—	380	—
1b	2.8	0.30	420	—
1c	4.6	0.20	470	1.2
1d	5.9	-0.13	580	0.8
2a	14.2	—	460	—
2b	111.2	0.08	550	1.2
2c	121.6	-0.03	567	2.6
2d	132.0	-0.36	589	0.6
3a	20.8	—	465	—
3b	161.0	0.18	556	1.6
3c	201.0	0.08	572	1.1
3d	246.0	-0.25	588	0.8

On the basis of cyclic voltametry, Mössbauer and other spectroscopic data", we believe that the bisferrocene moiety (3a) is unique in the ability of the two iron centres to interact electronically. A recent report¹² on similar functionalized ferrocenes supports this view that the $-C=N-$ linkage, indeed, allows for greater electronic conjugation. Extended Hückel calculations on these complexes show that the highest occupied molecular orbital is delocalized over the two iron centres in 3a. Oxidation of all the neutral compounds results in a tremendous increase in the p values. The measured P values for the partly oxidized complexes are an order of magnitude greater than those for the corresponding neutral molecules. Since the oxidizing ability varies in the order $TCNQ < DDQ < I_2$, and the measured hyperpolarizabilities of the complexes follow the reverse order, we have examined the electrode potentials ($\Delta E_{1/2}$) for the redox reactions. A remarkable correlation is obtained between the $\Delta E_{1/2}$ and P (Figure 2). As $\Delta E_{1/2}$ decreases in the positive sense, the free energy for electron transfer from the bisferrocene moiety to the acceptor decreases and only a charge transfer complex is formed. But this is accompanied by an increase in p . Since the ferrocene donors have low hyperpolarizabilities, the origin of the large P values must lie elsewhere in the partially oxidized complexes. It appears that the nonlinearity in these complexes results from differential electron transfer from the bisferrocene moiety to the oxidant in the ground and excited states, resulting in a significant change in the dipole moment between the two states. In other words, in the excited state the ability of the oxidized bisferrocene donor to accept an electron leads to a reversal in the direction of charge transfer leading to

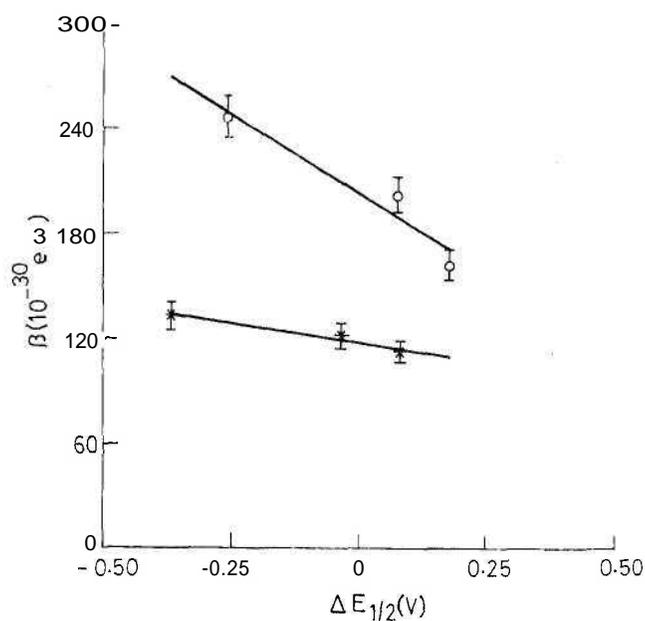


Figure 2. p (10^{-30} esu) vs $\Delta E_{1/2}$ (V) for compounds 2b-d and 3b-d.

a large $\delta\mu$ and hence large second-order nonlinearities result in these complexes.

The 460 nm band in the neutral ferrocenes is attributed primarily to a d-d transition which shifts to ~ 550 nm on oxidation. The absorption band extends up to + 50 nm around λ_{max} and this may contribute to the resonance enhancement of p through a two-photon mechanism. In the case of complexes containing TCNQ and DDQ, this band may also originate from TCNQ^- or DDQ^- respectively. Although the λ_{max} correlates linearly with β , no straightforward correlation between the absorbance at 532 nm (ϵ_{532}) and the measured P is observed. These molecules do not absorb at ~ 1064 nm unlike the mixed valence ruthenium complex³ and, therefore, a single photon dispersion in p is ruled out.

In summary, we have clearly demonstrated that partially oxidized ferrocenes formed by matching the redox potentials of neutral ferrocene moieties and an oxidant represent an entirely new class of complexes which exhibit large first-order hyperpolarizability. p for the corresponding neutral ferrocenes is, at least, an order of magnitude smaller than the ionic compounds and comparable to other ferrocenyl compounds studied in the past. Since a huge library of metallocenes and their oxidation potentials exist it is possible to design better partially ionic NLO materials based on the above guidelines. We are currently investigating this.

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