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A photoswitchable molecular wire with the dithienylethene (DTE) linker, (dppe)(η^5-C_5Me_5)Fe–C≡C–DTE–C≡C–Fe(η^5-C_5Me_5)(dppe)†

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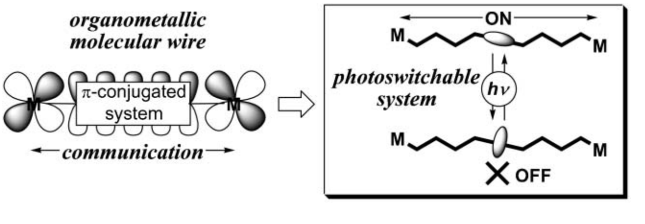
A redox-active diiron complex with the diethynylated dithienylethene (DTE) linker, (dppe)(η^5-C_5Me_5)Fe–C≡C–DTE–C≡C–Fe(η^5-C_5Me_5)(dppe), shows photochromic behaviour, which switches on and off the communication performance between the two metal centres.

Molecular electronics are regarded as one of the promising ways for miniaturization of electronic circuits leading to highly integrated electronic systems.[1,2] In order to build up a molecular circuit many molecular components such as wires, switches and transistors are needed to be developed and combined. As a result of extensive studies, various types of molecular wires have been developed so far. In particular, organometallic molecular wires consisting of a π-conjugated system bridging the redox active metal centres (*e.g.* polyynediyldimetal complexes, M–(C≡C)$_n$–M) turn out to be highly efficient (Scheme 1).[3–5] Although molecular switching systems have also been studied to a considerable extent,[6] examples of switching of the conducting and non-conducting states of molecular wires by stimuli are still rare. Herein we report a photoswitchable molecular wire containing the photochromic dithienylethene (DTE) unit;[7] the communication between the metal centres can be switched on and off by UV/visible light irradiation.



Scheme 1

The diiron complex **2** consisting of the diethynylated DTE spacer and the redox active Fe(η^5-C_5Me_5)(dppe) termini (abbreviated as ***Fe*** throughout this paper) was prepared by reaction of the corresponding terminal diacetylene **1** with ***Fe***Cl/KPF_6 in a THF–MeOH solvent mixture followed by KOBu^t-treatment, according to the conventional synthetic procedure *via* the cationic vinylidene intermediate established by Paul and Lapinte[4] (Scheme 2). Incorporation of the ***Fe*** fragments into the red product **2** and its symmetrical structure were supported by the NMR features (*e.g.* single resonances for the thienyl parts and the ancillary η^5-C_5Me_5 and dppe ligands),‡ and the open-structure was confirmed by (1) the spectroscopic features for the DTE moiety similar to those of the precursor **1**, (2) the lack of a visible absorption band characteristic of the closed form,[7] and (3) X-ray crystallography (Fig. 1).§ The acetylenic parts attached to the DTE core are σ-bonded to the iron fragments of the three-legged piano-stool structure, and the bridging π-conjugated system spans the two iron centres separated by 15.22 Å. The structural parameters for the ***Fe*** and DTE parts are comparable to those of the previously reported relevant compounds.[4,7] The two thiophene rings are arranged in an antiparallel fashion suitable for the photochemical ring closing process.[7]

When a THF solution of **2** was irradiated by a UV lamp,¶ a visible absorption band appeared at 774 nm, and the mixture reached a photostationary state after *ca.* 1 h (see the bottom-left figure in Scheme 2). On the basis of (1) the appearance of the visible band and (2) the deshielded ^{1}H NMR signals for the methyl groups attached to the thiophene rings characteristic of the closed form (δ_H(Me) 2.42 (*cf.* δ_H(Me) 1.94 (**2**)),[7] it was concluded that the UV-irradiation caused the ring closure of **2** giving the closed green isomer **3**,‡ which was isolated by fractional recrystallization. The isomer ratio at the UV-photostationary state was determined to be **2** : **3** = 1 : 3 on the basis of the intensity ratio of the Me signals (^{1}H NMR) for the two isomers. The attachment of the ***Fe*** groups improved the efficiency of the photochromic process compared to the starting alkyne **1**, which was left unchanged even after prolonged UV irradiation. On the other hand, irradiation of an equilibrated mixture of the isomers with visible light¶ caused a significant decrease of the visible absorption at 774 nm after *ca.* 3 h (7% compared to the UV-photostationary state) to regenerate the open isomer **2**, and thus the diiron-DTE complex **2** turned out to undergo photochromic behaviour *via* the reversible photochemical ring closure-opening processes (**2** ↔ **3**). The cycle can be repeated without noticeable deterioration.

