Metal-induced Aggregation-deaggregation Equilibrium Change in Calix[4]arene-appended Bisfullerenes

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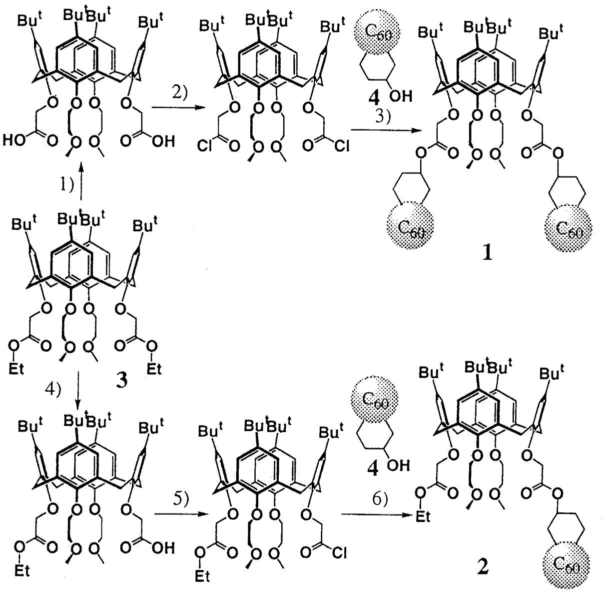
A calix[4]aryl ester containing two C_{60} groups changed the absorption spectra (and thus its visible color) upon changing the solvent from chloroform to chloroform : acetonitrile = 1 : 1 v/v or adding $NaClO_4$. The spectroscopic and light-scattering studies established that the unique behaviors can be rationalized in terms of an aggregation-deaggregation equilibrium change.

The exploitation of fullerene chemistry continues unabated.[1] One problem facing the C_{60} chemist is, however, that C_{60} tends to aggregate in solution,[2,3] which is highly solvent-dependent and makes the C_{60} chemistry complicated and less reproducible. In compound **1** two C_{60} groups are introduced into the same side of a calix[4]arene platform. Therefore, in polar solvents the aggregation of **1** is expected to occur more easily than that of **2** which has only one C_{60} group.[4] Moreover, the deaggregation of **1** may be induced in the presence of Na^+ ion because the solubility of such metal complexes should be improved in polar solvents.[5] In this paper, we report that the solubility change which eventually induces a novel color change really takes place.



Reagents: 1) Me_4NOH, H_2O, THF; 2) $SOCl_2$, pyridine, benzene; 3) **4**, pyridine, benzene; 4) CF_3COOH, $CHCl_3$; 5) $SOCl_2$, pyridine, benzene; 6) **4**, pyridine, benzene

Scheme 1. Synthesis routes and compounds used in this work.

Compounds **1** [meso-**1**, mp > 300 °C (decomp.); race-**1**, mp > 300 °C (decomp.): for symbols of meso and race see below] and **2** (mp 100.0-101.5 °C) were synthesized as shown in Scheme 1 and identified by IR, ^1H NMR and Mass [positive SIMS (*m*-nitrobenzylalcohol, $NaClO_4$): meso-**1**, *m/z* 2453 (M + Na^+); race-**1**, *m/z* 2453 (M + Na^+); **2**, *m/z* 1706 (M + Na^+)] spectral evidence and elemental analyses.

