Supporting Information

Fulvalene Derivatives Involving a Tetrabenzofluorene Unit: New Non-Planar Fulvalenes with a High Electron Affinity


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1. Experimental

2. X-ray crystallographic analysis

2.1. X-ray crystal structure of co-crystals of 2 and 4

Figure S1. ORTEP drawings of 2 and 4 in co-crystal (2:4 = 55:45) with ellipsoids shown at 50% probability.

2.2. X-ray crystal structure of 12

Figure S2. ORTEP drawings of 12 with ellipsoids shown at 50% probability.

3. Cyclic voltammetric measurements

Figure S3. Cyclic voltamograms of 4 in DMF (V vs. Ag/Ag+, in 0.1 M nBu4NClO4/DMF, scan rate 100 mV/s, +25 ºC, ferrocene used as a standard).

Figure S4. A cyclic voltamogram of 5 in DMF (V vs. Ag/Ag+, in 0.1 M nBu4NClO4/DMF, scan rate 100 mV/s, +25 ºC, ferrocene used as a standard).

Figure S5. A cyclic voltamogram of 6 in DMF (V vs. Ag/Ag+, in 0.1 M nBu4NClO4/DMF, scan rate 100 mV/s, +25 ºC, ferrocene used as a standard).

4. Theoretical Calculations (DFT).

Figure S6. HOMO, LUMO, energy level and twist structure of 7.

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Figure S9. HOMO, LUMO, energy level and twist structure of 6.

Figure S10. HOMO, LUMO, energy level and butterfly structure of 6.

5. 1H- and 13C-NMR spectra in CDCl3

Figure S11-S17. 1H-NMR spectra of 4—7 and 12, and 13C-NMR spectra of 4 and 12.

6. References
1. Experimental

**General:** All reactions of air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via syringe. Analytical thin-layer chromatography was performed using glass plates pre-coated with Merck Art. 7730 Kiesel-gel 60 GF-254. Thin layer chromatography plates were visualized by exposure to UV light. Organic solutions were concentrated by using rotary evaporation at \( \text{ca.} 15 \text{ Torr} \) obtained with a diaphragm pump. Column chromatography was performed with Merck Kiesel-gel 60. All reagents were commercially available and used without further purification unless otherwise noted. THF was purchased from Wako Chemical Co. and distilled from lithium aluminum hydride at 760 Torr under a nitrogen atmosphere before use.

Melting points were recorded on a Yanaco MP–S3 apparatus and reported uncorrected. EI mass spectra were measured on a Shimadzu GCMS-QP5050A. High-resolution mass spectra were measured on an Applied Biosystem Japan Ltd. Elemental analyses were obtained from Yanaco MT5 CHN corder. \( ^1 \)H and \( ^13 \)C NMR spectra were recorded on Bruker-Biospin DRX-500, and Jeol EX-270 FT spectrometers. \( ^1 \)H and \( ^13 \)C NMR spectral data for 4—7 and 12 were measured at 20 \( ^\circ \)C. IR spectra were obtained using a Shimadzu FTIR-8400 spectrometer. Electronic (UV-Vis) and fluorescence spectra in solution were recorded with Hitachi U-3500 and F2500 spectrophotometers, respectively. DFT calculations for 5—7 was carried out by using the B3LYP/6-31G(d) method with the Gaussian 09 program package.\(^{[1]}\)

Fluorene 8 was purchased from Kishida Kagaku, and tetrabenzofluorene 2\(^{[2]}\) and trimethylsiloxy-4-bromo-2,6-di(\( t \)-butyl)benzene\(^{[3]}\) were prepared using reported procedures.

**Tetrabenzo[a,c,g,i]fluoren-17-one (4):** TBF 2 (0.366 g, 1.00 mmol) was dissolved with aqueous \( \text{K}_2\text{CO}_3 \) (1.0 ml) and DMF (40 ml), and the solution was heated at 100 \( ^\circ \)C with bubbling air overnight. After cooling the reaction mixture, saturated aqueous ammonium chloride was added to
deposit a dark reddish solid. The solid was filtered and washed with ether to afford 4 (0.256 g, 0.700 mmol) in 70% yield.

\((4\text{-Oxy-2,6-di(t-butyl)cyclohexadienylidene})_\text{-17'-tetrabenzo[a,c,g,i]fluorenylidene}\) (5): To a solution of 4-bromo-2,6-di(t-butyl)trimethylsiloxybenzene (0.179 g, 0.50 mmol) in THF (20 ml) was added \(n\)-butyllithium (1.6 M hexane solution, 0.38 ml, 0.60 mmol) via syringe at –78 °C under N\(_2\). To the reaction mixture was added a solution of 4 (100 mg, 0.26 mmol) in THF (20 ml) via syringe, the mixture was allowed to warm to rt, and stirred overnight. The reaction mixture was quenched with aqueous ammonium chloride, and extracted with toluene. The organic layer was washed with water and brine, and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was evaporated under reduced pressure. The resulting pale yellow solid 10 was mixed with phosphoryl chloride (0.50 ml, 5.5 mmol) and pyridine (10 ml). The mixture was heated at 105 °C overnight. After cooling in an ice bath, the mixture was quenched with ice water, and extracted with toluene. The organic layer was washed with 2 M hydrochloric acid and brine, and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was evaporated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel (toluene/hexane =1/4) to afford 5 (0.015 g) in 10% yield.

