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First stable 7,7,8,8-tetraaryl-*o*-quinodimethane: isolation, X-ray structure, electrochromic response of 9,10-bis(dianisylmethylene)-9,10-dihydrophenanthrene†

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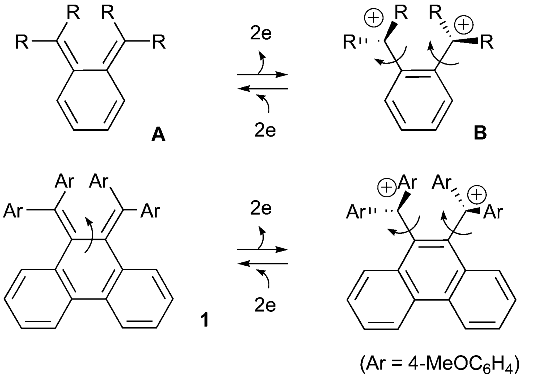
Oxidative cyclization of 2,2′-bis(dianisylethenyl)biphenyl yielded the dicationic salt of phenanthrene-9,10-diylbis(dianisylmethylium), which in turn afforded the severely congested title molecule as the first stable tetraaryl-*o*-quinodimethane derivative upon reduction.

o-Quinodimethane (oQDM; **A**, R = H) has been known as a short-lived reactive hydrocarbon and used as a versatile building block in synthetic chemistry.[1] From the viewpoint of multistage redox systems,[2] this skeleton serves as an attractive scaffold to construct a Wurster-type redox pair by attaching the proper end groups at the termini of the *exo*-methylene carbons (**A**, R = charge-stabilizing group).[3] Outstanding features of oQDM-based redox systems will be drastic geometric changes upon electron transfer when the end groups are bulky enough to adopt nonplanar structures. Thus, the two *exo*-methylenes in the neutral molecule will form a large torsion angle whereas the *o*-xylylene unit will become planar in the doubly charged ion to which the charged end groups being attached nearly perpendicularly as in **B** (Scheme 1). By considering the fact that such structural changes are favorable to constructing molecular response systems in terms of reversibility and bistability,[4,5] we have designed a novel electron donor **1** with four anisyl (4-$MeOC_6H_4$) groups as cation-stabilizing end groups. Two extra benzene rings are annelated to the oQDM skeleton in order to prevent **1** from diminishing by cyclization to the benzocyclobutene-type or triaryldihydroanthracene-type isomers.[6,7] Here we report the successful preparation of **1** as a first isolable member of tetraaryl-oQDMs along with its severely deformed structure determined by low-temperature X-ray analysis. A noteworthy feature is that **1** and 9,10-phenanthrenediyl dication $\mathbf{1}^{2+}$ constitute a reversible redox pair exhibiting an electrochromic response with vivid change in color.

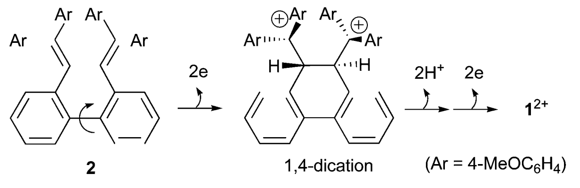
The reaction of 2,2′-bitolyl with BuLi in the presence of TMEDA gave 2,2′-bis(lithiomethyl)biphenyl,[8] which was then treated with 4,4′-dimethoxybenzophenone in THF. The resulting diol was treated with a catalytic amount of TsOH in refluxing benzene to give diolefin **2**[9] in 50% yield over two steps. According to the X-ray analysis,[10] **2** adopts a pseudo-C_2 symmetry with a twisting angle of 82.9° around the biphenyl axis (Figure S1†). Although the two benzylidene carbons are separated by 3.85 Å in this solid-state structure, the oxidative cyclization[11,12] proceeded smoothly as follows. Upon treatment of diolefin **2** with 4 equivalents of $NOBF_4$ in CH_2Cl_2, the dark purple powder of dicationic salt $\mathbf{1}^{2+}(BF_4^-)_2$[9] was obtained in 92% yield. When a smaller amount of oxidant was used, the same salt was obtained accompanied by recovery of the starting material **2**, suggesting that the 1,4-dication formed by 2e oxidation of **2** underwent facile deprotonation to **1** which is more easily oxidized under the reaction conditions to $\mathbf{1}^{2+}$ (Scheme 2).[11,13]

