Experimental Section

Conditions for ^{1}H NMR data: 250 MHz, CD_3CN, 25 °C, TMS; for ^{13}C NMR data: 63 MHz, CD_3CN, 25 °C, TMS.

G0 · 6 PF_6^-: ^{1}H NMR: $\delta = 8.92$ (d, $^3J(H,H) = 7.0$ Hz, 12H), 8.39 (d, $^3J(H,H) = 7.0$ Hz, 12H), 7.66(s, 3H), 5.83 (s, 6H), 4.68 (q, $^3J(H,H) = 7.3$ Hz, 6H), 1.65 (t, $^3J(H,H) = 7.3$ Hz, 9H); ^{13}C NMR: $\delta = 151.1$, 150.1, 146.2, 145.8, 135.3, 132.3, 127.8, 127.6, 64.0, 58.2, 16.0; elemental analysis calcd for $C_{45}H_{48}N_6P_6F_{36} \cdot 1H_2O$: C 34.63, H 3.23, N 5.39; found C 34.85, H 3.58, N 5.36.

G1 · 18 PF_6^-: ^{1}H NMR: $\delta = 8.93 - 8.90$ (m, 36H), 8.42 – 8.36 (m, 36H), 7.66(s, 9H), 7.64(s, 3H), 5.83 (s, 24H), 4.67(q, $^3J(H,H) = 7.3$ Hz, 12H), 1.65 (t, $^3J(H,H) = 7.3$ Hz, 18H); ^{13}C NMR: $\delta = 151.1$, 151.0, 150.1, 146.3, 146.2, 145.8, 135.3, 132.3, 132.2, 127.9, 127.8, 127.6, 64.0, 58.2, 16.0; elemental analysis calcd for $C_{138}H_{138}N_{18}P_{18}F_{108} \cdot 3H_2O$: C 35.18, H 3.08, N 5.35; found C 35.13, H 3.21, N 5.32.

G2 · 42 PF_6^-: ^{1}H NMR: $\delta = 8.93 - 8.90$ (m, 84H), 8.41 – 8.39 (m, 84H), 7.66 (br.s, 30H), 5.83 (s, 60H), 4.67(q, $^3J(H,H) = 7.3$ Hz, 24H), 1.64 (t, $^3J(H,H) = 7.2$ Hz, 36H); ^{13}C NMR: $\delta = 151.1$, 151.0, 150.1, 146.2, 145.7, 135.3, 135.2, 132.2, 132.1, 127.9, 127.8, 127.6, 64.0, 58.1, 15.9; elemental analysis calcd for $C_{324}H_{318}N_{42}P_{42}F_{252}* \cdot 5H_2O$: C 35.45, H 3.01, N 5.36; found C 35.23, H 3.01, N 5.33.

G3 · 90 PF_6^-: ^{1}H NMR: $\delta = 8.93 - 8.90$ (m, 180H), 8.42 – 8.39 (m, 180H), 7.67 (br.s, 66H), 5.83 (s, 132H), 4.67(q, $^3J(H,H) = 7.3$ Hz, 48H), 1.64 (t, $^3J(H,H) = 7.2$ Hz, 72H); ^{13}C NMR: $\delta = 151.1$, 151.0, 146.2, 145.7, 135.3, 135.2, 132.2, 127.9, 127.8, 127.6, 64.0, 58.1, 15.9; elemental analysis calcd for $C_{696}H_{678}N_{90}P_{90}F_{540} \cdot 23H_2O$: C 35.18, H 3.07, N 5.30; found C 35.02, H 3.18, N 5.23.

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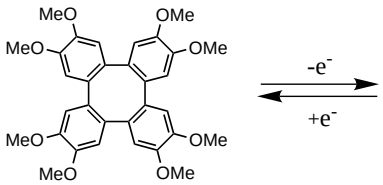
A Redox-Controlled Molecular Switch Based on the Reversible C–C Bond Formation in Octamethoxytetraphenylene**

Rajendra Rathore,* Pierre Le Magueres, Sergey V. Lindeman, and Jay K. Kochi*

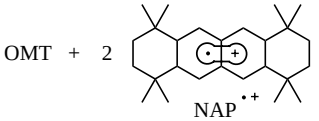
The design and synthesis of organic derivatives for molecular devices such as sensors, switches, electrical conductors, ferromagnets, electronic circuits, and nonlinear optical materials has been actively pursued in recent years. [1–3] Especially noteworthy are organic materials that exhibit changes in physical properties such as magnetism, conductivity, and optical response when triggered by external stimuli such as heat, light, or electrical potentials.[4] One of the approaches in designing such materials is to exploit electronic interactions in macrocyclic or supramolecular assemblies consisting of multiple redox-active components.[5] We now introduce a methoxylated tetraphenylene derivative as a potential molecular switch based on its dramatic color change upon the application of an electrical potential.

