Remarkable switching behavior of bimodally stimuli-responsive photochromic dithienylethenes with redox-active organometallic attachments†

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Organometallic dithienylethenes with the redox-active $M(\eta^5\text{-}C_5H_5)L_2$-type attachments (M = Fe, Ru; L = CO, PR_3) exhibit bimodally stimuli-responsive, photo- and pseudo-electrochromic behavior with the remarkable switching factors [K_C(closed)/K_C(open)] up to 5.4×10^3.

Switching functions play key roles in various aspects of molecular devices such as molecular electronics and molecular machines,[1] and chromism is regarded as an effective switching mechanism.[2] Application of stimuli (light, heat, pH *etc.*) to chromic compounds brings about changes of their geometrical and electronic structures, which eventually affect their physicochemical properties as typically indicated by the color change. Combination of a chromic system with other functional systems should lead to development of multimodally stimuli-responsive systems, which would be applied to sophisticated molecular devices such as multimodal switches and logic systems (Scheme 1).

Dithienylethene derivatives (DTE; Scheme 1), extensively studied by Irie, are recognized as highly efficient organic photochromic compounds with respect to such features as fast response, fatigue resistance and facile control of the color,[2] and we previously reported the photoswitchable DTE-based molecular wire **4** with the C≡C linkers [X = C≡C–Fe(η^5-C_5Me_5)(dppe)].[3] Herein we disclose DTE derivatives with the directly σ-bonded, redox-active organometallic $M(\eta^5$-$C_5H_4R)L_2$ attachments (**1–3**). It has been found that the DTE complexes exhibit not only bimodal switching behavior triggered by photo- and electrochemical stimuli but also remarkable switching performance much superior to that of **4**.

The organo–iron and –ruthenium DTE derivatives with the $M(\eta^5$-$C_5H_4R)(CO)_2$ fragments **1** (M/R = Fe/H (**1^Fe**), Ru/H (**1^Ru**)) were prepared by treatment of 1,2-di(5-lithio-2-methyl-thien-3-yl)perfluorocyclopentene with X–M(η^5-$C_5H_4R)(CO)_2$ [R = H (Cp), Me (Cp′)]. Subsequent photochemical ligand substitution reactions afforded the phosphine-substituted derivatives with the MCp(CO)(PPh₃) fragments **2** (M = Fe (**2^Fe**), Ru (**2^Ru**)) and the FeCp′(dppe) fragments **3′^Fe** (the Cp′ ligand
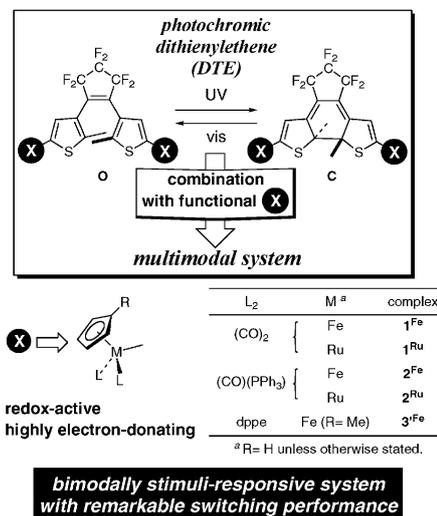
Scheme 1 Multimodally stimuli-responsive system.

was used to avoid the solubility problem of the Cp derivative).‡ The obtained yellow (Fe) and colorless DTE complexes (Ru) showed no intense visible absorption, and their spectroscopic data§ revealed attachment of the metal fragments as well as the symmetrical structures. It is notable for the four complexes characterized crystallographically§ (**1^Fe**, **1^Ru**, **2^Fe** and **3′^Fe**) that (i) the two thiophene rings are arranged in anti-parallel fashions suitable for the photochemical ring closure and (ii) the structural features associated with the DTE parts, including the distance between the 2- and 2′-thienyl carbon atoms to be connected upon photochemical ring closure, are similar to each other and comparable to those of organic derivatives. Thus the metal fragments even bulkier than the DTE cores do not affect the structural features of the DTE parts significantly.

