Synthesis and characterization of π-extended bowl-shaped π-conjugated molecules†‡

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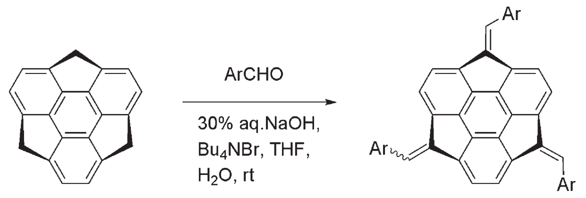
A series of π-extended bowl-shaped π-conjugated compounds were synthesized from sumanene and characterized, and among them the terthiophene derivative showed a remarkable red-shifted absorption and small band gap, which was rationalized by molecular orbital calculation.

The science of non-planar π-conjugated carbon molecules, represented by C_{60} and the carbon nanotube, has been attracting great interest due to their potential utility over interdisciplinary fields, such as electrical materials science, catalysis, and pharmaceutics. In this context, bucky-bowls are now considered to be another group of key materials in the science of curved π-conjugated carbon systems. Most of the investigation in bucky-bowl chemistry has focused on C_{5v} symmetric corannulene and its derivatives.[1] However, the methods to prepare functionalized corannulenes are still limited because the rim of corannulene consists of aromatic double bonds.[2] On the other hand, sumanene (**1**), a partial C_{3v} symmetric structure of fullerenes, is characterized by three benzylic positions, which may allow facile functionalization. In 2003, a synthesis of **1** under nonpyrolytic conditions was developed by our group.[3] Stereoselective trisilylation at the benzylic positions *via* the corresponding trianion was achieved to afford a single diastereoisomer.[4] X-ray analysis showed columnar π-stacking in a concave–convex fashion,[4] suggesting that **1** may be of potential utility as electrically active materials in the solid state. In order to develop sumanene-based bucky-bowl chemistry, the method for carbon–carbon bond formation at its benzylic positions is considered to be an urgent issue. In the present research, 1,2-addition of benzylic anions to various aldehydes was investigated to extend π-conjugation, which is also of interest in view of non-planar π-conjugated carbon chemistry. Herein, we describe the facile synthesis, characterization and DFT calculation of extended π-conjugation systems derived from sumanene.

The condensation of the benzylic anions of **1** with aldehydes was investigated to extend π-conjugation of **1** (Table 1). Various bases were examined for the condensation with benzaldehyde. The use of aqueous 30% NaOH solution as a base in the presence of tetrabutylammonium bromide and a minimum amount of THF gave **2a** quantitatively as both C_3 symmetric and unsymmetric diastereomers. Several substituted benzaldehydes (for **2b–f**) were employed for the condensation reaction to control the electronic state of the π-conjugated systems. Seven derivatives **2a–g** with extended π-conjugation were successfully synthesized in 68% to quantitative yield (Table 1).§ Condensation with [2,2′;5′,2″]terthiophene-5-carbaldehyde gave **2h**. The structures of these derivatives were supported by ^{1}H-NMR, ^{13}C-NMR and FAB-TOF mass spectrometry (HRMS). The color of **2a–f** was yellow in CH_2Cl_2 solution, whereas that of **2g** and **2h** was orange and red, respectively. The diastereomer ratio (C_3 symmetric and unsymmetric ones) of **2b** and **2c** was approximately 1 : 3, which was determined by the peak area of the methyl and methoxy groups of **2b** and **2c**, respectively, in the ^{1}H-NMR spectra.

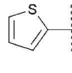
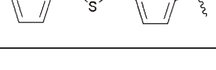
UV–vis and emission spectra of **2a–h** were measured in several solvents. Table 2 summarizes the absorption maxima, emission maxima and HOMO–LUMO band gaps. UV–vis and emission spectra of **1**, **2a**, **2g** and **2h** in CH_2Cl_2 solution are shown in Fig. 1a and Fig. 1b. The absorption maxima λ_{max} of **2a** were observed at 345 and 457 nm assignable to π–π*, which are 67 and *ca.* 150 nm red-shifted, respectively, as compared with those of **1**. On the other

Table 1 Synthesis of **2a–h**



Sumanene (**1**)

2a-h

	Ar	Isolated yield/%
2a	Ph	quant.
2b	4-MePh	quant.
2c	4-MeOPh	quant.
2d	4-ClPh	88
2e	4-CF_3Ph	68
2f	3,4,5-$(MeO)_3$Ph	79
2g		85
2h		57

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† Electronic supplementary information (ESI) available: Compound characterization data (^{1}H-, ^{13}C-NMR, IR and HRMS) for **2a–h**. See DOI: 10.1039/b701322a

‡ This paper is dedicated to the memory of the late Professor Emeritus Yoshihiko Ito.