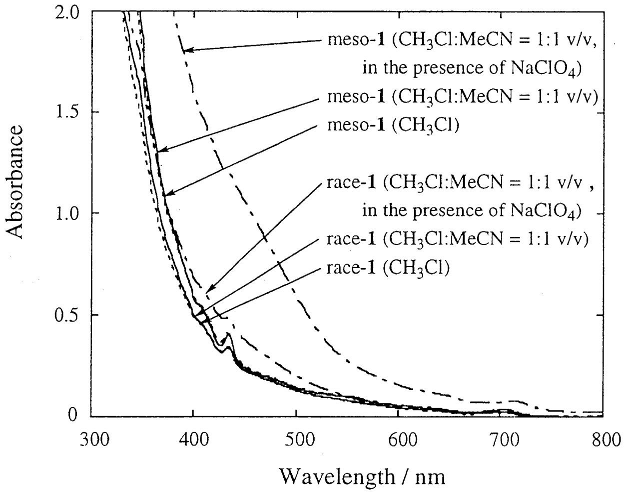


Figure 1. Absorption spectra of meso-**1** and race-**1** (5.00×10^{-5} M at 25 °C: —— in $CHCl_3$, — • — in $CHCl_3$:MeCN = 1:1 v/v, ······ in $CHCl_3$:MeCN = 1:1 v/v in the presence of $NaClO_4$ (1.00 M).

Compound **4** used in the last steps in Scheme 1 is racemic.[6] Thus, the product **1** should become either mesomeric (meso-**1**) or racemic (race-**1**). The TLC separation (silica gel, toluene : ethyl acetate = 20 : 1 v/v) gave two isolated products with $R_f = 0.38$ and 0.35 approximately in a 1 : 1 ratio. In ^1H NMR spectroscopy (25 °C, $CDCl_3$) the MeO protons for $R_f = 0.38$ appeared as one singlet peak (3.53 ppm) whereas those for $R_f = 0.35$ appeared as two singlet peaks (3.49 and 3.63 ppm). The results establish that the former is race-**1** and the latter is meso-**1**.

Firstly, we examined the solvent effect on the absorption spectra of meso-**1**, race-**1** and **2**. As shown in Figures 1 and 2, the significant spectral difference among these three compounds was not observed in chloroform. In chloroform : acetonitrile = 1 : 1 v/v and chloroform : methanol = 1 : 1 v/v which are poorer solvents for C_{60} than chloroform itself,[7] the absorbance for meso-**1** and race-**1** increased over wide wavelength region and the spectral change in meso-**1** was much greater than that in race-**1**. This spectral change was visually detectable as a color change from faint brown to deep brown. When $NaClO_4$ (10 M: 5.0 equivalents to **1** or **2**) was added to chloroform solutions of meso-**1**, race-**1** and **2**, the association with Na^+ could be detected by ^1H NMR spectroscopy,[8] but the solution color (faint brown) was unaffected. In contrast, when $NaClO_4$ was added to these poor mixed solvent solutions, the deep brown color disappeared in the chloroform-acetonitrile mixture but was affected to a smaller extent in the chloroform-methanol mixture (Figures 1 and 2). It is seen from Figures 1 and 2 that the spectral change in meso-**1** is again greater than that in race-**1**. The association constant for meso-**1** in chloroform : acetonitrile = 1 : 1 v/v determined from a plot of A_{434} *vs.* [$NaClO_4$] assuming the formation of a 1 : 1 complex was 2.29×10^3 M (correlation

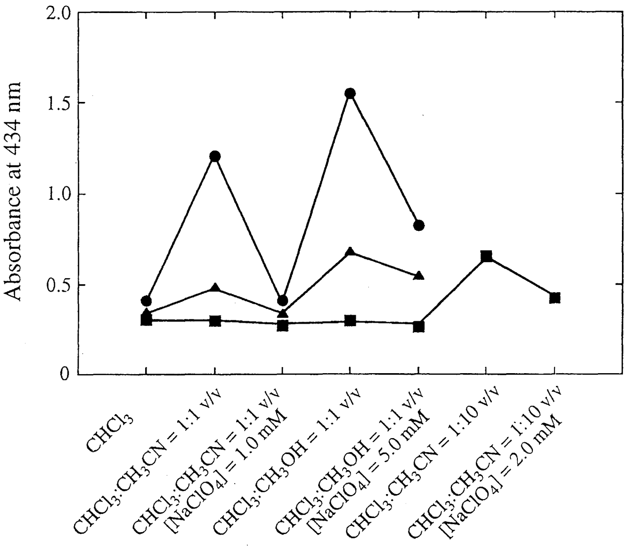


Figure 2. Solvent-induced and $NaClO_4$-induced spectral changes of meso-**1**, race-**1**, and **2** (●, meso-**1**, 5.00×10^{-5} M at 25 °C; ▲, race-**1**, 5.00×10^{-5} M at 25 °C; ■, **2**, 1.00×10^{-4} M at 25 °C).

coefficient > 0.99). For **2**, in contrast, such solvent-induced and $NaClO_4$-induced spectral changes were not observed (Figure 2).