The performance of the two isomeric forms as molecular wire was evaluated by the electrochemical method.[4]‖ An efficient molecular wire with two redox active termini shows two separated reversible redox waves, and from the separation of the two redox processes (ΔE) the comproportionation constant for the mixed valence species (K_C) can be obtained. K_C, regarded as a measure for the performance of molecular wires, is an equilibrium constant for the mixed valence species with respect to the two non-mixed valence species (in the present case, Fe(II)–Fe(II) + Fe(III)–Fe(III) ↔ 2 Fe(II)–Fe(III)). In the 1e-oxidized form of an efficient molecular wire the unpaired electron delocalizes widely over the π-conjugated system extended to the metal termini to give a larger

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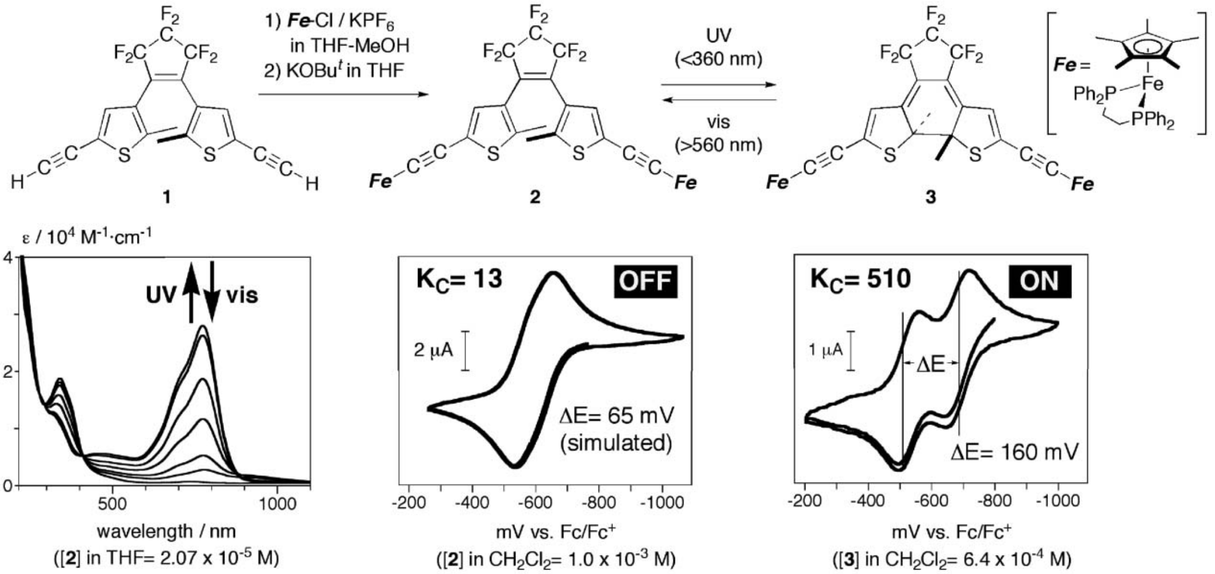
† Electronic supplementary information (ESI) available: Details of the X-ray crystallography of **2**·CH_2Cl_2 and DPV traces for **2** and **3**. See DOI: 10.1039/b614748h



Scheme 2

K_C value. The open form **2** showed a broad redox wave (Scheme 2) and, on the basis of the result of simulation, the separation of the two redox processes was estimated to be at most 65 mV, in other words, K_C is less than 13. Thus the CV measurement of the open isomer **2** indicated virtually no communication between the two iron centres. On the other hand, the closed isomer **3** exhibited two clearly separated reversible redox waves with ΔE = 160 mV (Scheme 2), which were also confirmed by a DPV measurement (included in ESI†) as well as simulation. The possibility that one of the two redox waves of **3** might be due to the organic bridging part can be eliminated by comparison with the closed isomer of the related thiophene-fused DTE compound reported by Irie and co-workers.[8] The redox waves observed for this compound ($E_{\mathrm{oxid}} >$ +0.28 V) appear in the region much more positive than those for **3**, and the substantial difference (>0.7 V) clearly indicates that the redox processes of **3** shown in Scheme 2 are metal-based. From the ΔE value, the K_C value for the closed isomer **3** with a 12 carbon atom bridge was determined to be 510, being significantly larger than those of the open form **2** and related diiron complexes containing a long carbon atom bridge.[4] Because it is known that the two isomers can be interconverted with least motions,[7] the changes of the reorganization associated with the photochromic processes and the solvation should be minimal for the present case and, therefore, the change of the K_C values should reflect the performance as molecular wire of the two isomers.