Table 2 Absorption maxima λ_{max} (nm), emission maxima λ_{max} (nm) and HOMO–LUMO band gaps (eV) of **1** and **2a–h**[a]

	Solvent	Absorption maxima λ_{max} (nm)		Emission maxima λ_{max} (nm)[b]	HOMO–LUMO band gaps (eV)[c]
1	CH_2Cl_2	278	307	376	3.82
2a	CH_2Cl_2	345	457	530	2.38
	CH_3CN	342	454		
	THF	345	457		
	toluene	347	461		
2b	CH_2Cl_2	353	464	534	2.35
2c	CH_2Cl_2	366	470	543	2.33
2d	CH_2Cl_2	352	464	537	2.33
2e	CH_2Cl_2	345	461	539	2.34
2f	CH_2Cl_2	363	461	548	2.32
2g	CH_2Cl_2	373	482	564	2.25
	CH_3CN	370	479		
	THF	373	482		
	toluene	375	485		
2h	CH_2Cl_2	434	545	650	1.99
	THF	435	545		
	toluene	436	544		

[a] Concentration: 1.0×10^{-4} M. [b] Excited at the longer wavelength of the absorption maxima. [c] Estimated from the absorption edges.

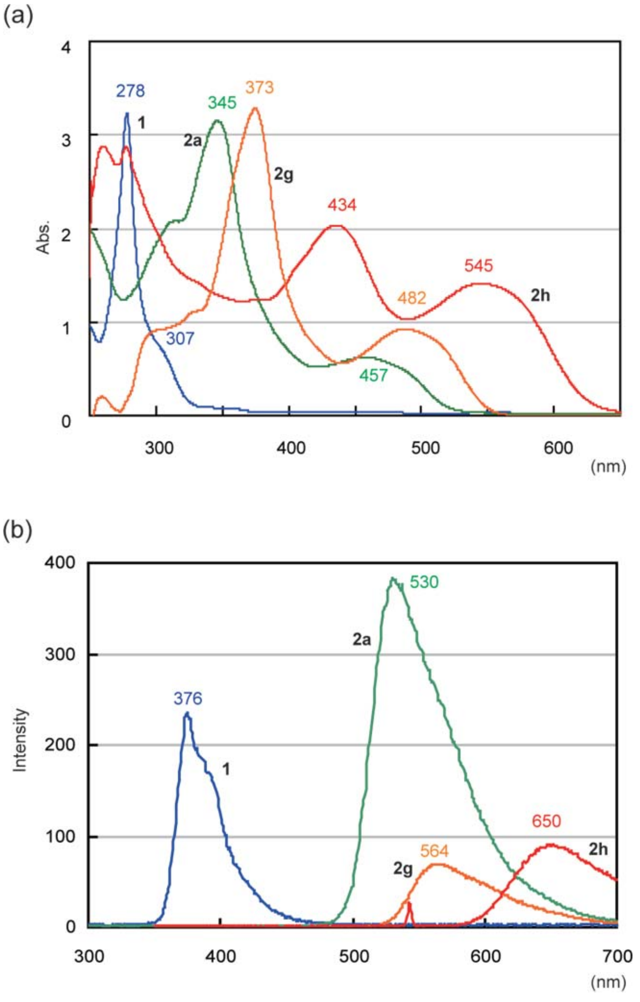
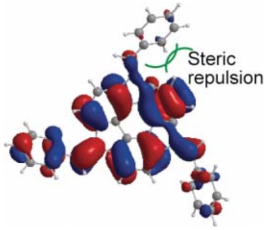
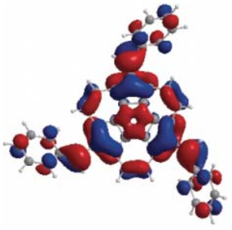
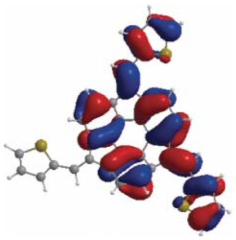
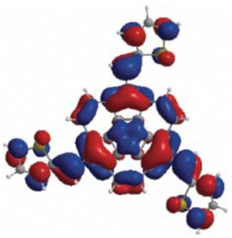
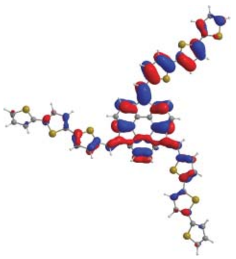
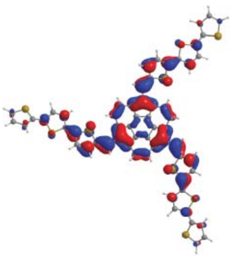