UV irradiation of the DTE complexes caused ring closure to form the purple- or deep-blue-colored closed isomers **C** showing the absorption maxima in the visible region (550–600 nm). But the efficiency turned out to be dependent on the metal and ancillary ligands (Scheme 2). In general, the ruthenium complexes cyclized more efficiently than the iron derivatives, and introduction of the phosphine ligands retarded the cyclization. The Fe-dppe derivative **3′^Fe** did not undergo the photochemical cyclization at all.

The closed isomers **C** were readily characterized on the basis of (i) the appearance of the visible absorptions and/or (ii) the

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† Electronic supplementary information (ESI) available: Typical preparative procedures, spectral data and crystallographic results. CCDC reference numbers 689366–689369. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b809318k

Scheme 2 Chromic behavior of the DTE complexes. For the ORTEP drawings of 2^{Fe} and $2^{Fe}C'^{2+}$, phenyl groups are omitted for clarity.

complex	photochemical conv. to **C** (%) [a]	λ_{max}(**C**) / nm [b]	electrochemical conv. to **C'$^{2+}$** (%)	K_C(**O**) [c]	K_C(**C**) [c]	$E_{1/2}^1$(**C**) / mV [d]	ΔE(**C**) / mV [c,d]	$\dfrac{K_C(\mathbf{C})}{K_C(\mathbf{O})}$ = SF [e]
1^{Fe}	45 % [f]	580	quant. [g]	~4	4.5×10^3	-78	216	1.1×10^3
1^{Ru}	60 %	552	quant. [g]	6.2	7.2×10^3	-60	228	1.2×10^3
2^{Fe}	~0 % [h]	590 [h]	quant. [g]	~4	1.6×10^4	-464	248	4.0×10^3
2^{Ru}	83 %	578	quant. [g]	~4	2.2×10^4	-430	256	5.4×10^3
$3'^{Fe}$	0 %	[i]	quant. [j]	85	7.5×10^4	-948	288	8.8×10^2

[a] the content of **C** at the photostationary state (UV irrad.). observed in C_6D_6 unless otherwise stated. [b] observed in toluene. [c] determined on the basis of the DPV data (anodic waves). [d] observed in CH_2Cl_2. [e] switching factor. [f] in acetone-d_6. [g] estimated on the basis of the CV data (see text). [h] The ring closure was not detected by NMR but by UV-vis. [i] not detected. [j] chemical oxidation with $[FeCp_2]PF_6$ (2 equiv.) (see text and note ¶).

^{1}H NMR changes.§ Furthermore $1^{Ru}C$ was characterized by X-ray crystallography (Scheme 2).§ The two thiophene rings in 1^{Ru} separated by 3.574(8) Å came closer to the distance of 1.543(7) Å ($1^{Ru}C$) within the range of σ-bonding interaction. The closed isomers **C** reverted to the open isomers **O** quantitatively upon visible-light irradiation.

The extent of the interaction between the two metal termini in the two isomeric forms was examined by an electrochemical method, *i.e.* in terms of K_C (conproportionation constant),[4] and then we encountered with a chemical process induced by oxidation. As typical examples, CV traces for 2^{Fe}, 2^{Ru} and $3'^{Fe}$ are shown in Fig. 1. For 2^{Ru} (trace c), a 2e-oxidation wave was observed at 273 mV (*vs.* $[FeCp_2]/[FeCp_2]^+$) but the corresponding reduction wave was not detected. Instead, two consecutive reduction waves were observed at −217 and −495 mV. Upon a subsequent anodic scan, two oxidation waves corresponding to the two consecutive reduction processes were detected. The two redox processes observed at $E_{1/2}$ = −430 and −174 mV turned out to be superimposable on those of the closed isomer $2^{Ru}C$ formed by the UV-irradiation of 2^{Ru}. These results are best interpreted in terms of oxidation-induced cyclization (Scheme 2). Because no wave was detected during the initial scan of 2^{Ru} in the range of 0––1300 mV (trace c), no species which is redox active in this scan range is present in the beginning. Upon oxidation the open isomer O^{2+} is converted into the closed isomer C'^{2+} spontaneously and quantitatively so as not to show the reduction wave for O^{2+}. Subsequent cathodic sweep causes appearance of the two redox waves for the formed dicationic closed isomer C'^{2+}, which shows CV waves identical to those of the neutral species **C**.

