

Preparation and characterization of a novel dumbbell-type [60]fullerene dimer containing a cyanine dye

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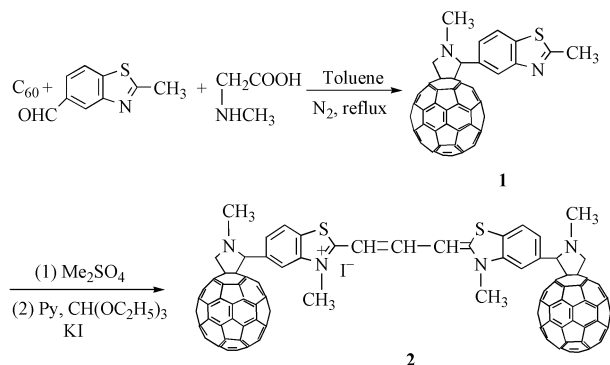
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Two [60]fullerene units were covalently linked by a cyanine dye to form a novel dumbbell-type molecule whose structure was observed by STM.

Fullerene chemistry has been developing rapidly because of the potential applications in materials science.¹ Covalently linked C₆₀ dyads have received much attention because the design of dyads bearing covalently linked strong electron donors or acceptors in close proximity to the C₆₀ surface provides a valuable approach to artificial photosynthesis and novel molecular electronic devices.² At present, much research focuses on the synthesis, characterization and properties of these covalently linked C₆₀ dyads:³ C₆₀-donor dyads such as TTF (tetrathiafulvalene) linked C₆₀, and C₆₀-acceptor dyads such as TCNQ (tetracyano-*p*-quinodimethane) linked C₆₀. However, the synthesis and characterization of dimers and oligomers containing two or more [60]fullerene units has been reported to a lesser extent,^{3,4} because they are more difficult to synthesize and characterize. To our knowledge, no compounds containing a cyanine dye covalently connected to two [60]fullerene units have been reported. Here, we report the synthesis, through the 1,3-dipolar cycloaddition reaction between azomethine ylides and [60]fullerene, of a novel dumbbell-type [60]fullerene dimer containing a cyanine dye, and its characterization, including STM observation of the structure.

Results and discussion

The synthesis of compound **1** is shown in Scheme 1. [60]Fullerene, sarcosine and 5-formyl-2-methylbenzothiazole are dissolved and stirred in dry toluene, followed by heating to reflux



Scheme 1

under nitrogen to give compound **1** in 60% yield (based on converted C₆₀). The dumbbell-type triad compound **2** is obtained in 15% yield through a coupling reaction of compound **1** to itself. The new compound **2** can be dissolved in chloroform, dichloromethane, 1,1,2-trichloroethane, DMF and DMSO, however, the solubility in these solvents is low.

All the spectroscopic data are consistent with the molecular structure of compound **1**. The redox potentials of compound **1** (Fig. 1) were determined by cyclic voltammetry in a dichloromethane solution containing 0.1 M TBAPF₆; the halfwave redox potentials at -0.69, -1.08 and -1.45 V are attributed to the C₆₀ moiety while the peaks at -0.40, -0.54, -0.92 and -1.29 V are attributed to the cyanine dye.

Compound **2** was characterized by FT-IR, UV-Vis, ¹H-NMR and MALDI-TOF mass spectra. In the FT-IR spectrum, a band due to C₆₀ is observed at 527 cm⁻¹, and the C-H stretching bands are at 2923, 2851 and 2783 cm⁻¹.

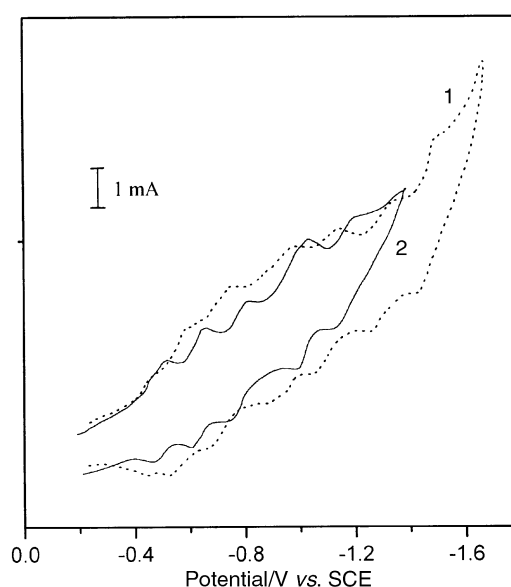


Fig. 1 The cyclic voltammograms of compounds **1** (dotted line) and **2** (solid line) in dichloromethane containing 0.1 M TBAPF₆ at room temperature, scan rate 100 mV s⁻¹.

