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Selective Synthesis of C_3 Symmetric Functionalized Sumanenes

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C_3 symmetric triformylsumanene was selectively synthesized from C_3 symmetric *syn*-tris(oxonorborneno)benzene, featuring ring-opening/closing metathesis reactions of *syn*-tris(methoxymethylnorbornadieno)benzene and DDQ oxidation. Triformylsumanene can be an intermediate to synthesize C_3 symmetric trisubstituted sumanenes by further transformation. Tris(ethoxycarbonylethenyl)sumanene was prepared through the Horner–Wadsworth–Emmons reaction. Its optical and electrochemical behaviors were investigated.

Since the synthesis of sumanene (**1**) in 2003,[1] the unique properties of **1** have been revealed such as the columnar crystal packing structure, bowl inversion, and electron conductivity.[2,3] To explore the physical properties as well as applications, the functionalization of the sumanene structure by introduction of substituents is necessary. Among such substituted sumanene derivatives, C_3 symmetric trisubstituted sumanenes are an attractive derivative for our purpose to study the properties because of the simpler analysis and discussion of the properties than those of unsymmetrical examples, the tripled effect of substituents, the suitable structure for the intermolecular interaction with guest molecules or for the control of the crystal morphology,[4] and so on. Nevertheless, the lack of a strategy for the regioselective introduction of functional groups has severely restricted further application. Multiple bromination at aromatic rings of **1** affords a mixture of the regioisomers, which are separated and purified with difficulty.[2f] Therefore at present there is no rational route to C_3 symmetric functionalized buckybowls starting from C_{3v} symmetric **1** (Figure 1). To solve this problem, we adopted a synthetic strategy to convert a C_3 symmetric precursor to C_3 symmetric substituted sumanenes. We have already achieved the selective synthesis of C_3 symmetric trimethylsumanene, controlling the regiochemistry of substituents as well as the bowl chirality.[2d] Here, we expand the strategy to the selective synthesis of C_3 symmetric triformylsumanene **2**, which can be a more versatile intermediate for various trisubstituted sumanenes (Figure 1). As an example, preparation of tris(ethoxycarbonylethenyl)sumanene **3** through the Horner–Wadsworth–Emmons reaction is also reported.

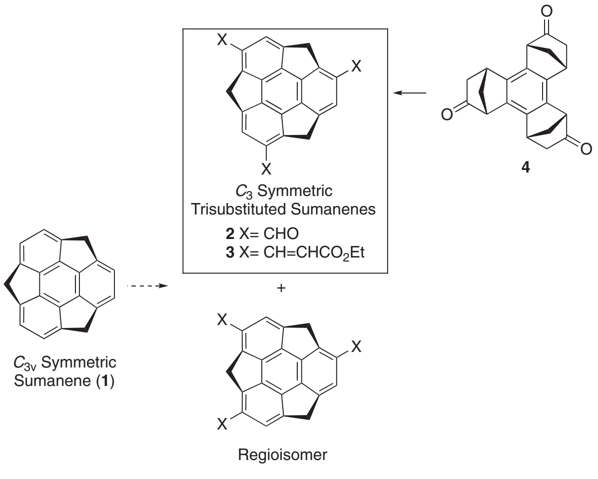
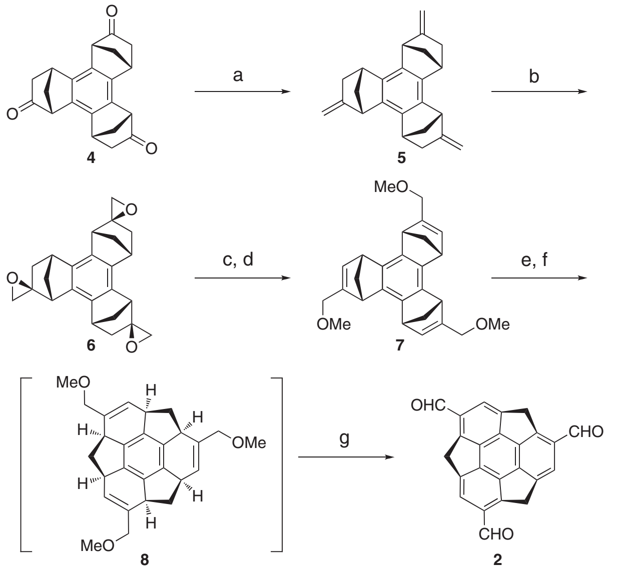


Figure 1.