Upon treatment of $\mathbf{1}^{2+}(BF_4^-)_2$ with excess Zn powder in DME, the deep purple color disappeared rapidly, and oQDM **1**[9] was isolated as surprisingly stable yellow cubes in 92% yield after recrystallization from CH_2Cl_2–hexane. Its thermal stability was demonstrated by quantitative recovery after refluxing for 24 h in toluene with no signs of electrocyclization to its isomers.[14] In order to determine the detailed structural features of the first isolable derivative of 7,7,8,8-tetraaryl-oQDM, its X-ray analysis was conducted at −150 °C (Fig. 1).[10] The most striking feature is the large torsion angle of 63.4° for the Ar_2C=C–C=CAr_2 unit although the twisting angle of the biphenyl skeleton is only 19.3°.[15] Such deformation is surely induced to avoid the anomalous proximity of two inner anisyl groups, which are still close enough for π–π interaction: they are overlapped in a face-to-face manner with an interplanar distance of 3.35 Å and a dihedral angle of 13.2°. The closest contact between the aromatic carbons of opposite sides is 3.19 Å, which is much shorter than the sum of the van der Waals radii (3.40 Å).[16]

The observed deformation as well as intramolecular π–π interaction seem to be responsible for raising the HOMO level of **1** (E^{ox} +0.78 V *vs.* SCE in MeCN; 2e process) compared with **2** (+1.00 V). In fact, oQDM was easily oxidized to reproduce dication $\mathbf{1}^{2+}$, which was isolated as BF_4^- or $SbCl_6^-$ salt in 78% and 87% respective yield upon treatment with 2 equivalents of $NOBF_4$ or $(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$. The reduction potential of $\mathbf{1}^{2+}$ was observed in the far cathodic region (+0.28 V), and the separation by 0.5 V corresponds to the electrochemical bistability of this couple. Such a large shift of redox peaks as well as one-wave 2e



Scheme 1 Redox pairs based on the oQDM skeleton.



Scheme 2 Oxidative cyclization of **2** to $\mathbf{1}^{2+}$.

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† Electronic supplementary information (ESI) available: ORTEP drawings of $\mathbf{1}^{2+}$ and **2**. See http://www.rsc.org/suppdata/cc/b4/b405837b/

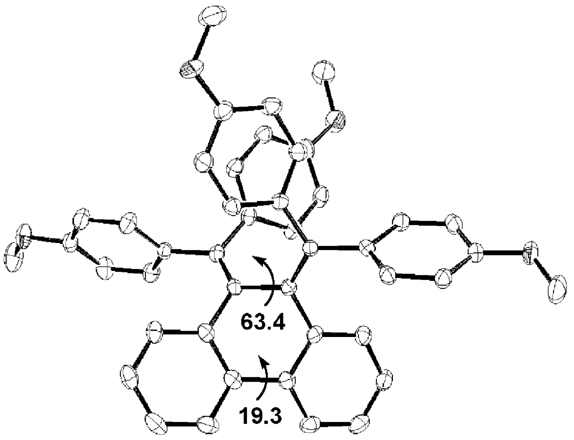

Fig. 1 ORTEP drawing of **1** determined by X-ray analysis of $CHCl_3$ solvate at −150 °C.

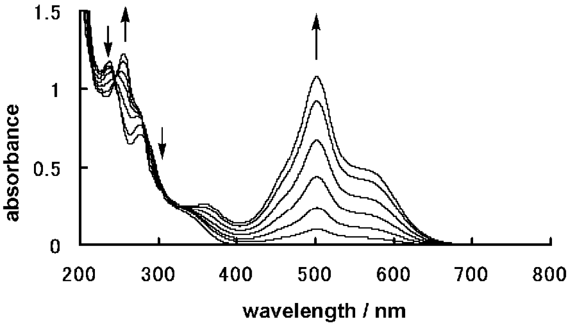

Fig. 2 Continuous changes in the UV–Vis spectrum of **1** (3 mL, 1.52×10^{-5} mol dm^{-3} in MeCN containing 0.5 mol dm^{-3} Bu_4NBF_4) upon constant-current electrochemical oxidation (28 μA, 10 min interval) to $\mathbf{1}^{2+}$.

oxidation process have been commonly observed in the dynamic redox pairs[5] undergoing reversible C–C bond making/breaking[4] or drastic structural changes.[17] Preliminary X-ray analysis on the dicationic salt $\mathbf{1}^{2+}(I_3^-)_2$ suggests that its phenanthrene unit adopts a planar structure.[18]

Not only the geometries but also their colors change drastically during the interconversion between **1** and $\mathbf{1}^{2+}$. Thus, when the electrochemical oxidation of **1** was followed using UV–Vis spectroscopy, the continuous and clean conversion was observed as shown in Fig. 2 with the development of a huge absorption band in the visible region (λ = 400–650 nm), demonstrating that this couple can serve as a new electrochromic material with high electrochemical bistability. Studies on other stable oQDMs are now under way.

