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Fulvalene Derivatives Containing a Tetrabenzofluorene Unit: New Nonplanar Fulvalenes with High Electron Affinity

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Kenta Yamada^a Hiroshi Shibamoto^a Yusuke Tanigawa^a Hiroyuki Ishikawa^a Jun-ichi Nishida^a Chitoshi Kitamura^b Hiroyuki Kurata^c Takeshi Kawase^{*a}

^a Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

kawase@eng.u-hyogo.ac.jp

^b Graduate School of Engineering, University of Shiga Prefecture, 2500, Hassaka-cho, Hikone, Shiga 522-8533, Japan

^c Department of Environmental and Food Science, Faculty of Environmental and Information Science, Fukui University of Technology, Gakuen 3-6-1, Fukui 910-8505, Japan

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Abstract 17*H*-Tetrabenzo[a,c,g,i]fluoren-17-one possessing a nonplanar, helicene-like structure was efficiently prepared by aerial oxidation of 17*H*-tetrabenzo[a,c,g,i]fluorene under mild basic conditions. A quinone methide and an unsymmetrical fulvalene containing a tetrabenzofluorene unit were synthesized from the ketone. Treatment of 17-bromotetrabenzo[a,c,g,i]fluorene with a base afforded a symmetric fulvalene as an air-sensitive blue solid. Electrochemical analyses revealed that these compounds have high electron affinities.

Key words conjugation, nonplanar π -systems, tetrabenzofluorenes, fulvalenes, electron acceptors, polycycles

 π -Extended fulvalene derivatives have received much attention as electron-accepting π -conjugated materials.¹ For example, Wudl and co-workers recently reported the application of an arene-fused pentafulvalene derivative 1 (Figure 1) as an electron-transporting material for organic photovoltaic cells.² 17*H*-Tetrabenzo[a,c,g,i]fluorene (**2**, R = H; TBF), a π -extended fluorene derivative, was first synthesized by De Ridder and Martin in 1960.³ Later, a crystallographic analysis of 2 revealed that the TBF framework has a nonplanar helicene-like structure in the crystals.⁴ We recently synthesized a series of 17,17-dialkyltetrabenzofluorenes 3 (R = methyl to hexyl) that show intense blue fluorescence, not only in solution, but also in the solid state.⁵ Moreover, we have reported unique fluorescence properties for 3,14-bis(4-nitrophenyl)-17,17-dipentyl-17H-tetrabenzo[a,c,g,i] fluorene.⁶ In this context, fulvalene derivatives containing a TBF unit would appear to be intriguing compounds with unique electronic properties; however, no examples have been synthesized to date.⁷



17*H*-Tetrabenzo[*a*,*c*,*g*,*i*]fluoren-17-one (**4**; Figure 1) can be regarded as a versatile synthetic intermediate for the construction of the corresponding fulvalene derivatives. Although **4** is known,³ its chemical and physicochemical properties have not been fully explored because of the long and complicated synthesis procedure. Here, we report the synthesis and physicochemical properties of fulvalene derivatives **5**–**7**, together with an improved synthesis and the crystal structure of **4** (Figure 1).

Because aerial oxidation of fluorene **8** under basic conditions is an efficient method for the synthesis of 9*H*-fluoren-9-one (**9**),⁸ we examined the aerial oxidation of 17*H*tetrabenzo[a,c,g,i]fluorene (**2**) under various basic conditions. After several failures, we finally found that mild basic conditions (K₂CO₃ in DMF at 100 °C) efficiently led to 17*H*tetrabenzo[a,c,g,i]fluoren-17-one (**4**), which was obtained as dark reddish crystals in 60–70% yield (Scheme 1). Chromatographic purification on a silica gel column provided **4** in a pure form;⁹ however, owing to the poor solubility of **4** in common organic solvents and the formation of co-crystals with the starting material **2**, the purification of large quantities of **4** is somewhat difficult.