\(9\text{-Fluorenylidene-17'-tetrabenzo[a,c,g,i]fluorenylidene}\) (6): To a solution of fluorene (0.166 g, 1.0 mmol) in THF (20 ml) was added \(n\)-butyllithium (1.6 M hexane solution, 0.63 ml, 1.0 mmol) via syringe at 0 °C under N\(_2\). To the reaction mixture was added a solution of 4 (100 mg, 0.26 mmol) in THF (20 ml) via syringe and stirred for 1 h. To the reaction mixture was added phosphoryl chloride (0.50 ml, 5.5 mmol). The solvent was evaporated under reduced pressure. To the resultant was added pyridine (15 ml). The solution was heated at 105 °C overnight. After cooling in an ice bath, the mixture was quenched with ice water, and extracted with chloroform. The organic layer was washed with 2 M hydrochloric acid and brine, and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was evaporated under reduced pressure. The resulting crude product was purified with column
chromatography on silica gel (CH$_2$Cl$_2$/hexane =1/1) to afford 6 (0.007 g) in 5% yield.

17-Bromo-17H-tetrabenzo[a,c,g,i]fluorene (12): TBF 2 (0.366 g, 1.0 mmol) and NBS (212 mg, 1.0 mmol) were dissolved with CH$_2$Cl$_2$ (30 ml), and the solution was stirred at rt for 2 h. After washing the reaction mixture with water and brine, the reaction mixture was dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure. The resulting dark reddish solid was rinsed with diethyl ether to afford 12 (0.267 g) in 60% yield.

17,17'-Bis(tetrabenzo[a,c,g,i]fluorenylidene) (7): TBF bromide 12 (0.100 g, 0.23 mmol) and potassium t-butoxide (47 mg, 0.47 mmol) were stirred at rt for 10 min in THF (5 ml) under N$_2$. The reaction mixture was quenched with water and extracted with toluene. The organic layer was separated, washed with brine and dried over anhydrous Na$_2$SO$_4$. The solution was concentrated under reduced pressure using an evaporator. The resulting black solid was rinsed with toluene/hexane (1:1) with heating at 40 °C to give 7 (0.040 g) in 50% yield.
2. X-ray crystallographic analysis

2.1. X-ray crystal structure of co-crystals of 2 and 4

Figure S1. ORTEP drawings of 2 and 4 in co-crystal (2:4 = 55:45) with ellipsoids shown at 50% probability.

A co-crystal of 2 and 4 (2:4 = 55:45 whose occupancy was refined) for X-ray analysis was obtained by slow evaporation from corresponding toluene/hexane solutions. X-ray diffraction data were collected on a Rigaku Rapid Auto diffractometer with graphite-monochromated MoKα (λ = 0.71070 Å) radiation, Φ and ω scans to a maximum 2θ value of 55.0°. The structures were solved by a direct method using SIR2004. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F² using SHELXL97. Hydrogen atoms of 2 and 4 were positioned geometrically and refined using a riding model. All calculations were performed using the WinGX program package.

2:4 (55:45): Crystal System = Monoclinic, a = 18.384(6) Å, b = 5.0933(15) Å, c = 19.237(6) Å, β = 90.656(4)°, V = 1801.1(10) Å³, Space Group = P2/c, Z value = 4, μ(MoKα) = 0.084 mm⁻¹, T = 223 K, R1[ I > 2σ (I) ] = 0.0608, wR2(all data) = 0.2139, GOF = 0.881, Refl./param=3775/0/272.

CCDC-950544 contains the supplementary crystallographic data for this paper.
2.2. X-ray crystal structure of 17-bromo-17H-tetrabenzo[a,c,g,i]fluorene 12

Figure S3. ORTEP drawings of 12 with ellipsoids shown at 50% probability.

A single crystal of 12 for X-ray analysis was obtained by slow evaporation from a toluene/hexane solution of 12. X-ray diffraction data were collected on a Rigaku Rapid Auto diffractometer with graphite-monochromated MoKα (λ = 0.71070 Å) radiation, Φ and ω scans to a maximum 2θ value of 55.0°. The structures were solved by a direct method using SIR2004. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on $F^2$ using SHELXL97. Hydrogen atoms of 12 were positioned geometrically and refined using a riding model. All calculations were performed using the WinGX program package.