Similar behavior was noted for all other derivatives. It is notable that the Fe-dppe derivative $3'^{Fe}$,¶ which did not
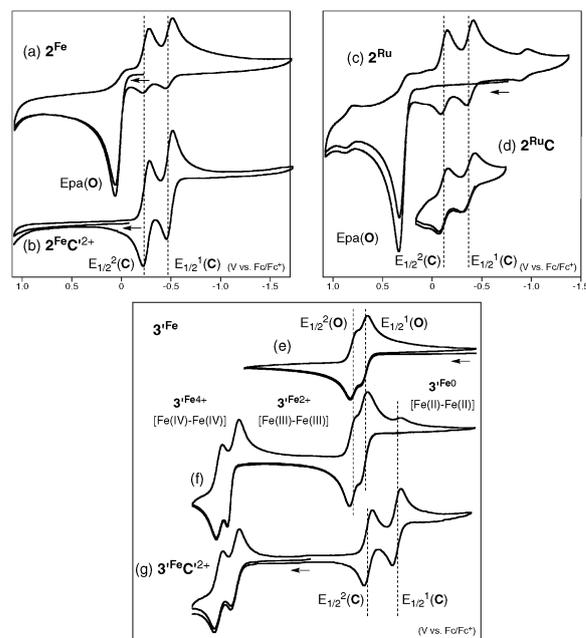
Fig. 1 CV traces for (a) 2^{Fe}, (b) $2^{Fe}C'^{2+}$, (c) 2^{Ru}, (d) a photo-equilibrated mixture of $2^{Ru}O/C$ (scanned only for the range for $2^{Ru}C$), (e) $3'^{Fe}O$ (0.6 ↔ −1.7 V), (f) $3'^{Fe}O$ (1.1 ↔ −1.7 V) and (g) $3'^{Fe}C'^{2+}$. ([complex] = ~1×10^{-3} M, [NBu$_4$PF$_6$] = 0.1 M, observed in CH_2Cl_2.)

undergo the photochemical ring closure at all, cyclized quantitatively upon oxidation. Furthermore, in the cases of 2^{Fe} and $3'^{Fe}$, the deep-green, dicationic species $[2^{Fe}C'^{2+}](PF_6)_2$ and $[3'^{Fe}C'^{2+}](PF_6)_2$ were isolated upon chemical oxidation with $[FeCp_2]PF_6$ (2 equiv.). To be noted is the diamagnetism of C'^{2+} resulting from coupling of the radical centers. X-ray crystallography of $[2^{Fe}C'^{2+}](PF_6)_2$§ revealed (i) C–C bond formation between the two thiophene rings at the 2- and 2'-positions (C–C: 1.518(9) Å), (ii) the double bond character of the Fe=C moieties (1.852(5), 1.871(6) Å; cf. 1.979(4) Å (2^{Fe})) and (iii) the change of the pattern of the bond alternation in accord with the canonical form C'^{2+} depicted in Scheme 2. The carbene–metal substructure is also supported by the highly deshielded ^{13}C NMR signal for $[3'^{Fe}C'^{2+}](PF_6)_2$ located at δ_C 281.7 (t, $J_{P–C}$ = 26 Hz). The isolated dications $2^{Fe}C^{2+}$ and $3'^{Fe}C'^{2+}$ showed two redox waves identical to those observed for the closed components generated by oxidation-induced cyclization of the open isomers 2^{Fe} and $3'^{Fe}$ respectively (Fig. 1; traces b and g),§ evidencing occurrence of the ring closure of 2^{Fe} and $3'^{Fe}$ upon 2e-oxidation.¶ Because the closed species C'^{2+} are so stable even under reduction or irradiation conditions as not to undergo cycloreversion, the closed structure otherwise prone to open even by weak daylight can be firmly "locked" by the electrochemical method and thus the present system is regarded as a pseudo-electrochromic system.