Octamethoxytetraphenylene[6] (OMT) was prepared from a readily available 1,2-dimethoxybenzene derivative (veratrole) in excellent yield using standard synthetic procedures (see Experimental Section). This saddle-shaped macrocycle with cofacial phenylene groups (established by X-ray crystallography) shows a striking electrochromic behavior with a color change from yellow to red, which is completely reversible over multiple redox cycles [Eq. (1)].[7]



OMT, yellow "dark red" (1)

The dramatic color change upon electrooxidation of OMT can also be achieved by a variety of chemical oxidants such as aromatic radical cations,[8] nitrosonium cation,[9] or triethyloxonium hexachloroantimonate.[10] For example, a blue solution of a octahydronaphthacene radical cation[11] ($NAP^{\bullet+}$) turns dark red immediately upon the addition of neutral OMT [Eq. (2)]. In order to establish the stoichiometry of this



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redox reaction, a dichloromethane solution of $NAP^{\bullet+}$ ($\lambda_{max} = 672$ nm, $\varepsilon = 9300\,M^{-1}cm^{-1}$) was treated with incremental amounts of neutral OMT and the resulting UV/Vis spectral changes are shown in Figure 1. The three well-defined isosbestic points ($\lambda_{max} = 350$, 420, and 610 nm) clearly establish the concomitant reduction of $NAP^{\bullet+}$ and oxidation of neutral OMT. That the final spectrum remains unchanged upon the addition of OMT beyond 0.5 equivalents establishes the redox stoichiometry as shown in Equation (2).[12]

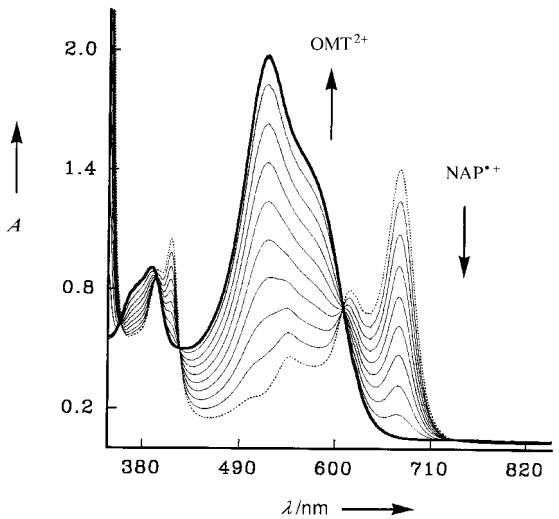

Figure 1. Spectral changes attendant upon an incremental addition of neutral OMT (2.2×10^{-4} mmol) to a 0.15 mM solution of $NAP^{\bullet+}$ (4.5×10^{-4} mmol) in dichloromethane at 25 °C.

The resulting dark-red product is thus identified as octamethoxytetraphenylene dication (OMT^{2+}) with an intense absorption band at $\lambda_{max} = 521$ nm and a high molar absorptivity of $\varepsilon_{521} = 31\,000\,M^{-1}cm^{-1}$ (in dichloromethane). Similarly, the simple dissolution of a 2:1 mixture of the well-known one-electron oxidant $NO^+SbCl_6^-$ and neutral OMT in dichloromethane at $-20\,^\circ C$ immediately results in a red solution with an identical absorption spectrum; and the quantitative formation of OMT^{2+} according to Equation (3) is determined spectrophotometrically.[13]

$$OMT + 2\,NO^+ \longrightarrow OMT^{2+} + 2\,NO \qquad (3)$$

It is important to note that the transformation of OMT to OMT^{2+} is initiated by well-known one-electron oxidants [see Eq. (2) and (3)]. As such, the oxidation of OMT to its dication can also be achieved by photoinduced electron transfer (PET) using tetrachlorobenzoquinone (chloranil; $E^0_{red} = 0.02$ V vs. SCE) as the electron acceptor. For example, the pale-yellow mixture of neutral OMT and chloranil in dichloromethane in the presence of trifluoroacetic acid (ca. 1%) is stable in the dark for prolonged periods; however, upon a brief exposure to a mercury lamp it immediately develops the characteristic red color of the dication.[14] Note that the use of strongly oxidizing 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; $E^0_{red} = 0.60$ V vs. SCE) instead of chloranil, under otherwise identical conditions, affords the dication OMT^{2+} even in the dark in excellent yield.[15]