12: Crystal System = Orthorhombic, $a = 13.4455(17)$ Å, $b = 15.948(2)$ Å, $c = 18.163(2)$ Å, $V = 3894.7(9)$ Å³, Space Group = $P_{bac}$, $Z$ value = 8, $\mu$(MoKα) = 2.125 mm⁻¹, $T = 223$ K, $R1[I>2\sigma(I)] = 0.0904$, $wR2$(all data) = 0.3118, GOF = 1.466, Refl./param= 4821/0/271. CCDC-1474664 contains the supplementary crystallographic data for this paper.
3. Cyclic voltammetry

Figure S3. Cyclic voltamograms of 4 in DMF (V vs. Ag/Ag⁺, in 0.1 M nBu₄NClO₄/ DMF, scan rate 100 mV/s, +25 °C, ferrocene used as a standard).

Figure S4. Cyclic voltamograms of 5 in DMF (V vs. Ag/Ag⁺, in 0.1 M nBu₄NClO₄/ DMF, scan rate 100 mV/s, +25 °C, ferrocene used as a standard).

Figure S5. Cyclic voltamograms of 6 in DMF (V vs. Ag/Ag⁺, in 0.1 M nBu₄NClO₄/ DMF, scan rate 100 mV/s, +25 °C, ferrocene used as a standard). The irreversible reduction wave at 1.4 V is ascribed to contaminated oxygen, because the wave varies with N₂ gas bubbling. Because of low concentration of 6, the wave of oxygen could not be deleted.
4. DFT Calculations.

4.1 Twisted form of 7

Figure S6. HOMO, LUMO, energy level and a twist form of 7 by the DFT calculation.

4.2. Butterfly form of 7

Figure S7. HOMO, LUMO, energy level and a butterfly form of 7 by the DFT calculation.

Table 1. The data of calculations of twist and butterfly forms of 7.
Optimized structures | Twist form | Butterfly form
--- | --- | ---
Calculation Type | FOPT | FOPT
Calculation Method | RB3LYP | RB3LYP
Basis Set | 6-31G(d) | 6-31G(d)
Charge | 0 | 0
Spin | Singlet | Singlet
E(RB3LYP) (a.u.) | –2229.50134052 | –2229.48574474
RMS Gradient Norm (a.u.) | 0.00000115 | 0.00000275
Dipole Moment (Debye) | 0.4395 | 0.000
Point Group | C1 | C1

Table 2. The absorption maxima, the first oxidation and reduction potentials, and HOMO, LUMO, and HOMO-LUMO gap of 4—7.

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<th>compound</th>
<th>λ_{max} nm</th>
<th>E_{i}^{ox} (V)</th>
<th>E_{i}^{red} (V)</th>
<th>LUMO (eV)</th>
<th>HOMO (eV)</th>
<th>HOMO-LUMO gap (eV)</th>
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<tr>
<td>4</td>
<td>530</td>
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<td>5</td>
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<td>6</td>
<td>545</td>
<td>+0.46</td>
<td>–1.16</td>
<td>2.40 (Butterfly) 2.91 (Twist)</td>
<td>5.00 (Butterfly) 5.10 (Twist)</td>
<td>2.60 (Butterfly) 2.09 (Twist)</td>
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<tr>
<td>7</td>
<td>641</td>
<td>+0.54</td>
<td>–0.65</td>
<td>2.48 (Butterfly) 3.22 (Twist)</td>
<td>4.94 (Butterfly) 5.01 (Twist)</td>
<td>2.60 (Butterfly) 1.79 (Twist)</td>
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4.3 Optimized structure of quinone methide 5.

Figure S8. HOMO, LUMO, energy level and a butterfly form of 5 by the DFT calculation. Because of low energy barrier between butterfly and twist structures, the calculations for optimized structure of 5 provides only the butterfly form.

Figure S9. HOMO, LUMO, energy level and a twist form of 6 by the DFT calculation.
Figure S10. HOMO, LUMO, energy level and a butterfly form of 6 by the DFT calculation.

Table 3. The data of calculations of twist and butterfly forms of 6.

<table>
<thead>
<tr>
<th>Optimized structures</th>
<th>Twist form</th>
<th>Butterfly form</th>
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5. $^1$H-NMR spectra in CDCl$_3$

Figure S11. $^1$H-NMR spectrum of 4.

Figure S12. $^{13}$C-NMR spectrum of 4.
Figure S13. $^1$H-NMR spectrum of 5.

Figure S14. $^1$H-NMR spectrum of 6.
Figure S15. $^1$H-NMR spectrum of 12.

Figure S16. $^{13}$C-NMR spectrum of 12.
Figure S17. $^1$H-NMR spectrum of 7.
6. References