The MALDI-TOF mass spectrum shows a molecular ion peak at m/z 2014.02 ($[M - H]^+$ for $C_{145}H_{27}N_4S_2I$, calc. 2015.08). The halfwave redox potentials determined by CV at -0.62 and -1.01 V arise from the C_{60} while the peaks at -0.50 , -0.76 and -1.16 V come from the cyanine dye.

The cyclic voltammetry measurements of compounds **1** and **2** show, in addition to the reduction waves corresponding to the reduction steps of the [60]fullerene unit, the presence of reversible two- and one-electron reduction waves for the cyanine dyes. The first reduction potentials for these fulleropyrrolidines are remarkably shifted to more positive values in comparison with the parent C_{60} .

Fig. 2 shows the UV-Vis spectra of compounds **1** and **2** and of the pure cyanine dye. As can be seen, the UV-Vis spectrum of compound **2** displays strong absorptions corresponding to cyanine dye and [60]fullerene moieties. In compound **2**, the maximum in absorption at 582 nm, arising from the cyanine dye in the compound, shows a significant redshift of 25 nm relative to the absorption of pure cyanine dye at 557 nm.⁵

The molecular structure of compound **2** was also studied by STM. Fig. 3(a) shows a typical atomic resolution STM image of the highly oriented pyrolytic graphite (HOPG) surface, with a lattice parameter $a = 2.5 \pm 0.5$ Å, which correlates with the value of $\sqrt{3} d_{C-C} = 2.46$ Å.⁶ After placing a drop of a 10^{-3} mM solution of **2** onto HOPG, a single molecular image of compound **2** was obtained, as shown in Fig. 3(b). Fig. 3(c) shows a linear array of compound **2** on the HOPG surface. Fig. 3(c) also shows that the center-to-center distance of the C_{60} molecules is nearly 22–23 Å. The molecules appear as a bent bridge chain with an angle of 63° . The intermolecular distance is relatively uniform with an average distance of about

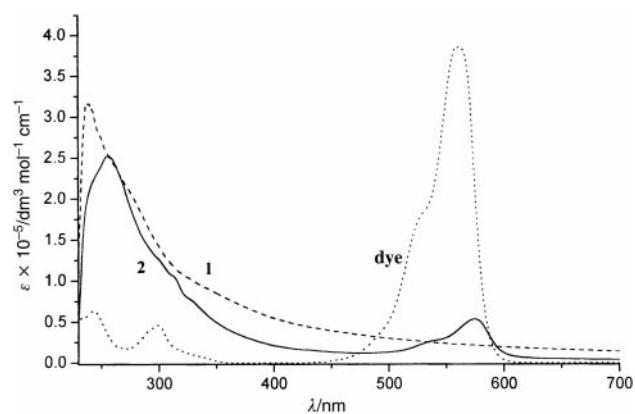


Fig. 2 The UV-Vis spectra of **1** (dashed line), **2** (solid line) and the cyanine dye (dotted line) in dichloromethane and acetonitrile at room temperature.

3.4–3.7 nm, which is much longer than the typical intermolecular distance in van der Waals crystals (0.3–0.5 nm). This kind of molecular alignment is probably induced by a molecular charge effect. As shown in Scheme 1, compound **2** is charged, with an iodine counteranion; therefore, electrostatic forces between molecules may induce such an arrangement. Fig. 3(d) is a magnification of Fig. 3(c), giving a much clearer picture of the molecular array.