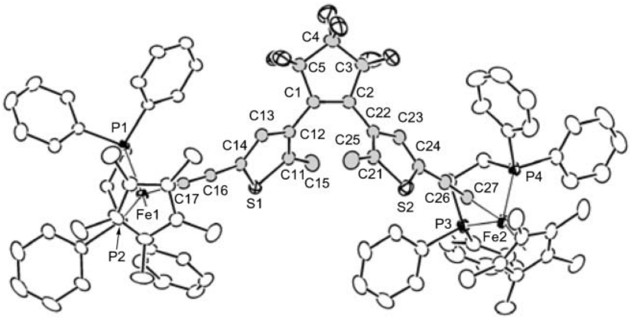
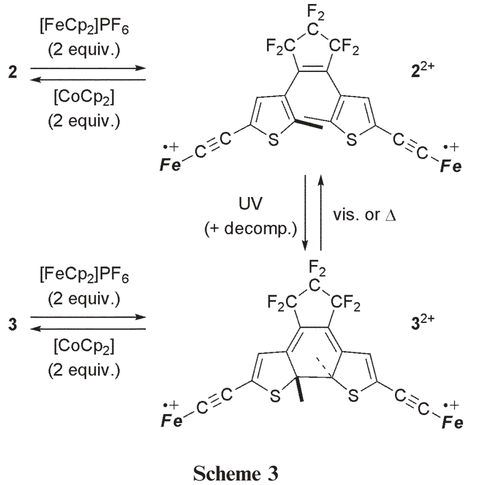


Fig. 1 An ORTEP plot for **2** drawn with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å): Fe1–C17 1.896(4), Fe2–C27 1.877(4), S1–C11 1.726(4), S1–C14 1.742(4), S2–C21 1.739(5), S2–C24 1.747(5), C1–C2 1.354(5), C1–C12 1.474(5), C2–C22 1.471(6), C11–C12 1.380(6), C11–C15 1.497(6), C12–C13 1.425(6), C13–C14 1.379(6), C14–C16 1.424(5), C16–C17 1.210(5), C21–C22 1.372(7), C21–C25 1.511(7), C22–C23 1.433(6), C23–C24 1.364(6), C24–C26 1.416(6), C26–C27 1.227(6), C11···C21 3.644(6).

It is also found that (1) 2e-oxidized species $\mathbf{2}^{2+}(\mathrm{PF_6}^-)_2$ and $\mathbf{3}^{2+}(\mathrm{PF_6}^-)_2$ exhibit photochromic behaviour and (2) $\mathbf{3}^{2+}(\mathrm{PF_6}^-)_2$ undergoes thermal ring opening (Scheme 3), while redox-promoted chromic behaviour of DTE derivatives has precedents.[9]

In conclusion, we report that the communication property of the organometallic molecular wire with the photochromic DTE linker (**2**/**3**) can be switched on and off in a reversible manner by UV and visible light irradiation: **2** (OFF) ↔ **3** (ON). The open form **2** is virtually an insulator (K_C < 13), and the ratio of the communication performance of the ON and OFF states, K_C(ON; **3**)/K_C(OFF; **2**), is as large as 39. The ON/OFF ratio is much larger than previously reported wire-like compounds,[10] while performance of



Scheme 3

the chromic behaviour is yet to be improved. The large difference in the K_C values for the two isomeric forms should be ascribed to the different conjugation patterns of the bridging parts. The open form **2** contains cross-conjugation at the thiophene–perfluorocyclopentene junctions, whereas the closed form **3** contains the fully π-conjugated system, through which the two iron centres can communicate effectively, as is also indicated by the significant lower energy shift of the ν(C≡C) vibration (2039 cm^{-1} (**2**) → 1986 cm^{-1} (**3**)) as well as the shift of the first redox potential (−580 mV (**2**) → −671 mV (**3**)).

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Notes and references

‡ *Selected spectroscopic data*: for **2**: δ_P (in C_6D_6) 92.5, δ_H (in C_6D_6) 8.05–7.85, 7.40–7.00 (40H, m, Ph), 6.69 (2H, s, thiophene), 2.70–2.40 (m, PCH_2), 1.90–1.60 (m, PCH_2), 1.94 (6H, s, Me in C_4HS–Me), 1.46 (30H, s, η^5-C_5Me_5), IR (KBr) ν(C≡C) 2039 cm^{-1}, λ_{max}/nm ($\varepsilon/\text{M}^{-1}\text{ cm}^{-1}$ in THF) 364 (1.85×10^4). For **3**: δ_P (in C_6D_6) 91.3, δ_H (in C_6D_6) 8.10–7.50, 7.40–7.00 (40H, m, Ph), 6.15 (2H, s, thiophene), 2.70–2.40 (m, PCH_2), 2.42 (6H, s, Me in C_4HS–Me), 1.90–1.60 (m, PCH_2), 1.39 (30H, s, η^5-C_5Me_5) IR (KBr) ν(C≡C) 1986 cm^{-1}, λ_{max}/nm ($\varepsilon/\text{M}^{-1}\text{cm}^{-1}$) 336 ($1.70 \times 10^4$), 470 ($7.98 \times 10^3$), 774 ($4.37 \times 10^4$).

