Synthesis and Mesomorphic Property of Novel Discotic C_{60}-Triphenylene Derivative

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Abstract: By reacting monohydroxytriphenylene **2** with 1,6-dibromohexane and then condensating with 4-hydroxybenzaldehyde, triphenylene derivative with mono-aldehyde group **4** was prepared in ideal yield. Further treating compound **4** with C_{60} and sarcosine, the novel discotic C_{60}-triphenylene derivative **5** was prepared by 1,3-dipolar cycloaddition in a yield of 35%. DSC analysis and observation with polarized optical microscopy indicated that compound **5** possessed mesomorphic property.

Keywords: 1,3-dipolar cycloaddition, fullerene, liquid crystal, synthesis, triphenylene.

Fullerene has received considerable attention and much research interest due to its unique structure and interesting properties [1-3]. Many functional groups have been introduced, often region- or stereoselectively, for tuning of the physical properties of C_{60} and for construction of supramolecular architectures [4-6]. Among all kinds of C_{60} derivatives, the discotic molecule-substituted C_{60} derivatives showed interesting properties, especially, liquid crystal properties. Up to now, few C_{60} derivatives with discotic-molecular groups and their liquid crystal properties were studied. In 1998, Deschenaux reported the first mesomorphic C_{60}-ferrocene derivative [7]. Tian synthesized a C_{60}-perylene derivative in 2004 [8]. Nakanishi prepared a series of uncommon liquid C_{60} derivatives with 2,4,6-tris(alkyloxy) benzal groups in 2006 [9]. Lately, Geerts described the synthesis of mesogenic phthalocyanine-C_{60} [10]. Triphenylene was one of the most important discotic molecules with exciting mesomorphic properties. However, due to the difficult *muti*-step synthetic procedures, only two C_{60}-triphenylene derivatives were obtained by Bingel-type reaction with outstanding liquid crystal properties of self-assembled columns [11, 12]. Besides these two researches, the studies on the synthesis and properties of other C_{60}-triphenylene derivatives are unknown so far. In this paper, we wish to report the design and synthesis of a new kind of C_{60}-triphenylene derivative by 1, 3-dipolar cycloaddition of the azomethine ylide generated *in situ* from aldehyde and sarcosine.

1, 3-dipolar cycloaddition was a typical reaction for preparing C_{60} derivatives [5], however, this reaction was not applied to preparing C_{60}-triphenylene derivative so far. Thus, we designed a synthetic route using this reaction to prepare novel C_{60}-triphenylene **5** as demonstrated in Scheme **1**. The monohydroxytriphenylene **2** was prepared by oxidation of 1, 2-dipentyloxylbenzene with $FeCl_3$ and then selective ether cleavage with B-bromocatechol-boronane following literature method [13]. Reacting compound **2** with excess 1, 6-dibromohexane under K_2CO_3/MeCN system afforded ω-bromo-substituted triphenylene **3** in 70% yield after column chromatography. Subsequently, the triphenylene derivative **4** with terminal aldehyde group was prepared in 75% yield by condensating compound **3** with 4-hydroxybenzaldehyde in K_2CO_3/MeCN system after column chromatography. Further, by treating compound **4** with sarcosine and C_{60} in refluxing toluene, the novel discotic C_{60}-triphenylene derivative **5** was obtained in 35% isolated yield *via* 1,3-dipolar cycloaddition of azomethine ylides to C_{60} after column chromatography. Although the *muti*-step synthetic procedures and purification with column chromatography, novel discotic C_{60}-triphenylene derivative **5** was still obtained in reasonable yield. To the best of our knowledge, compound **5** was the first example of discotic C_{60}-triphenylene derivative **5** obtained by 1,3-dipolar cycloaddition, although other two C_{60}-triphenylene derivatives were synthesized by Bingel-type reaction [11, 12].

