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Reversible switching of the first hyperpolarisability of an NLO-active donor–acceptor molecule based on redox interconversion of the octamethylferrocene donor unit

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Compound 1, containing an octamethylferrocene donor linked to a nitrothiophene acceptor *via* an ethenyl linker, shows a static first hyperpolarisability β_0 of 95(±10) × 10^{-30} esu, which is reduced to 10(±2) × 10^{-30} esu on oxidation of the octamethylferrocene unit; this provides for a simple redox-based switching of the NLO characteristics of the compound.

Compounds displaying non-linear optical (NLO) properties are of considerable interest because of their possible applications in the emerging technologies of optoelectronic and photonic devices.[1] Second-order NLO effects, including second-harmonic generation, and especially electro-optic modulation are important in interfacing massive amounts of electronic data to wideband optical communication. At the molecular level, the efficiency for electro-optic modulation is determined by the second-order non-linear polarisability, also called the first hyperpolarisability, β. A large value of β is generally associated with molecules which have a donor/conjugated bridge/acceptor (D-π-A) structure, such that there is a long-range charge-transfer transition from one end to the other and consequently a substantial difference between the ground-state and excited-state dipole moments.

The ability to switch the NLO response of a molecule 'on' and 'off' reversibly by a simple controllable perturbation would add significant value to the utility of NLO molecules, from the point of view of developing molecular photonic devices whose properties can be switched by modifying one of the component parts.[2] Despite the large number of molecules with large first hyperpolarisabilities, there are remarkably few examples in which such reversible switching has been demonstrated. Of these the majority depend on isomerisation or tautomerisation of the molecule, such that the nature of the conjugated bridge linking the donor and acceptor termini undergoes a substantial change.[3] A more appealing method of controlling the second-order NLO response of a molecule would be a reversible redox change, in which either the donor (D) unit is oxidised or the acceptor (A) unit is reduced. The result in either case would be a loss of the charge-transfer capability and a consequent drop in the hyperpolarisability β.[2] To date there is a single example of this in the literature, from the group of Coe, comprising a $\{Ru(NH_3)_5\}^{2+}$ donor linked to a viologen-like acceptor; the value of β decreased by an order of magnitude on one-electron oxidation of the Ru terminus. Subsequent re-reduction of the Ru terminus completely restored the SHG properties of the compound.[4]

We describe here a new molecule for second-order NLO applications (**1**) which contains an octamethylferrocene donor unit and a nitrothiophene acceptor, linked by an ethenyl bridge. The reversible octamethylferrocene–octamethylferrocenium couple, at modest potential, provides an ideal route for redox-based switching of the hyperpolarisability. Compounds which contain ferrocene units as the electron donor, with a single conjugated side-arm linked to an acceptor unit, have been exceptionally popular for studying SHG in the last decade.[5] The redox activity of the ferrocene donor unit however has not until now been exploited for switching purposes; use of the octamethylferrocene unit in **1** will both enhance its electron-donor properties compared to ferrocene, and will reduce the redox potential to make redox-based switching more facile.

Compound **1** was prepared in good yield† by a Wittig reaction between 1′,2,2′,3,3′,4,4′,5-octamethylferrocenylmethyltriphenylphosphonium bromide[6] and 5-nitro-2-thiophenecarbaldehyde in tetrahydrofuran (THF); the crystal structure is in Fig. 1.‡ The cyclopentadienyl ring of the donor, the ethenyl bridge, and the nitrothiophene acceptor are essentially coplanar which will clearly optimise end-to-end charge-transfer *via* the conjugated system. The electronic spectrum in CH_2Cl_2 (Fig. 2)

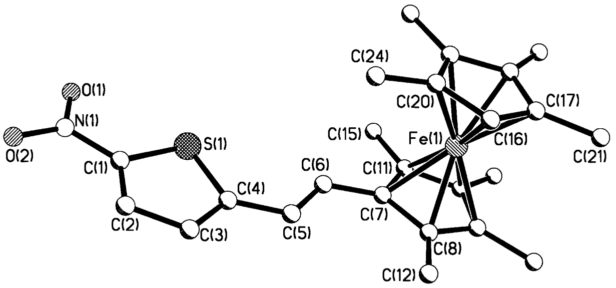

Fig. 1 Crystal structure of **1** together with selected bond distances. The structure of the complex cation of $[\mathbf{1}]^+(PF_6)\cdot CH_2Cl_2$ is essentially identical, and the bond distances for this are given in square parentheses after the corresponding value for **1**. Fe–C (average) 2.05 [2.10], N(1)–O(1) 1.242(4) [1.232(3)], N(1)–O(2) 1.228(4) [1.235(3)], N(1)–C(1) 1.423(4) [1.428(3)], C(1)–C(2) 1.354(5) [1.356(4)], C(2)–C(3) 1.405(4) [1.401(3)], C(3)–C(4) 1.377(4) [1.379(3)], C(1)–S(1) 1.719(3) [1.718(2)], C(4)–S(1) 1.738(3) [1.731(2)], C(4)–C(5) 1.442(4) [1.446(3)], C(5)–C(6) 1.348(4) [1.336(3)], C(6)–C(7) 1.449(4) [1.461(3)] Å.