The intensely colored OMT^{2+} dication is highly stable in dichloromethane at ambient temperature and the dark-red single crystals can be readily isolated after precipitated by the slow diffusion of toluene into the solution at $-23\,^\circ C$. X-ray crystallography establishes the hexacyclic structure of the novel dicationic OMT^{2+} (Figure 2). Comparison of the

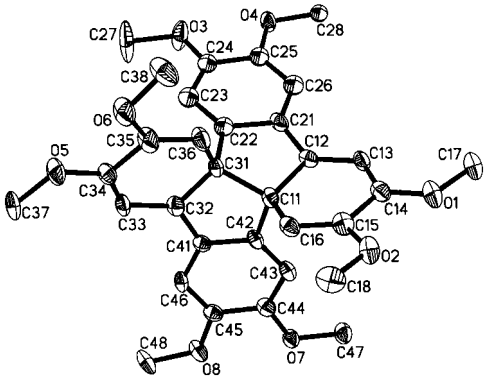

Figure 2. ORTEP diagram showing the fused hexacyclic structure of OMT^{2+} (hydrogen atoms and the $SbCl_6^-$ anion are omitted for clarity).

structures of neutral and dicationic OMT reveals the change from the saddle-shaped eight-membered ring in OMT to the *cis*-fused bicyclo[3.3.0]octane framework of OMT^{2+}. The two-electron oxidation of OMT leads to the spontaneous formation of a C–C bond between the *ipso*-carbons C1 and C5 of opposite phenylene rings (C1–C5 = 1.56 Å, Figure 3[16]). The C–C bond formation is accompanied by (1) the sp^2 to sp^3 rehybridization of C1 and C5[17] and (2) the formation of a pair of cationic cyclohexadienyl rings which show considerable quinoidal distortion.[18]

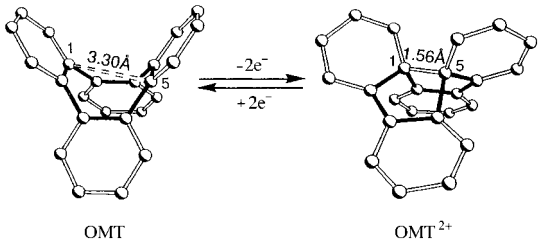

Figure 3. Structural changes in the oxidation of OMT to OMT^{2+} with concomitant bond formation between C1 and C5 of the OMT ring. Atoms C1 and C5 are represented in Figure 2 as C11 and C31, respectively.

The reversibility of the redox-controlled structural change (Figure 3) is established by voltammetric analysis. Thus, oxidation of OMT shows an irreversible cyclic voltammogram (Figure 4a) in which the anodic peak at $E_{ox} = 1.25$ V (vs. SCE) corresponds to the oxidation of OMT to OMT^{2+}, whereas the cathodic peak at $E_{red} = 0.25$ V (vs. SCE) on the return scan represents the reduction of OMT^{2+} to OMT.[7] Such an assignment is further verified by the reduction of dark-red OMT^{2+} (prepared from two equivalents of $NO^+PF_6^-$) which leads to an irreversible voltammogram with identical peak potentials as shown in Figure 4b. The cyclic voltammograms

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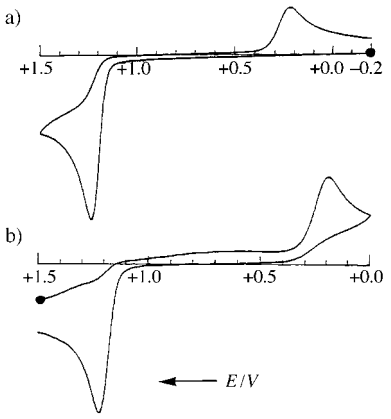
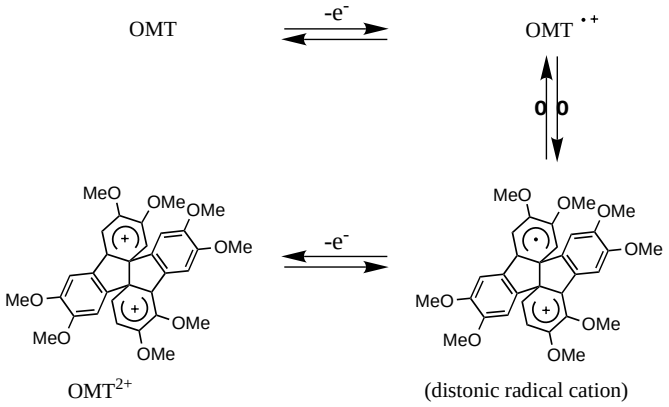