The electrochemical ring closure can be interpreted by taking into account coupling on an alternative resonance structure O'^{2+} with two radical centers at the tertiary 2- and 2'-thienyl carbon atoms (Scheme 2).[5]

The K_C values were then determined on the basis of the DPV data (Scheme 2). The K_C values for the open isomers O are very small, in some cases, being close to the theoretical minimum for a statistical mixture (4). On the other hand, the closed isomers C show two well-separated reversible redox waves as can be seen from Fig. 1. The $K_C(C)$ values increase significantly, as the ancillary ligands (L_2) become more electron-donating (cf. $E_{1/2}^1(C)$: the first oxidation potentials of the closed isomers C). The Ru and phosphine derivatives show better performance compared to the Fe and CO derivatives respectively; in particular, the K_C value for the Fe-dppe derivative $3'^{Fe}C$ turns out to be as large as 7.5×10^4.

Furthermore the extent of the communication between the two metal centers can be switched by factors of up to 5.4×10^3 ($= K_C(C)/K_C(O)$) by the photo- and electrochemical stimuli. Organic derivatives with electron-donating substituents showed similar bimodal behavior but the oxidized species were not always satisfactorily characterized as in the present work and the switching function was not studied in detail.[6]

In conclusion, the present study reveals that (i) the ring opening-closing cycles of the organometallic DTE derivatives $1–3$ can be achieved by a combination of the photochemical and electrochemical protocols and (ii) the K_C values for the closed isomers ($K_C(C)$) and the switching factors ($SF = K_C(C)/K_C(O)$) are even remarkably larger than those for the derivative 4 with the C≡C linkers, which was regarded as the molecular switch with the highest performance ($K_C(C) = 5.1 \times 10^2$; $SF = 39$) when it was reported by us.[3] The $K_C(C)$ and SF values for the compounds reported herein are magnificently larger than those

of 4 by factors of ~ 150 ($3'^{Fe}$: $K_C(C)$) and ~ 140 (2^{Ru}: SF) respectively. The excellent performance should result from (i) the carbon linkage of $1–3$ (8 C atoms) being shorter than that of 4 (12 C atoms) and (ii) the oxidized form C'^{2+} being strongly stabilized by the electron-donating metal fragments through contribution of the carbene structures.

Notes and references

‡ The Ru-analogue 3^{Ru} could not be obtained by the analogous method.
§ For spectroscopic and crystallographic data, see ESI.† CCDC 689366 (1^{Ru}), CCDC 689367 ($1^{Ru}C$), CCDC 689368 (2^{Fe}), CCDC 689369 ($[2^{Fe}C'^{2+}](PF_6)_2$).† The crystallographic results for 1^{Fe} and $3'^{Fe}$ will be reported in a forthcoming full paper.
¶ The behavior of $3'^{Fe}$ was slightly different. The CV scan in the range of -1.7–0.6 V showed completely reversible two consecutive 1e-redox processes around 0.5 V ($3'^{Fe} \leftrightarrow 3'^{Fe2+}$) with no indication of cyclization (Fig. 1, trace e). A further anodic scan (trace f), however, revealed another 2e-redox waves around 0.8 V corresponding to $3'^{Fe2+} \leftrightarrow 3'^{Fe4+}$ and, upon a subsequent cathodic scan, a small peak identical to the cathodic peak of the first redox process of $3'^{Fe}C^{2+}$ (trace g) was detected, indicating partial ring closure upon 4e-oxidation. Although $[FeCp_2]^+$ is not strong enough for the 4e-oxidation of $3'^{Fe}$ as judged by the redox potentials, attempted oxidation with $[FeCp_2]PF_6$ (2 equiv.) led to quantitative formation of $[3'^{Fe}C^{2+}](PF_6)_2$. The observed results may be interpreted in terms of the rate of the ring closing process of $3'^{Fe2+}$ being slower than the CV time scale but substantial with respect to the time scale of preparative experiments. Accordingly, in contrast to the CO complexes 1 and 2, the electron-donating dppe ligand in 3 can stabilize the electron-deficient dicationic intermediate O^{2+} effectively so that the radical coupling on it occurs at a rate slower than the CV time scale.

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