Slow evaporation of a solution of a mixture of **2** and **4** in hexane–toluene provided dark reddish prismatic co-crystals of **2** and **4** in a 55:45 ratio, as determined by ¹H NMR spectroscopy. An X-ray crystallographic analysis of the co-crystal surprisingly showed that its crystal parameters¹⁰ were almost identical to those of a known crystal of **2**.⁴ The TBF moieties in **2** and **4** have the same helicene-like structure with a C_2 symmetry in the co-crystal; the spatial relationship between the carbonyl group in **2** and the methylene group in **4** is disordered statistically in the molecular

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Scheme 1 (a) Synthesis of 9*H*-fluoren-9-one (**9**) from 9*H*-fluorene (**8**)^{8a} and of (b) 17*H*-tetrabenzo[a,c,g,i]fluoren-17-one (**4**) from 17*H*-tetrabenzo[a,c,g,i]fluorene (**2**)

structure. Figure 2 shows an ORTEP drawing of **4** and the molecular packing of **2** and **4**. The dihedral angle between the A and B ring planes is 37.93(0.07)°. The molecules form a columnar packing in the crystals in which **2** and **4** are located randomly. The results imply that the presence of a carbonyl oxygen has neither steric nor electronic effects in the crystals.

Treatment of ketone **4** with 4-lithio-2,6-di(*tert*-butyl)-1-(trimethylsiloxy)benzene, derived from 4-bromo-2,6-di(*tert*-butyl)-1-(trimethylsiloxy)benzene,¹¹ afforded alco-hol **10** upon the usual acidic workup. Dehydration of **10** with phosphoryl chloride in refluxing pyridine led to the quinone methide **5**⁹ as a deep-reddish solid in 10% yield from **4** (Scheme 2).

We also examined the synthesis of 17-(9H-fluoren-9-ylidene)-17H-tetrabenzo[a,c,g,i]fluorene (6), by using a similar procedure. We assumed that the reaction of**4**with



Figure 2 ORTEP drawing of **4** with thermal ellipsoids at the 50% probability level (left) and the molecular packing (right) of a co-crystal of **2** and **4** (**2**/**4** = 55:45).

the fluorenyl anion would give the alcoholate intermediate **11**, because the dark-red color of **4** in the reaction mixture disappeared. However, the usual acidic workup gave the recovered starting materials. We therefore quenched **11** directly with phosphoryl chloride, without an acidic workup, and then concentrated the resulting mixture under reduced pressure. The residue was dissolved in pyridine, and the solution was heated at reflux to afford fulvalene **6**⁹ in 5% yield as a deep-purple solid (Scheme 3). The poor yields of **5** and **6** are due to the rather low solubilities of compounds **4–6** and reaction intermediates **10** and **11** in common organic solvents.

Several known procedures for the synthesis of 9,9'-bifluorene^{1b} were used in attempts to produce 17,17'-bi(17*H*tetrabenzo[*a,c,g,i*]fluorenylidene) (**7**); however, all these procedures failed when ketone **4** was used as a starting material. For example, under McMurry reaction conditions (Ti-Cl₄/Zn/THF), deoxygenative reduction of **4** occurred to afford **2** as the sole isolated product. Finally, **7**⁹ was success-