C_3 symmetric *syn*-tris(oxonorborneno)benzene **4** was prepared by our reported Pd-catalyzed *syn*-selective cyclotrimerization of enantiopure iodonorbornenes.[5,9] Methoxymethyl group was introduced as a convertible substituent in the following steps (Scheme 1). Carbonyl groups of **4** were transferred to methylene groups by the Wittig reaction, giving **5** in 94% yield. Oxidation of **5** with dimethyldioxirane at low temperature afforded the corresponding epoxide **6** as a major isomer in 72%. The methoxymethyl-substituted *syn*-tris(norbornadieno)benzene **7** was obtained by ring-opening of **6** with LDA and subsequent protection of the thus-formed hydroxy groups. Ring-opening metathesis reaction of **7** with Grubbs' catalyst (PCy$_3$)$_2$Cl$_2$-Ru=CHPh under ethylene atmosphere resulted in a mixture of several products which were formed by partial ring-opening and



Scheme 1. Reagents and conditions: (a) BuLi 350 mol %, MePPh$_3$I 360 mol %, THF, rt, 4 h, 94%; (b) dimethyldioxirane 600 mol %, acetone, −70–−60 °C, 3 d, 72%; (c) LDA 800 mol %, THF, −40 °C–rt, 16 h; (d) NaH 400 mol %, MeI 400 mol %, THF/DMF, rt, 11 h, 81% from **6**; (e) (PCy$_3$)$_2$Cl$_2$Ru=CHPh 200 mol %, ethylene, CH$_2$Cl$_2$, 40 °C, 10 h; (f) (PCy$_3$)$_2$-Cl$_2$Ru=CHPh 60 mol %, CH$_2$Cl$_2$, 40 °C, 10 h; (g) DDQ 900 mol %, H$_2$O, CH$_2$Cl$_2$, rt, 6 h, 7%.

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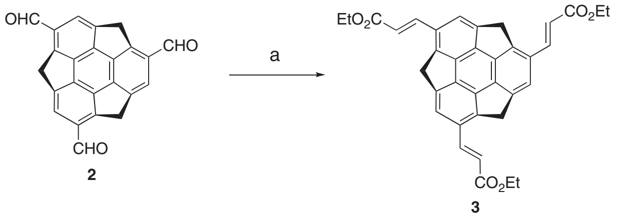

Scheme 2. Reagents and conditions: (a) $(EtO)_2P(O)CH_2CO_2Et$ 600 mol %, Cs_2CO_3 1000 mol %, THF, rt, 2 d, 67%.

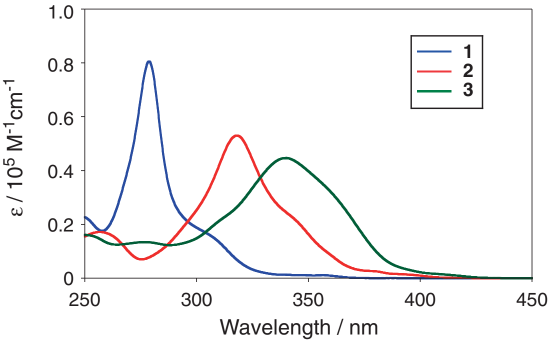

Figure 2. UV–vis absorption spectra of **1** (blue), **2** (red), and **3** (green) in CH_2Cl_2 (1.0×10^{-5} M).

-closing metathesis reactions. The mixture was retreated with Grubbs' catalyst under argon atmosphere and underwent ring-closing metathesis reaction, giving desired hexahydrosumanene **8**. Due to its air-sensitiveness, **8** was subsequently dehydrogenated by DDQ without isolation. Methoxymethyl groups were also oxidized by excess DDQ in one pot, giving triformylsumanene **2** successfully. The formyl groups of **2** show the chemical shift of 10.08 ppm in ^{1}H NMR, that of 191.7 ppm in ^{13}C NMR, and the C=O stretching band of 1685 cm^{-1} in IR, all of which are comparable in the values of the formyl group of 1-fluorenecarboxaldehyde (10.23 ppm in ^{1}H NMR, 192.8 ppm in ^{13}C NMR, 1688 cm^{-1} in IR).