Molecular mechanics calculations for compound **2** were performed using the DREIDING 2.21 force field. The calculated distance between the two [60]fullerene units is 21.22 Å and the angle between the two pyrrolidene rings is 58.8° . The

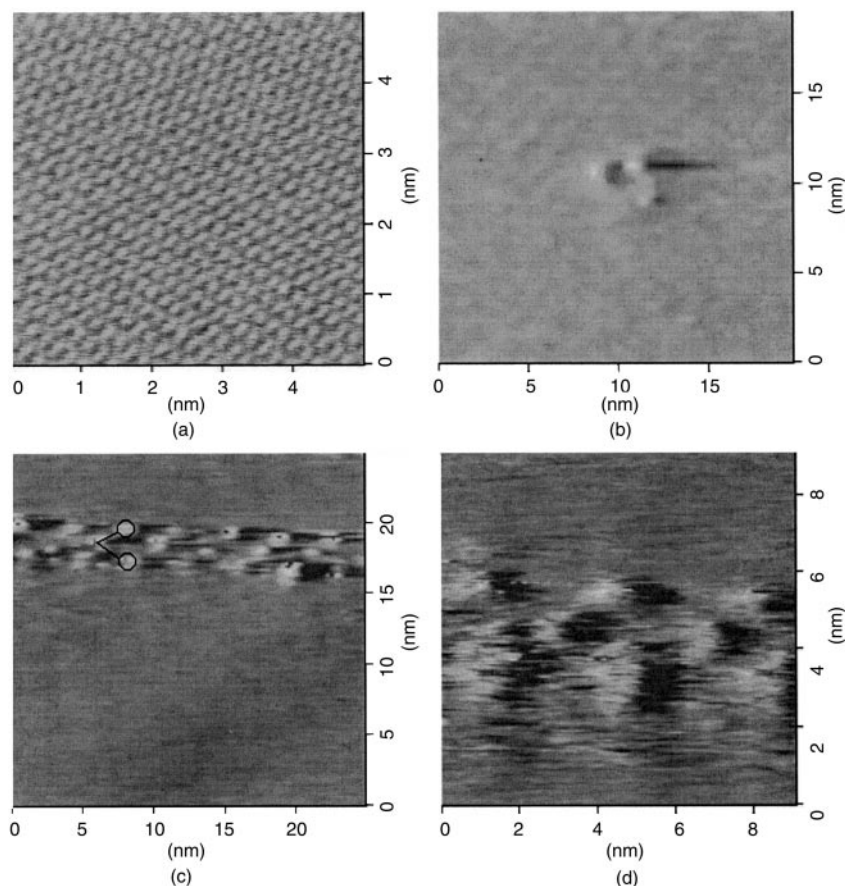


Fig. 3 (a) Atomic resolution STM 5 nm \times 5 nm current image of HOPG, $I = 0.62$ nA, $V_b = 0.008$ V; (b) 20 nm \times 20 nm STM image of a single molecule of compound **2**; (c) 25 nm \times 25 nm STM image of an orderly self-organized array of molecules of **2**; (d) 9 nm \times 9 nm zoomed image of (c). For (b)–(d) $I = 0.12$ nA and $V_b = 0.08$ V.

calculated results are roughly in agreement with the experimental values obtained by STM.

In conclusion, we have synthesized a novel dumbbell-type C₆₀ dimer containing a cyanine dye. All of the spectroscopic studies and STM images are consistent with the proposed molecular structure. Further studies on the characterization, properties and possible applications of the products are ongoing in our laboratory.

Experimental

Methods

Cyclic voltammetry. All the CV experiments were performed at room temperature in solutions containing 0.1 M TBAPF₆ as supporting electrolyte and with a Pt disk of 3 mm diameter as the working electrode. The counter-electrode was a Pt plate and an SCE was used as the reference electrode. The concentration of compounds **1** and **2** was 10⁻⁴ M. The solutions were magnetically stirred for 5 min, then argon was purged through the working solutions for 3 min to deoxygenate them prior to the electrochemical experiments. During measurements, Ar gas was kept above the solutions.