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fully obtained by treating 17-bromo-7*H*-tetrabenzo[a,c,g,i]fluorene (**12**) with potassium *tert*-butoxide in THF.¹² The starting bromide **12**⁹ was prepared by treatment of **2** with NBS in CH₂Cl₂ (Scheme 4). Because **7** is rather air-sensitive in solution, it gradually decomposed during column chromatography on silica gel to form ketone **4**. Therefore, the best method for the isolation of **7** is crystallization from a toluene extract by adding hexane as a less-polar solvent. Even in the solid state, **7** converted slowly into **4** under air; however, it can be stored for a long period under an inert atmosphere. Fulvalenes exist in two conformations: the twist and butterfly forms. Unfortunately, good single crystals of fulvalenes have not been obtained because of their low solubilities. To gain insight into the structural features, we performed density functional theory (DFT) calculations [B3LYP/6-31G(d)].¹³ The calculations predicted that the twist forms of **6** and **7** are stable conformations; the twist angles between two cyclopentadienyl rings are 54.7° and 50.3°, respectively (Figure 3 and Figure S9). The energies of the twist forms are 41 and 13 kJ mol⁻¹ lower, respectively, than those of the corresponding butterfly forms (Figure S10 and Tables S1–S3).¹⁴ On the other hand, the stable conformation of the quinone methide **5** is the butterfly form (Fig-



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ure S8). The conformational isomers of **7** should exist as enantiomeric and diastereomeric isomers as a result of the helicene-like TBF moieties; however, isomerization should occur rapidly at ambient temperature because of relatively low racemization barrier of the TBF framework ($\Delta G^{\ddagger} \approx 60$ kJ·mol⁻¹).⁵ The susceptibility of **7** to oxygen could be due to its highly twisted structure; however, the compound gave clear ¹H NMR signals in CDCl₃ at room temperature, showing that the diradical character is almost negligible at ambient temperatures.



Figure 4 shows the absorption spectra of 4-7 in CH₂Cl₂. Fulvalenes 5-7 were obtained as dark reddish, purple, or

blue compounds. The long-wavelength-absorption maxima $[\lambda_{max} \text{ nm } (\epsilon)]$ of the fulvalenes [**5**: 529 (6300), **6**: 545 (13600), **7**: 641 (14800)] exhibit bathochromic and hyperchromic shifts with the extension of their π -electron frameworks.



The order of the bathochromic shift is in good agreement with the HOMO–LUMO energy gaps of the predicted stable twist or butterfly conformational isomers of **5–7** (Table 1). The low-energy bands for these compounds should arise from intramolecular charge-transfer transitions. Actually, large spatial separations were observed between the HOMO and LUMO in these molecules (Figures S6–S10). On the other hand, the ketone **4**, as a cyclopentadienone derivative, shows a characteristic weak long-wavelength-absorption band. The λ_{max} value for **4** [530 nm (900)] exceeds that of tetraphenylcyclopentadienone by 28 nm,¹⁵ probably as a result of the high planarity of the molecules of **4**.

Table 1	Calculated HOMO and LUMO Energies and HOMO-LUMO En-
ergy Gap	s of 4–7 ^a , Together with Observed HOMO–LUMO Energy Gaps

Compound	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE_{cal}^{b} (eV)	ΔE_{obs}^{c} (eV)
4	-5.35	-2.67	2.68	1.90
5	-5.26	-2.92	2.34	2.07
6 (twist)	-5.00	-2.91	2.09	1.94
6 (butterfly)	-5.10	-2.40	2.60	
7 (twist)	-5.01	-3.22	1.79	1.66
7 (butterfly)	-4.94	-2.48	2.60	

^a Calculated by the DFT method [B3LYP/6-31G(d)].

 $^{b}\Delta E_{cal} = E_{LUMO} - E_{HOMO} [B3LYP/6-31G(d)].$

^c From the low-energy absorption edge of the absorption spectra in CH₂Cl₂.

The electrochemical properties of 4-7 were examined by cyclic voltammetry (CV) in DMF, and the result was summarized in Table 2. The cyclic voltammogram of 5 exhibits one reversible two-electron reduction wave, one irreversible one-electron reduction wave, and one irreversible oxidation wave, whereas that of 6 shows two reversible reduction waves and one irreversible oxidation wave. Comparison with the redox potentials of $\mathbf{4}^{16}$ showed that the radical cations and dianions of 5 and 6 are highly stabilized as a result of the extension of the π -electron system. Moreover, the cyclic voltammogram of 7 exhibits two reversible and two pseudo-reversible reduction waves and one irreversible oxidation wave. Thus, 7 shows an overall five-step redox behavior (Figure 5). In comparison with the electron affinities of **5** and **6**, the electron affinity of **7** is considerably enhanced by the extension of the π -electron system. The results are in good agreement with the predicted LUMO energy levels for the stable conformations of **5–7** (Table 1).