The structures of new compounds **3**, **4** and **5** were characterized by element analyses, UV, IR, ESI-MS, ^{1}H NMR and ^{13}C NMR spectra. The UV spectrum of compound **5** was showed in Fig. (**1**). It could be seen the typical absorption features of mono-fulleropyrrolidine at 256, 309 and 432 nm. The ESI-MS spectrum of compound **5** showed corresponding molecular ion peak at 1626.48. The ^{1}H NMR spectrum of compound **5** was showed in Fig. (**2**) and all the protons in compound **5** were assigned well. Especially, the typical split of NCH_2 (a and a') on pyrrole ring and ArH (c and d) were observed clearly. Although the ^{13}C NMR spectrum of compound **5** showed complicated peaks in 133~148 ppm due to the overlapped signals of carbon on the skeleton of triphenylene and C_{60}, the peaks of NCH_2 at 68.04 ppm and 69.05 ppm, NCH_3 at 40.08, NCH at 83.27 ppm certainly supported the structure of compound **5**. All these typical characterization of spectrum were similar to structures of mono-fulleropyrrolidine in literatures [4, 6, 12, 13].

The mesomorphic behavior of compound **5** was preliminarily studied by DSC and the phase texture was investigated

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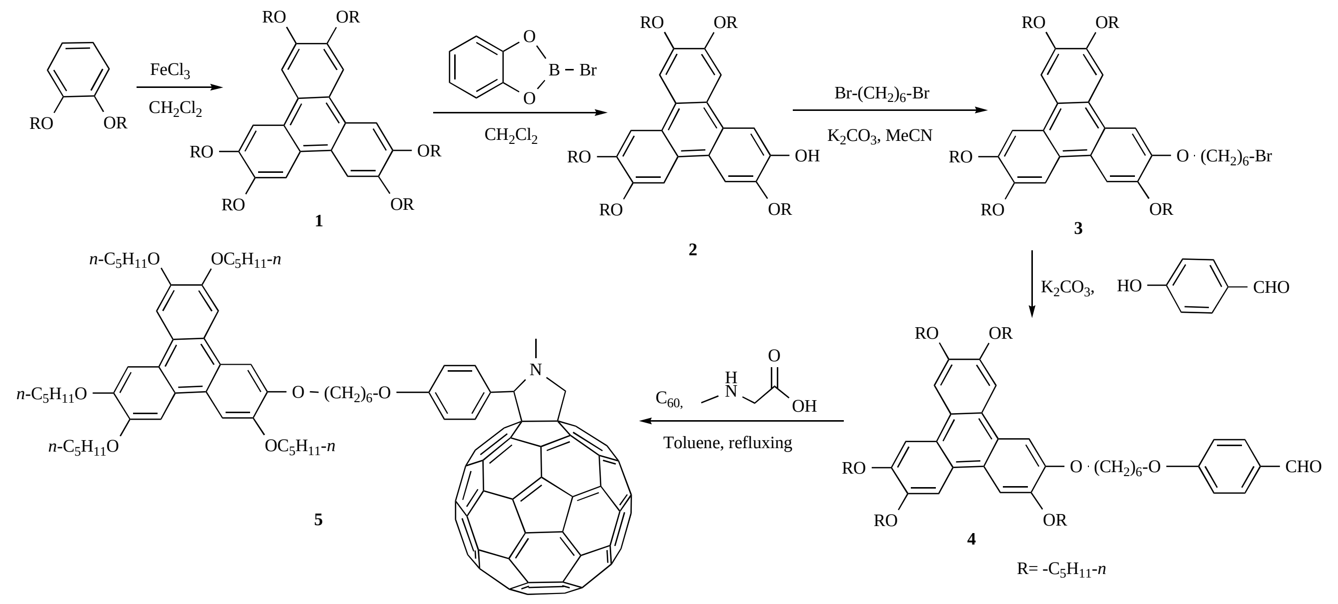

Scheme 1. The synthetic route of triphenylene-C_{60} derivative **5**.

under polarized optical microscopy. Results showed that compound **5** possessed mesomorphic property, which was confirmed by the two endothermic peaks at 76.6°C and 90.6°C in the DSC measurement and the mesomorphic texture under POM at 85°C as showed in Fig. (**3**). The in-depth studies on liquid crystal properties and electrochemistry property based on the large conjugation action between triphenylene unit and C_{60} unit, will be investigated in the following work.