STM experiments. Scanning tunneling microscope (STM) images were obtained with a SPA300HV STM unit (Seiko Instruments, Inc.), operated in air at room temperature, using Pt/Ir tips. Atomic scale images were obtained in the 2 channel simultaneous scan mode; the images shown here are the raw current topography data. A freshly cleaved, highly oriented pyrolytic graphite (HOPG) surface was imaged first. Tip voltage and tunneling current applied to HOPG were fixed at +80 mV and 0.62 nA, respectively, while those applied to organic samples were fixed at +80 mV and 0.12 nA. As is commonly reported when measuring molecular organic single films, very low values of the tunneling current were sufficient. Scanning speeds were adjusted within 8–16 Hz.

Molecular mechanics calculations. All the calculations, structures and 3D models were performed and visualized on a Silicon Graphics O₂ workstation using the program Cerius², version 3.0, developed by Molecular Simulations Inc. (San Diego, CA, USA).

Syntheses

Compound 1. Compound **1** was prepared by the following method:⁷ 10.6 mg (0.06 mmol) of 5-formyl-2-methyl-benzothiazole, 28.8 mg of [60]fullerene and 7.1 mg of sarcosine were dissolved in 40 ml of dry toluene. The resulting solution was stirred and refluxed for 6 h under nitrogen. After cooling to room temperature, the brown solution was concentrated on a rotary evaporator. The raw solid product was purified by column chromatography on silica gel eluted with a mixed solvent of toluene and ethyl acetate (8 : 1 v/v, R_f = 0.68) to give 9.1 mg of compound **1** in a yield of 25% (yield 60% based on converted C₆₀). Selected data for compound **1**: ¹H-NMR (300 MHz, CDCl₃, 25 °C) δ_H: 2.84 (s, 3H), 2.88 (s, 3H), 4.35 (d, 1H), 5.22 (d, 2H), 7.13 (t, 2H), 7.9 (s, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ_C: 168.81 (C=N), 153.22, 152.39, 147.43,

146.40, 146.33, 146.23, 146.03, 145.85, 145.77, 145.66, 145.50, 145.42, 145.36, 144.91, 144.55, 144.39, 143.15, 142.76, 142.69, 142.35, 142.26, 142.18, 142.05, 141.74, 141.58, 140.26, 135.75, 136.68, 125.88, 123.66, 122.30, 83.53, 68.95, 68.48, 39.99, 20.09; UV-Vis (CH₂Cl₂) λ_{max}/nm: 256, 327, 430; MALDI-TOF *m/z*: 923.07 [M – H]⁺; FT-IR ν/cm⁻¹: 2946, 2780, 1644, 1525, 1428 (C₆₀), 1177, 1024, 527 (C₆₀).

Compound 2. Compound **2** was synthesized as follows: 54 mg (0.06 mmol) of compound **1** and 1 ml of dimethyl sulfate were placed in a 5 ml bottle flask. The mixture was stirred and heated at 140 °C under nitrogen for 2 h. The mixture was cooled to room temperature and diethyl ether was added to the solution. The precipitate was filtered off and transferred to a 5 ml round-bottom flask containing 3 ml of pyridine, 100 mg of ethyl orthoformate and 200 mg of potassium iodide; the combined mixture was stirred and heated to reflux under nitrogen for 4 h. The pyridine was evaporated by rotary evaporation and crude compound **2** was obtained. The crude compound **2** was washed with ethanol and benzene using a Soxhlet apparatus to give the pure compound **2** [TLC indicated only one spot, R_f = 0.6, using chloroform–methanol (5 : 1 v/v) as the developing agent]. The yield was about 15%. Selected data for compound **2**: ¹H-NMR (300 MHz, CDCl₃, 25 °C) δ_H: 2.90 (s, 3H), 2.99 (s, 3H), 3.31 (s, 6H), 4.64 (s, 2H), 4.81 (s, 2H), 5.75 (s, 1H), 5.94 (s, 1H), 7.48 (t, 1H), 7.51 (d, 1H), 7.54 (d, 1H), 8.05 (d, 2H), 8.35 (d, 2H), 8.88 (s, 1H), 9.07 (s, 1H); UV-Vis (CH₂Cl₂) λ_{max}/nm: 256, 574; MALDI-TOF *m/z*: 2014.02 [M – H]⁺; FT-IR ν/cm⁻¹: 2923, 2851, 2783, 1634, 1533, 1456, 1429 (C₆₀), 1392, 1249, 1211, 1181, 1023, 796, 527 (C₆₀).

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