Tabl	e 2	Redox Potentials	s of 4–7 ª
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Compound	E ^{ox}	$E_1^{\rm red}$	E_2^{red}	$E_3^{\rm red}$	$E_4^{\rm red}$
4	+0.95 ^b	-1.28	-1.94	-	-
5	+0.59 ^b	-1.30		-1.90 ^b	-
6	+0.46 ^b	-1.16	-1.68	-	-
7	+0.54 ^b	-0.65	-0.97	-1.22	-1.50 ^b

a Volts versus Ag/Ag⁺ in 0.1 M Bu₄NClO₄/DMF; scan rate 100 mV/s, Fc/Fc⁺ = 0 V.

^b Peak potentials.

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In conclusion, we have developed an effective preparation of 17*H*-tetrabenzo[*a*,*c*,*g*,*i*]fluoren-17-one (**4**) and we have described the synthesis and physicochemical properties of the fulvalene derivatives 5-7. Crystallographic analysis revealed a helicene-like nonplanar structure for 4. Whereas compounds **4–6** are stable dark-red or purple crystals, the symmetric fulvalene 7 is a rather-air-sensitive blue solid. Electrochemical measurements revealed that the fulvalenes presented here are new and efficient electron acceptors. In particular, 7 acts as a five-stage redox system with high electron affinity. The novel electronic properties of 7 are explained in terms of its highly twisted structure as well as its extended π -electron system, as predicted by DFT calculations.¹⁷ Further studies are underway on the applicability of tetrabenzofluorene derivatives in the design of other π -conjugated systems, as well as on their potential use in organic electronic materials.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561478.

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(9) 17H-Tetrabenzo[a,c,g,i]fluoren-17-one (4)

Dark-red prisms; yield: 256 mg (70%); mp 284.0–286 °C (Lit.² 295 °C). IR (KBr): 3072w, 3057w, 1697s, 1425m, 1095m, 748s, 729s, 718s cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 7.64–7.84 (m, 8 H), 8.31 (d, J = 8.2 Hz, 2 H), 8.69 (d, J = 7.9 Hz, 2 H), 8.78 (d, J = 8.6 Hz, 2 H), 9.23 (d, J = 8.6 Hz, 2 H). ¹³C NMR (125.8 MHz, CDCl₃): δ = 122.75, 123.95, 124.85, 125.88, 126.46, 126.58, 126.95, 127.63, 128.46, 128.55, 128.94, 131.60, 134.71, 146.93, 197.44. MS (EI): m/z (%): 380 [M⁺] (100), 352 [M–CO]⁺ (35), 350 (38). UV/Vis (CH₂Cl₂): λ_{max} (ϵ , M⁻¹-cm⁻¹) = 321 (29500), 336 (33500), 423 (2320), 530 (900) nm.

3,5-Di-tert-butyl-4-(17H-tetrabenzo[a,c,g,i]fluoren-17-ylidene)cyclohexa-2,5-dien-1-one (5)