Why is such a color change induced in poorer solvents or in the presence of $NaClO_4$? C_{60}-Derivatives covalently-linked to ionophoric crown ethers or cryptands have been synthesized.[3,5,9-11] However, alkali metal cations bound to these ionophoric sites cannot directly affect the absorption spectra of the C_{60} moiety. Thus, the first possible rationale is an *intramolecular* event which features the distance change between two C_{60}'s. The second possible rationale is an *intermolecular* event which features the aggregation-deaggregation. To estimate the feasibility of the second possibility, we measured the molecular-weight in solution by a light-scattering method (Otsuka Electronics DLS-7000). In chloroform the formation of the aggregate particle was not observed for meso-**1**, race-**1** and **2**. Since the smallest particle diameter detectable by this method is 10 nm, one can regard that they exist discretely in chloroform. In the mixed solvents meso-**1** and race-**1** aggregate into the particles with 240-390 nm diameter (Table 1). On the other hand, the particle formation was not observed for **2** even in these mixed solvents. When $NaClO_4$ was added, the particles of meso-**1** and race-**1** in the chloroform-acetonitrile mixture disappeared but those in the chloroform-methanol mixture were scarcely affected. Therefore, the behaviors observed in absorption spectroscopy and light-scattering commonly support the view that the second possibility is responsible for the unique color change.

If the color change is attributable to the intermolecular event, it should be also observable for **2** in the high **2** concentration or in high acetonitrile concentration solution. To corroborate this we increased the acetonitrile percentage in chloroform and finally found that the similar color change can be induced at [**2**] = 1.00 X 10^{-4} M in chloroform : acetonitrile = 1 : 10 v/v (Figure 2).

Table 1. Average particle sizes (nm) determined by a light-scattering method at 25 °C in the absence and the presence of $NaClO_4$ (M)[a]

Compound	$CHCl_3$	$CHCl_3$-MeCN (1 : 1 v/v)		$CHCl_3$-MeOH (1 : 1 v/v)	
	[$NaClO_4$] = 0	[$NaClO_4$] = 0	2.0	[$NaClO_4$] = 0	10.0
Meso-**1**	N. d.	280±80	N. d.	390±180	400±250
Race-**1**	N. d.	240±50	N. d.	250±50	270±140
2	N. d.	N. d.	N. d.	N. d.	N. d.

[a] N. d. denotes that the formation of aggregated particles was not detected.

In conclusion, this paper demonstrates that **1** bearing both solvophobic C_{60} groups and a solvophilic calix[4]arene moiety within a molecule acts as a unique amphiphilic compound in certain organic solvents. The solvatochromic color change thus observed is primarily ascribable to a change in the aggregation-deaggregation equilibrium induced by solvents or added $NaClO_4$. Thus, the paper clearly indicates that the reproducible data about the solution properties of C_{60} derivatives are obtainable only when the aggregation properties are well understood. We believe, as future prospects, that this system may be useful not only as a novel metal sensing system but also as a new methodology to control the aggregation properties of C_{60} derivatives.

References and Notes

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8 400 MHz, 25 °C, $CDCl_3$: δ_H (ppm) values of Ar*H*, $C_{60}CH_2C\mathit{H}O$ and $C_{60}CH_2C\mathit{H}$ in the absence (and the presence) of $NaClO_4$ are 6.66 (7.22), 6.30 (6.56) and 2.73 (3.05) for meso-**1**, 6.67 (7.17), 6.29 (6.54) and 2.69 (3.03) for race-**1** and 6.72 (7.13), 6.24 (6.95) and 2.69 (3.02) for **2**. The assignments were accomplished according to 2D-COSY.
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