Notes and references

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7 According to PM3 calculations on model compounds, 9,10-bis(diphenylmethylene)-9,10-dihydrophenanthrene **1′** (Ar = Ph) has a smaller heat of formation (192.25 kcal mol^{-1}) than the corresponding cyclobutene derivative, 1,2-dihydro-1,1,2,2-tetraphenylcyclobuta[l]phenanthrene **3′** (208.12 kcal mol^{-1}). Although 9,9a-dihydro-9,9,10-triphenylanthracene is much more stable than 7,7,8,8-tetraphenyl-oQDM or 1,1,2,2-tetraphenylbenzocyclobutene,[6] this is not the case for the dibenzo analogues. The dihydroanthracene-type isomer was predicted to have the higher heat of formation (216.18 kcal mol^{-1}) than **1′** and **3′**, probably due to the steric repulsion between phenyl substituents and fused benzene rings.

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9 Physical data of new compounds are as follows. **1**: mp 97–98 °C, ^{1}H NMR (acetone-d$_6$) δ 7.89 (2 H, d, J = 7.5 Hz), 7.29 (2 H, dd, J = 7.5, 7.5 Hz), 7.14 (2 H, d, J = 7.5 Hz) 6.75–6.83 (16 H, m), 3.84 (6 H, s), 3.72 (6 H, s); UV–Vis (MeCN) λ_{max} 325sh (log ε 4.04), 276 (4.67), 239 (4.75) nm. $\mathbf{1}^{2+}(BF_4^-)_2$: mp 172–174 °C, ^{1}H NMR (CD_3CN) δ 9.07 (2 H, d, J = 8.4 Hz), 7.94 (2 H, dd, J = 8.4, 8.4 Hz), 7.54–7.60 (10 H, m), 7.41 (2 H, d, J = 8.4 Hz), 7.06 (8 H, AA′XX′), 4.03 (12 H, s); UV–Vis (MeCN) λ_{max} 550sh (log ε 4.50), 502 (4.76), 366 (4.11), 272 (4.48), 254 (4.65) nm. **2**: mp 191–192 °C, ^{1}H NMR ($CDCl_3$) δ 7.23 (2 H, d, J = 7.5 Hz), 7.15 (2 H, dd, J = 7.5, 7.5 Hz), 7.06 (4 H, AA′XX′), 6.95 (2 H, dd, J = 7.5, 7.5 Hz), 6.83–6.88 (6 H, m), 6.77 (4 H, AA′XX′), 6.43 (2 H, s), 6.43 (4 H, AA′XX′), 3.79 (6 H, s), 3.70(6 H, s).

10 Crystal data for $\mathbf{1}\cdot(CHCl_3)_2$: $C_{46}H_{38}Cl_6O_4$, M 867.52, tetragonal $I\bar{4}$ (No. 82), a = 27.728(4), c = 11.005(2) Å, U = 8461.0(1) Å^3, D_c (Z = 8) = 1.362 g cm^{-1}, T = 123 K, μ = 4.49 cm^{-1}. The final R value is 0.052 for 3232 independent reflections with $I > 3\sigma I$ and 509 parameters. Esds for bond lengths and angles are 0.006–0.008 Å and 0.4–0.5° for non-hydrogen atoms. Due to the orientational disorder of the solvent in the crystal, several positional parameters were fixed in the final least-squares cycle. CCDC 237042. Data for **2** : $C_{44}H_{38}O_4$, M 630.78, orthorhombic *Pbca* (No. 61), a = 10.1566(7), b = 18.671(1), c = 35.302(2) Å, U = 6694.5(8) Å^3, D_c (Z = 8) = 1.252 g cm^{-1}, T = 153 K, μ = 0.79 cm^{-1}. The final R value is 0.039 for 4939 independent reflections with $I > 3\sigma I$ and 433 parameters. Esds for bond lengths and angles are 0.002–0.003 Å and 0.1–0.2° for non-hydrogen atoms. The ORTEP drawing of **2** is given as Figure S1 in the ESI. CCDC 237043. See http://www.rsc.org/suppdata/cc/b4/b405837b/ for crystallographic data in .cif format.

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14 Photoirradiation of **1** caused its isomerization to the 9,10-dihydroanthracene skeleton by electrocyclization and a subsequent 1,3-H shift. The details will be published as a full paper in due course.

15 The PM3 calculation on 9,10-bis(diphenylmethylene)-9,10-dihydrophenanthrene **1′** reproduced the values for these angles (59.7° and 18.8°, respectively) so nicely that the observed solid-state structure is intrinsic to this skeleton but not due to the crystal packing force.

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18 Crystal data: $C_{44}H_{36}O_4I_6$, M 1390.2, triclinic $P\bar{1}$, a = 11.502(2), b = 11.612(2), c = 19.688(3) Å, α = 84.567(4), β = 88.131(4), γ = 84.500(4)°, U = 2604.9(7) Å^3, D_c (Z = 2) = 1.773 g cm^{-1}, T = 293 K. Due to the severe disorder of the iodine atoms, the R value is still quite high (11.3%) (Fig. S2, ESI). We are now trying to obtain other dication salts with different counter anions.