Black-red prisms; yield: 15 mg (10%); mp 293–294 °C. FT-IR (KBr): 719s, 747s, 870m, 1256m, 1364m, 1456w, 1620s (C=O), 2859w, 2947m, 3077w cm⁻¹. ¹H NMR (500 MHz, CDCl₃): $\delta = 1.18$ (s, 18 H), 7.61–7.66 (m, 6 H), 7.73 (t, J = 7.8 Hz, 2 H), 7.90 (s, 2 H), 8.22 (t, J = 8.3 Hz, 2 H), 8.48 (d, J = 8.3 Hz, 2 H), 8.74 (t, J = 8.3 Hz, 2 H), 8.77 (d, J = 8.3 Hz, 2 H). MS (EI): m/z (%): 570 [M + 2]⁺ (100), 569 [M + 1]⁺ (10), 568 [M⁺] (20). HRMS (ESI): m/z [M + 1]⁺ calcd for C₄₃H₃₇O: 569.2839; found: 569.2851. UV/Vis (CH₂Cl₂): λ (ϵ , M⁻¹·cm⁻¹) = 301 (26500), 358 (27000), 452 (20500), 529 (6300) nm. ¹³C NMR spectra for **5–7** could not be recorded because of the low solubilities of these compounds. **17** (**M** Eluoren 9 wildenc) **17** H tatrabarate c a silfurence

17-(9H-Fluoren-9-ylidene)-17H-tetrabenzo[a,c,g,i]fluorene (6)

Black-violet prisms; yield: 7 mg (5%); mp >300 °C. FT-IR (KBr): 733s, 1429w, 1447m, 3034w, 3064w cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 6.90 (t, J = 7.2 Hz, 2 H), 7.09 (t, J = 7.2 Hz, 2 H), 7.15 (t, J = 7.6 Hz, 2 H), 7.38 (t, J = 7.6 Hz, 2 H), 7.42 (d, J = 7.6 Hz, 2 H), 7.56 (t, J = 7.6 Hz, 2 H), 7.65 (d, J = 7.7 Hz, 2 H), 7.69 (t, J = 7.6 Hz, 2 H), 7.93 (d, J = 8.3 Hz, 2 H), 8.33 (d, J = 8.3 Hz, 2 H), 8.59 (d, J = 8.1 Hz, 2 H), 8.68 (d, J = 8.1 Hz, 2 H). HRMS (ESI): m/z [M⁺] calcd for C₄₂H₂₄: 528.1881; found: 528.1873. UV/Vis (CH₂Cl₂): λ (ϵ , M⁻¹·cm⁻¹) = 303 (29600), 342 (13100), 359 (12100), 545 (13600) nm.

17-Bromo-17H-tetrabenzo[a,c,g,i]fluorene (12)

Dark-red prisms; yield: 267 mg (60%); mp 255–256 °C. FT-IR (KBr): 1125, 1157, 1435, 1447, 3069 cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 6.58 (s, 1 H), 7.62–7.81 (m, 4 H), 8.43 (d, J = 7.6 Hz, 4 H), 8.64 (d, J = 7.9 Hz, 4 H), 8.81 (t, J = 7.6 Hz, 4 H). ¹³C NMR (125.8 MHz, CDCl₃): δ = 44.35, 123.35, 123.78, 124.81, 125.48, 126.80 (2C), 127.01, 127.71, 127.79, 128.05, 131.00, 132.48, 136.40, 140.04.

The structure was confirmed by the X-ray crystallographic analysis; see Figure S3 in the Supporting Information.

17,17'-Bi(17H-tetrabenzo[a,c,g,i]fluorenylidene) (7)

Dark-blue leaflets; yield: 40 mg (50%); mp >300 °C. IR (KBr): 1495, 1564, 1607, 2851, 2920, 2957, 3038, 3073 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 6.72 (t, J = 7.7 Hz, 4 H), 7.64–7.71 (m, 12 H), 7.96 (d, J = 8.2 Hz, 4 H), 8.42 (d, J = 8.2 Hz, 4 H), 8.49 (d, J =

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7.9 Hz, 4 H), 8.63 (d, J = 7.9 Hz, 4 H). MS (EI): m/z 728. HRMS (ESI): m/z [M⁺] calcd for C₅₈H₃₂: 728.2499; found: 728.2505. UV/Vis (CH₂Cl₂): λ (ϵ , M⁻¹·cm⁻¹) = 312 (29500), 370 (17400), 495 (3300), 641 (14800) nm.

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