Figure 4. a) The initial positive-scan cyclic voltammogram of 5 mM neutral OMT and b) the initial negative-scan cyclic voltammogram of 5 mM $OMT^{2+}(PF_6^-)_2$ at 25 °C in anhydrous dichloromethane containing 0.2 M $n Bu_4N^+PF_6^-$ at a scan rate of $\upsilon = 200\ mV\,s^{-1}$.

in Figure 4 can both be repeated at least 100 times without any sign of degradation, and this electrochemical behavior is symptomatic of a chemically reversible but electrochemically irreversible redox system.[19]

The cyclic voltammograms in Figure 4 can be readily simulated[20] according to an ECE mechanism (Scheme 1)[21] based on the spectroscopic and structural data. Thus, one-electron oxidation of OMT generates its radical cation which undergoes an intramolecular C–C bond formation to yield a distonic radical cation.[22] It is the distonic nature of this rearranged radical cation which facilitates the removal of a second electron at a much lower potential[23] and leads to the formation of stable dication OMT^{2+}.



Scheme 1. Proposed mechanism of the oxidation of OMT to its corresponding dication.

The facile, electrochemically controlled interconversion between OMT and its dication (Figure 3) via the two-electron redox change thus satisfies the three most important criteria for the construction of molecular switches, namely bistability, reversibility, and ready detection owing to the accompanying intense color changes.

Experimental Section

Synthesis of OMT: Crystalline 2,2′-dibromo-3,4,3′,4′-tetramethoxybiphenyl was readily prepared from 1,2-dibromo-3,4-dimethoxybenzene (synthesized from veratrole) and *n*-butyllithium using a standard procedure[24] [m.p. 151–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.87$ (s, 6H), 3.92 (s, 6H), 6.77 (s, 2H), 7.12 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.31, 56.36, 114.07, 115.22, 134.13, 148.15, 149.26$; GC-MS: $m/z = 432$ (M^+)]. Following a literature procedure,[25] 2,2′-dibromo-3,4,3′,4′-tetramethoxybiphenyl (7.58 g, 17.5 mmol) was suspended in anhydrous diethyl ether (200 mL) and the mixture was cooled to −78 °C. A 2.5 M solution of *n*-butyllithium in hexane (15.5 mL, 38.6 mmol) was added dropwise and the dark yellow mixture was stirred for 1 h. Anhydrous cupric chloride (4.7 g, 35 mmol) was added and the resulting green mixture was slowly warmed to room temperature and stirred overnight. Aqueous workup afforded a yellow residue which was filtered through a pad of silica gel with ether/dichloromethane (1/1) as the eluent. The resultant product (ca. 10% 2,3,6,7-tetramethoxybiphenylene together with OMT) is further purified by recrystallization from ether to afford pure OMT as pale yellow prisms (1.7 g). Yield 46%, m.p. 260–262 °C (ether); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.82$ (s, 24H), 6.66 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.99, 112.42, 134.02, 147.85$; GC-MS: m/z: 544 (M^+); elemental analysis: calcd for $C_{32}H_{32}O_8$: C 70.57, H 5.92; found: C 70.28, H 5.52.

X-ray crystallography: The intensity data were collected on a Siemens SMART diffractometer equipped with a CCD detector using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at −150 °C. The structures were solved by direct methods[26] and refined by full-matrix least-squares procedures.

Crystal data for OMT [$2C_{32}H_{32}O_8 \cdot C_{16}H_{16}O_4$]. A suitable crystal ($0.8 \times 0.6 \times 0.5$ mm) of OMT and 2,3,6,7-tetramethoxybiphenylene as a 2:1 complex was obtained by recrystallization from ethanol/dichloromethane at 0 °C. $M_r = 1361.44$, triclinic, space group $P\bar{1}$, $a = 11.2651(2)$, $b = 12.4218(3)$, $c = 13.3150(2)$ Å, $\alpha = 96.350(1)$, $\beta = 109.833(1)$, $\gamma = 92.559(1)°$, $\rho_{calcd} = 1.303\ Mg\,m^{-3}$, $V = 1735.20(6)$ Å^3, $Z = 1$. The total number of reflections measured were 25533, of which 15301 reflections were symmetrically nonequivalent. Final residuals were $R1 = 0.0718$ and $wR2 = 0.1288$ for 15286 reflections with $I > 2\sigma(I)$.