Fig. 1 (a) UV–vis spectra and (b) emission spectra of **1**, **2a**, **2g** and **2h** in CH_2Cl_2 (1.0×10^{-4} M).

hand, there is relatively little difference in the absorptions λ_{max} of **2a–f**. These findings indicate that the substituent effect of the phenyl group to π-conjugation is not so strong. In contrast, the thiophene derivatives **2g** and **2h** showed red-shifted absorptions as compared with those of the benzylidene derivatives. Especially, a remarkable red-shift was observed with **2h** (λ_{max}: 434 and 545 nm), strongly suggesting expanded π-conjugation. Excitation spectra showed that the emission of these compounds is derived from the longest absorption band in the corresponding spectrum. HOMO–LUMO band gaps are estimated from the absorption edges. The band gaps of the benzylidene derivatives **2a–f** appeared in the range of 2.32–2.35 eV, while that of **1** was 3.82 eV. The difference in the band gap values between **1** and **2a–f** is 1.47–1.50 eV. The smaller value was observed with the thiophene derivative **2g** (2.25 eV), and **2h** exhibited the minimum band gap (1.99 eV). In the emission spectra, strong emission was observed with **2a**. On the other hand, the emission intensity of **2g** and **2h** was decreased as shown in Fig. 1b. The solvent effect in UV–vis spectra was investigated in **2a**, **2g** and **2h** using CH_2Cl_2, CH_3CN, THF and toluene, but the observed difference in different solvents was quite small in each spectrum (Table 2).

To discuss the results obtained from the spectroscopic experiments, computational studies were carried out using the B3LYP density functional theory method.[5] Both geometry optimization and single-point energy calculation were performed using a 6-311G** basis set for **1** and **2a–g**, and a 6-31G** basis set for **2h**. The orbital diagrams of the C_3 isomers of **2a**, **2g** and **2h** are drawn in Table 3. Although HOMO and LUMO of **1** are doubly

Table 3 Orbital diagrams of HOMO and LUMO in **2a**, **2g** and **2h**

	Orbital diagrams	
	HOMO	LUMO
2a		
2g		
2h		

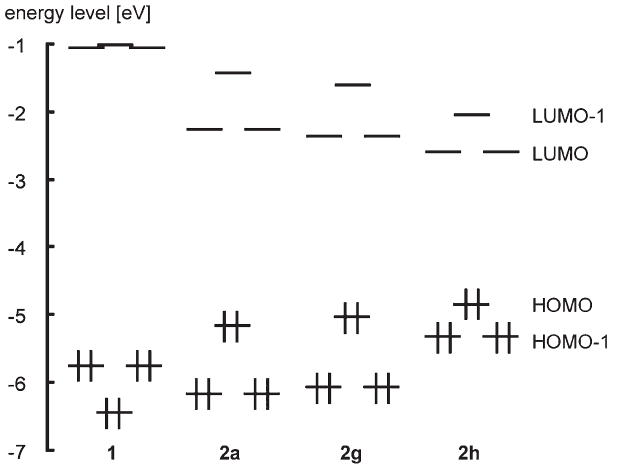


Fig. 2 Energy levels of HOMO-1, HOMO, LUMO and LUMO-1 of **1**, **2a**, **2g** and **2h** calculated by the B3LYP DFT method (6-311G** for **1**, **2a** and **2g**, 6-31G** for **2h**).