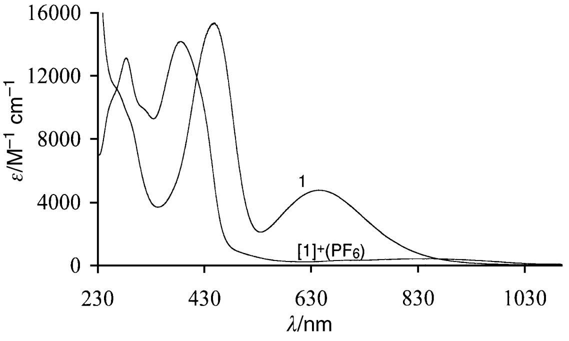

Fig. 2 Electronic spectra of **1** and $[\mathbf{1}]^+(PF_6)$ in CH_2Cl_2.

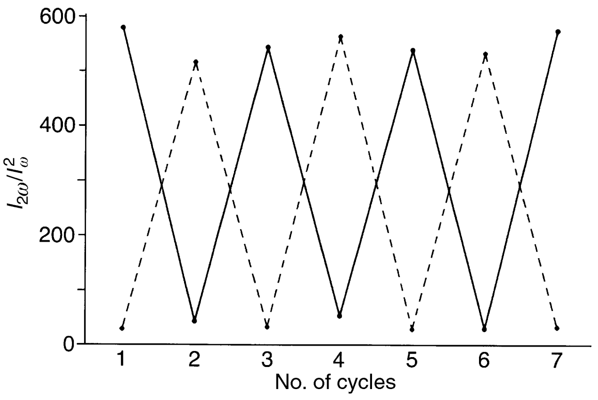

Fig. 3 Redox switching of the hyper-Raleigh scattering response between **1** and [**1**]$^+$ in CH_2Cl_2 (concentration of samples, 4 × 10^{-5} M). The solid line shows the response obtained starting with **1** and then alternately oxidising and re-reducing it; the dotted line shows the response obtained starting with [**1**]$^+$(PF_6) and then alternately reducing and re-oxidising it. The parameter plotted on the *y*-axis ($i_{2\omega}/I^2_{\omega}$) is proportional to β^2.

shows transitions at 644 nm and 447 nm which we ascribe to the two relevant D $\longrightarrow$ A charge-transfer transitions;[7] in agreement with this, both transitions are strongly solvatochromic, with the absorption maxima changing from 586 and 409 nm respectively in hexane, to 655 and 453 nm respectively in dimethyl sulfoxide. Compound **1** undergoes a reversible octamethylferrocene–octamethylferrocenium redox interconversion at -0.30 V *vs.* the ferrocene–ferrocenium couple in THF. Accordingly, one-electron oxidation of **1** by treatment with 1 equiv. of ferrocenium hexafluorophosphate in MeCN afforded [**1**]$^+$(PF_6) in high yield.§ This complex has also been structurally characterised,‡ and the structure of the complex cation [**1**]$^+$ is essentially identical to that of **1** apart from minor changes in the Fe–C bond distances (see caption to Fig. 1). In the oxidised complex [**1**]$^+$ the charge-transfer transitions of **1** are absent, replaced by the characteristic weak LMCT transition of the ferrocenium unit at 851 nm (Fig. 2).

We used the hyper-Raleigh scattering method[8] to measure the first hyperpolarisability β of **1** and [**1**]$^+$ in CH_2Cl_2 solution using a 1064 nm laser. The value of β obtained for **1** [316 (±32) × 10^{-30} esu] is much greater than that for [**1**]$^+$ [25 (±5) × 10^{-30} esu], as we would expect based on the above arguments. Part of this change is however ascribable to the fact that the value of **1** is resonantly enhanced due to absorption by the CT transitions in the region of the second harmonic of the excitation laser at 532 nm; this effect is not so significant for [**1**]$^+$ whose absorbance at this wavelength is much lower. Consequently the two-level model[9,10]¶ was used to derive the static hyperpolarisability (β_0) in each case, and β_0 values of 95 (±10) × 10^{-30} and 10 (±2) × 10^{-30} esu were obtained for **1** and [**1**]$^+$(PF_6) respectively. Thus, compound **1** has a SHG efficiency about one order of magnitude greater than does [**1**]$^+$.