Crystal data for OMT^{2+} [$C_{32}H_{32}O_8^{2+} \cdot 2SbCl_6^- \cdot 2CH_2Cl_2$]. A suitable crystal ($0.3 \times 0.2 \times 0.15$ mm) was obtained by a slow diffusion of hexane into a dichloromethane solution of dark-red OMT^{2+} at −23 °C. $M_r = 1383.33$, monoclinic, space group $P2_1/c$, $a = 17.1786(10)$, $b = 10.0095(5)$, $c = 29.460(2)$ Å, $\beta = 90.577(1)°$, $\rho_{calcd} = 1.814\ Mg\,m^{-3}$, $V = 5065.4(5)$ Å^3, $Z = 4$. The total number of reflections measured were 30818, of which 12612 reflections were symmetrically nonequivalent. Final residuals were $R1 = 0.0741$ and w$R2 = 0.1431$ for 12563 reflections with $I > 2\sigma(I)$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133990 and CCDC-133991. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[6] The disk-shaped hexamethoxytriphenylene is planar and has been extensively studied owing to its liquid-crystalline properties. However, its higher homologue octamethoxytetraphenylene (OMT) is heretofore unknown.

[7] Note that the dark-red solution obtained upon electrooxidation of OMT was EPR-silent. Either an electroreduction or a treatment of the red-colored solution with zinc dust led to the recovery of neutral OMT in quantitative yield.

[8] Radical cation salts derived from annelated hydroquinone ethers ($E^0_{red} = 1.1 - 1.3$ V vs. SCE) are useful one-electron oxidants, see: R. Rathore, J. K. Kochi, *J. Org. Chem.* **1994**, *60*, 4399.

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[11] The stable radical cation of 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene ($E^0_{red} = 1.34$ V vs. SCE) is readily prepared as the crystalline hexachloroantimonate salt using $NO^+SbCl_6^-$ as one-electron oxidant: R. Rathore, P. Le Magueres, J. K. Kochi, unpublished results.

[12] The redox stoichiometry in Equation (2) is further confirmed by coulometry at a constant potential of 1.25 V (vs. SCE) in dichloromethane (containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte) at 0 °C.

[13] The identity of liberated NO gas is confirmed by UV/Vis and IR spectroscopy, see refs. [8, 9].

[14] Note that photoexcited chloranil is a powerful one-electron oxidant ($E^0_{red} = 2.15$ V vs. SCE) and readily oxidizes a variety of aromatic donors to their radical cations, see: R. Rathore, S. M. Hubig, J. K. Kochi, *J. Am. Chem. Soc.* **1997**, *119*, 11468.

[15] Compare: R. Rathore, J. K. Kochi, *Acta. Chem. Scand.* **1998**, *52*, 114.

[16] Methoxy groups are omitted for the sake of clarity.

[17] The pertinent bond angles [°] in OMT^{2+} around C11 and C31 are: C12-C11-C31 105.2, C12-C11-C42 112.6, C16-C11-C12 114.7, C16-C11-C42 106.4, C16-C11-C31 116.8, C42-C11-C31 100.5, C32-C31-C11 105.1, C32-C31-C22 106.5, C36-C31-C32 114.1, C36-C31-C11 117.8, C36-C31-C22 110.7, C11-C31-C22 101.3.

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[21] A similar ECE mechanism is applicable to other (oxidative) biaryl syntheses, see: A. Ronlan, O. Hammerich, V. D. Parker, *J. Am. Chem. Soc.* **1973**, *95*, 7132.

[22] The distonic radical cations have ample literature precedent in the synthesis of a variety of biaryls, see: O. Hammerich, V. D. Parker, *Adv. Phys. Org. Chem.* **1984**, *20*, 55, and references therein. The rate of formation of the distonic radical cation (Scheme 1) is estimated to be $k > 10^6\ s^{-1}$ based on time-resolved absorption measurements upon diffusional electron-transfer quenching of photoexcited chloranil, see ref. [14]. Thus, the transient spectrum obtained 1 μs after laser excitation (10 ns) of chloranil (8 mM) in the presence of OMT (10 mM) shows an absorption band at 450 nm with a shoulder at 420 nm, characteristic of a chloranil radical anion, as well as a band at 370 nm and a weak (broad) absorption at about 660 nm. The latter two absorptions are tentatively assigned to the spectrum of the distonic radical cation since it lacks the characteristic absorption wavelengths of the radical cations of either the dimethoxybenzenes or the methoxylated biphenyls (see: T. Shida, *Electronic Absorption Spectra*, Elsevier, New York, **1988**).

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