degenerate,[6] HOMO and LUMO-1 are doubly degenerate in the case of **2a**, **2g** and **2h** (Fig. 2). The orbital diagram of **2a** suggests that the π-conjugation at external double bonds is suppressed to some extent due to the steric repulsion between the *ortho*-hydrogen of the phenyl group and the aromatic hydrogen of the sumanene moiety (Table 3, HOMO of **2a**). The dihedral angle between the *exo*-double bond and the phenyl plane of **2a** was 29.6°. On the other hand, π-conjugation in **2g** and **2h** was extended from the sumanene moiety to the end of thiophene without the steric repulsion as observed with **2a** (Table 2). In the optimized geometry of **2g** and **2h**, the dihedral angles between the *exo*-double bond and the thienyl plane were 12.1° and 11.4°, respectively, which are much smaller than that of **2a** (29.6°). These results explain the observations in the spectroscopic experiments described above. The tendency of HOMO–LUMO band gaps is also similar to that of the experimental band gaps.

In summary, a facile synthetic method for π-extension at the benzyl positions of sumanene (**1**) was developed using a condensation reaction under mild basic conditions, and the spectroscopic characterization of the π-extended bowl-shaped π-conjugated compounds was investigated. The thiophene derivatives, especially **2h**, showed a remarkable red-shifted absorption and small band gap, which was rationalized by molecular orbital calculation. This study provides a useful route to synthesize a non-planar π-conjugated system based on sumanene. The application to electronic devices is now under investigation.

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Notes and references

§ General procedure for the preparation of π-extended sumanenes **2a–h**: To a 10 mL two-necked reaction bottle were added sumanene (**1**, 5 mg, 0.019 mmol) and Bu_4NBr (6 mg, 0.0095 mmol). After evacuation and purging with Ar for several times, THF (0.1 mL) and 30% aqueous NaOH solution (1 mL) (degassed water was used to prepare the NaOH solution) were added. After stirring for 3 min, ArCHO (5 equiv.) was introduced. After stirring at room temperature for 12 h, the reaction mixture was diluted with water (*ca.* 3 mL), and extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous NH_4Cl and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica-gel chromatography (pentane–CH_2Cl_2) to give the desired product.

1 For accounts, see: (*a*) P. W. Rabideau and A. Sygula, *Acc. Chem. Res.*, 1996, **29**, 235; (*b*) G. Mehta and H. S. P. Rao, *Tetrahedron*, 1998, **54**, 13325; (*c*) Y.-T. Wu and J. S. Siegel, *Chem. Rev.*, 2006, **106**, 4843; (*d*) V. M. Tsefrikas and L. T. Scott, *Chem. Rev.*, 2006, **106**, 4868.
2 Functionalization of corannulenes, see: (*a*) T. J. Seiders, E. L. Elliott, G. H. Grube and J. S. Siegel, *J. Am. Chem. Soc.*, 1999, **121**, 7804; (*b*) A. Sygula, G. Xu, Z. Marcinow and P. W. Rabideau, *Tetrahedron*, 2001, **57**, 3637; (*c*) D. V. Preda and L. T. Scott, *Tetrahedron Lett.*, 2000, **41**, 9633; (*d*) G. H. Grube, E. L. Elliott, R. J. Steffens, C. S. Jones, K. K. Baldridge and J. S. Siegel, *Org. Lett.*, 2003, **5**, 713.
3 H. Sakurai, T. Daiko and T. Hirao, *Science*, 2003, **301**, 1878.
4 H. Sakurai, T. Daiko, H. Sakane, T. Amaya and T. Hirao, *J. Am. Chem. Soc.*, 2005, **127**, 11580.
5 A Gaussian 03 suite of programs was used for the calculations. M. J. Frisch, *et al.*, *Gaussian 03, revision C.02*; Gaussian, Inc.: Wallingford CT, 2004.
6 U. D. Priyakumar and G. N. Sastry, *J. Phys. Chem. A*, 2001, **105**, 4488.