§ *Crystallographic data* for $\mathbf{2}\cdot CH_2Cl_2$ (at −60 °C): $C_{92}H_{86}F_6P_4S_2Cl_2Fe_2$, $M_r = 1678.3$, monoclinic, space group $P2_1/n$, $a = 42.28(2)$, $b = 16.460(8)$, $c = 12.019(5)$ Å, $\beta = 90.39(2)°$, $V = 8364(6)$ Å^3, $Z = 4$, $D_c = 1.333$ g cm^{-3}, $R1 = 0.0817$ (refined on F^2) for 13 064 data ($I > 2\sigma(I)$) and 985 parameters. CCDC 623567. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614748h

¶ UV and visible light irradiations were performed with an Ushio high-pressure mercury lamp (UM-452; $\lambda < 360$ nm with a U-360 cutoff filter) and a Soma Kogaku Xe lamp (150 W; $\lambda > 560$ nm with an O-56 cut-off filter), respectively. UV-vis spectra shown in Scheme 2 were recorded after UV irradiation for 0, 2, 4, 24, 40, 56 and 80 min.

‖ Electrochemical measurements (CV and DPV) were made on a BAS 100B/W analyzer and performed with a Pt electrode for CH_2Cl_2 solutions of the samples ($\sim 1 \times 10^{-3}$ M) in the presence of an electrolyte (Bu_4NPF_6; 0.1 M) at r.t. under an inert atmosphere. The scan rates were 100 mV s^{-1} (CV) and 20 mV s^{-1} (DPV). After the measurement, ferrocene (Fc) was added to the mixture and the potentials were calibrated with respect to the Fc/Fc$^+$ redox couple. *Data*: for **2**: $E_{1/2}{}^1 = -580$ mV, $E_{1/2}{}^2 = -515$ mV; for **3**: $E_{1/2}{}^1 = -671$ mV, $E_{1/2}{}^2 = -511$ mV.

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9 Treatment of **2** and **3** with 2 equivalents of $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ afforded the corresponding 2e-oxidized dicationic species, $\mathbf{2}^{2+}(PF_6{}^-)_2$ (green powder) and $\mathbf{3}^{2+}(PF_6{}^-)_2$ (dark purple powder), respectively. $\mathbf{3}^{2+}(PF_6{}^-)_2$ was converted into $\mathbf{2}^{2+}(PF_6{}^-)_2$ over the course of 6 h as revealed by ^{31}P NMR measurements of samples of $\mathbf{3}^{2+}(PF_6{}^-)_2$ taken at appropriate time intervals and reduced by $[Co(\eta^5\text{-}C_5H_5)_2]$. The interconversion between $\mathbf{2}^{2+}(PF_6{}^-)_2$ and $\mathbf{3}^{2+}(PF_6{}^-)_2$ was also promoted by UV- and visible light-irradiation in a manner similar to the neutral species and it is noted (1) the photochemical conversion of $\mathbf{3}^{2+}(PF_6{}^-)_2$ into $\mathbf{2}^{2+}(PF_6{}^-)_2$ was faster than that of the thermal process and (2) UV irradiation of $\mathbf{2}^{2+}(PF_6{}^-)_2$ gave $\mathbf{3}^{2+}(PF_6{}^-)_2$ together with unidentified decomposed products. Furthermore thermal ring opening of 1e-oxidized species $\mathbf{3}^{+}(PF_6{}^-)$ *in situ* generated by addition of 1 equivalent of $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ turned out to be sluggish compared to $\mathbf{3}^{2+}(PF_6{}^-)_2$. For similar redox-promoted chromic behaviour of organic DTE derivatives, see ref. 8. See also: T. Koshido, T. Kawai and K. Yoshino, *J. Phys. Chem.*, 1995, **99**, 6110; A. Peters and N. R. Branda, *J. Am. Chem. Soc.*, 2003, **125**, 3404; X.-H. Zhou, F.-S. Zhang, P. Yuan, F. Sun, S.-Z. Pu, F.-Q. Zhao and C.-H. Tung, *Chem. Lett.*, 2004, **33**, 1006; A. Peters and N. R. Branda, *Chem. Commun.*, 2003, 954.

10 For the related diruthenium complex with the same linker, which was σ-bonded to the phenyl group in the cyclometalated $Ru(bipy)_2(pp)$ fragments (pp = phenylpyridine),[6a] $[(bipy)_2Ru(pp\text{–}C{\equiv}C\text{–}DTE\text{–}C{\equiv}C\text{–}pp)Ru(bipy)_2](PF_6)_2$, the switching could not be detected by the electrochemical method [K_C(closed)/K_C(open) = 12/11 = 1.1] but by the electronic coupling (V_{ab} = 0.025 eV) obtained by analysis of the intervalence charge transfer band.