The thus-obtained triformylsumanene **2** is a suitable intermediate to prepare various C_3 symmetric trisubstituted sumanenes through the transformation of formyl groups. As a first example of derivatization, **2** was converted by the Horner–Wadsworth–Emmons reaction with $(EtO)_2P(O)CH_2CO_2Et$ to prepare a conjugated ester **3** in 67% yield (Scheme 2).[9]

The UV–vis absorption spectra and fluorescence spectra of **1**, **2**, and **3** in CH_2Cl_2 are shown in Figures 2 and 3, respectively. The absorption maxima are red-shifted in the order of **1** (279 nm), **2** (318 nm), and **3** (340 nm). The emission maximum also shows the red shift of **1** (376 nm), **2** (424 nm), and **3** (437 nm). Redox potentials of **1** and **3** (vs. Fc/Fc$^+$) were determined by cyclic voltammetry (CV)[6,7] and the HOMO/LUMO potentials of **1** and **3** (Me ester instead of Et ester)[8] were calculated by DFT calculation (B3LYP/6-31G(d)) (Table 1). CV of **1** and **3** shows irreversible cathodic peaks at $E_p{}^c = -3.27$ and -2.26 V and irreversible anodic peaks at $E_p{}^a = 1.00$ and 1.12 V, respectively. The difference ($E_p{}^a - E_p{}^c$) of **1** and **3** shows 4.27 and 3.38 V, respectively. The higher reduction/oxidation potentials of **3** and the narrower difference ($E_p{}^a - E_p{}^c$) of **3** than those of **1** are consistent with the corresponding calculated lower LUMO/HOMO potentials and narrower HOMO–LUMO gap (ΔE) of **3** (Me ester) than those of **1**. The calculated HOMO and LUMO orbitals of **3** (Me ester) are delocalized on the core sumanene skeleton as well as the unsaturated ester substituents (Figure 4).

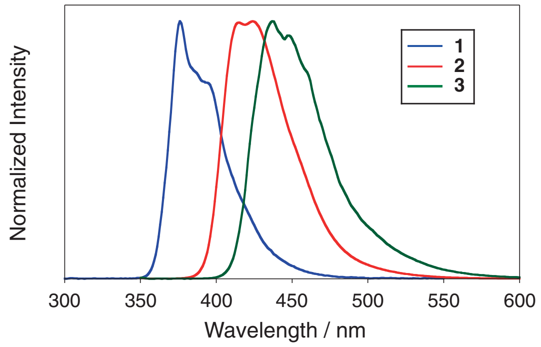

Figure 3. Fluorescence spectra ($\lambda_{ex} = 280$ nm) of **1** (blue), **2** (red), and **3** (green) in CH_2Cl_2 (1.0×10^{-5} M).

Table 1. Reduction ($E_p{}^c$) and oxidation ($E_p{}^a$) potentials (vs. Fc/Fc$^+$), the difference ($E_p{}^a - E_p{}^c$) of **1** and **3** by CV and the calculated HOMO and LUMO potentials, the HOMO–LUMO gaps (ΔE) (B3LYP/6-31G(d)) of **1** and **3** (Me ester)

	Cyclic voltammetry			Calculation		
	$E_p{}^c$/V	$E_p{}^a$/V	$E_p{}^a - E_p{}^c$/V	LUMO/V	HOMO/V	ΔE/V
1	−3.27	1.00	4.27	−0.72	−5.48	4.76
3	−2.26	1.12	3.38	−2.10[a]	−5.89[a]	3.79[a]

[a]Calculated value for **3** (Me ester).

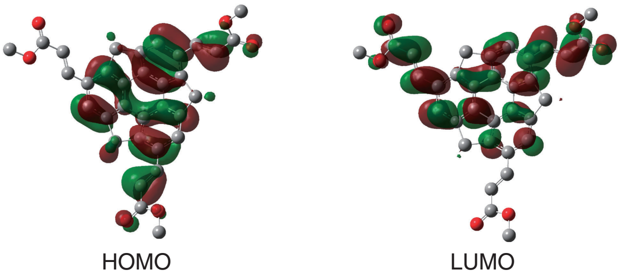

Figure 4. Calculated HOMO and LUMO orbitals (B3LYP/6-31G(d)) of **3** (Me ester).

As described above, we have succeeded in the selective synthesis of C_3 symmetric triformylsumanene **2**, which can be a versatile intermediate for various substituted sumanenes. As an example, we also demonstrated the extension of π-conjugation through the Horner–Wadsworth–Emmons reaction. Substituted sumanene derivatives with C_3 symmetry obtained by this synthetic strategy will help us to investigate the fundamental properties of buckybowls as well as the application to material sciences.

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6 Conditions of CV: 0.1 M Bu_4NClO_4 THF (reduction) and CH_3CN (oxidation), scan rate = $100\,mV\,s^{-1}$, glassy carbon electrode. CV of **2** was not measured because of the poor solubility in THF, DMF, or CH_3CN.

7 CV of **1** in CH_3CN or DMF has been reported: P. Zanello, S. Fedi, F. F. de Biani, G. Giorgi, T. Amaya, H. Sakane, T. Hirao, *Dalton Trans.* **2009**, 9192.

8 DFT calculation of **3** was conducted for the Me ester instead of the Et ester to minimize the calculation cost.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.