The redox interconversion of **1** and [**1**]$^+$ thus provides a basis for an effective switch of the second-order NLO properties of the complex. The switching effect is illustrated in Fig. 3, which shows (solid line) the alternation in the value of the first hyperpolarisability as a sample of **1** is alternately oxidised (by addition of Bu_4NBr_3) and then reduced (by addition of hydrazine). Exactly similar results were obtained starting with [**1**]$^+$ and alternately reducing and oxidising it (dotted line). Given the large number of D–π–A complexes based on ferrocenyl donors which have been prepared for NLO studies,[5] this redox-based switching is clearly of wide applicability for the development of switchable NLO materials.[2]

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Notes and references

† To a mixture of 1′,2,2′3,3′,4,4′,5-octamethylferrocenylmethyltriphenylphosphonium bromide (1.75 g, 2.68 mmol) and dry THF (100 cm^3) under N_2 at -78 °C was added potassium *tert*-butoxide (0.33 g, 2.94 mmol). The red suspension was allowed to warm up to 0 °C and was stirred for 30 min at this temperature, after which time 5-nitro-2-thiophenecarbaldehyde (0.50 g, 3.21 mmol) was slowly added. The resulting green solution was stirred at room temperature for 3 h. After quenching with water and removal of solvents *in vacuo*, chromatographic purification (alumina, 1 : 1 diethyl ether–hexane) afforded pure **1** (0.87 g, 72%). Found: C, 63.8; H, 6.7; N, 3.1%; $C_{24}H_{29}FeNO_2S$ requires C, 63.9; H, 6.4; N, 3.1%. EIMS: *m/z* 451 (M^+, 100%). ^1H NMR (300 MHz, $CDCl_3$) δ 1.62, 1.66, 1.82, 1.95 (all 6 H, s, CH_3 groups attached to Cp rings), 3.35 (1 H, s, CH of Cp), 6.73 (1 H, d, J = 16 Hz, C*H*=CH), 6.82 (1 H, d, J = 4 Hz, thienyl CH), 6.99 (1 H, d, J = 16 Hz, CH=C*H*), 7.80 (1 H, d, J = 4 Hz, thienyl CH).

‡ *Crystal data*: for $C_{24}H_{29}FeNO_2S$: M = 451.4, monoclinic, space group $P2_1/n$, a = 14.960(2), b = 9.4435(18), c = 15.639(4) Å, β = 102.200(14)°, U = 2159.4(8) $Å^3$, Z = 4, D_c = 1.388 Mg m^{-3}, μ(Mo-Kα) = 0.815 mm^{-1}, $F(000)$ = 952, T = 173 K, 4930 independent reflections with $2\theta < 55°$. Refinement of 270 parameters converged at final $R1$ = 0.0393, $wR2$ = 0.1155. For $C_{24}H_{29}FeF_6NO_2PS{\cdot}CH_2Cl_2$: M = 681.3, triclinic, space group $P\bar{1}$, a = 10.2058(9), b = 12.1655(11), c = 13.0266(11) Å, α = 73.439(2), β = 68.807(2), γ = 77.176(2)°, U = 1432.6(2) $Å^3$, Z = 2, D_c = 1.579 Mg m^{-3}, μ(Mo-Kα) = 0.906 mm^{-1}, $F(000)$ = 698, T = 173 K, 6498 independent reflections with $2\theta < 55°$. Refinement of 396 parameters converged at final $R1$ = 0.0390, $wR2$ = 0.0968. X-Ray measurements were made using a Bruker SMART CCD area-detector diffractometer; structure solution and refinement was with the SHELXTL program system version 5.1, 1998. CCDC 182/1853. See http://www.rsc.org/suppdata/cc/b0/b008056j/ for crystallographic files in .cif format.

§ To a solution of **1** (0.15 g, 0.33 mmol) in N_2-purged dry MeCN was added ferrocenium hexafluorophosphate (0.107 g, 0.32 mmol) and the mixture was sonicated in an ultrasound cleaning bath for 15 min. After evaporation of the solvent the residue was washed several times with ether until the filtrate was colourless, and was then dried yielding pure [**1**]$^+$(PF_6) (0.18 g, 91%). Found: C, 47.9; H, 5.1; N, 2.3%; $C_{24}H_{29}FeF_6NO_2PS$ requires C, 48.3; H, 4.9; N, 2.4%. FABMS: *m/z* 451 ($M^+ - PF_6$, 100%).

¶ One of the referees has pointed out that the two-level model (ref. 9) cannot be applied with accuracy to ferrocenyl-based systems such as these in which two charge-transfer processes contribute to β (ref. 7). This is true, however because of its simplicity and the lack of readily applicable alternatives it remains in wide use as long as its limitations are understood (ref. 10).

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