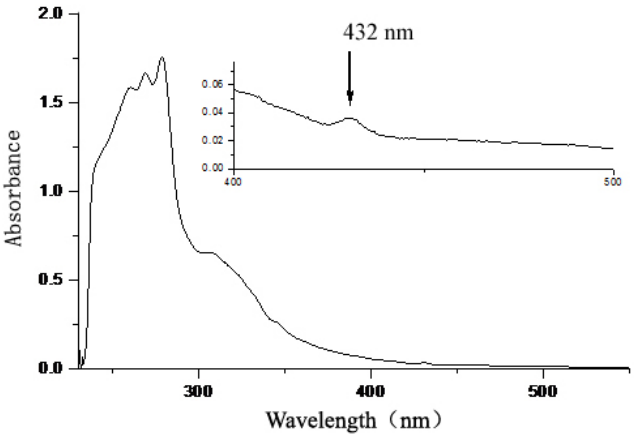

Fig. (1). UV-vis absorption spectrum of novel discotic C_{60}-triphenylene derivative **5**.

The Procedure for Synthesis of Compound 3

Compound **2** (1.35 g, 2 mmol) and 1,6-dibromohexane (1.22 g, 5 mmol) with K_2CO_3 (0.97g, 7 mmol) were refluxed in 50 mL acetonitrile overnight and purged with N_2. After reaction, the mixture was filtered and evaporated to dryness by rota-vapor. Then the mixture was further purified by column chromatography (SiO_2 100-200 mesh, petroleum ether / CH_2Cl_2 (10:1, *V*/*V*) as eluant). Compound **3** was obtained as gray soft solid in yield of 70%. Compound **3**: ^1H NMR (600 MHz, $CDCl_3$) δppm: 0.98 (t, 15H, *J* = 6.6Hz, CH_3), 1.42~1.98 (m, 38H, CH_2), 3.46 (t, 2H, *J* = 6.0Hz, $BrCH_2$), 4.23 (t, 12 H, *J* = 6.6Hz, OCH_2), 7.84 (s, 6H, ArH); MS *m*/*z* (%): 836.24 (M^+, 100). Anal. calcd for $C_{49}H_{73}O_6Br$: C 70.22, H 8.78; found C 70.15, H 8.84.

The Procedure for Synthesis of Compound 4

Compound **3** (0.84 g, 1 mmol) and 4-hydroxybenzaldehyde (0.31 g, 2.5 mmol) with K_2CO_3 (0.35 g, 2.5 mmol) were refluxed in 50 mL MeCN overnight and purged with N_2. After reaction, the mixture was filtered and evaporated to dryness by rotavapor. Then the mixture was further purified by column chromatography (SiO_2 100-200 mesh, petroleum ether / CH_2Cl_2 (5:1, *V*/*V*) as eluant). The compound **4** was obtained as grayish solid in yield of 75%. Compound **4**: ^1H NMR (600 MHz, $CDCl_3$) δppm: 0.98 (t, 15H, *J* = 6.6Hz, CH_3), 1.44~1.96 (m, 38H, CH_2), 4.07 (t, 2H, *J* = 6.0Hz, OCH_2) , 4.24 (m, 12 H, OCH_2), 6.98 (d, 2H, *J* = 8.4Hz, ArH), 7.81 (d, 2H, *J* = 8.4Hz, ArH), 7.84 (s, 6H, ArH), 9.87 (s, 1H, ArCHO); MS *m*/*z* (%): 878.68 (M^+, 100). Anal. calcd for $C_{56}H_{78}O_8$: C 76.50, H 8.94; found C 76.44, H 8.89.

The Procedure for Synthesis of Compound 5

A mixture of compound **4** (0.44g, 0.5 mmol), C_{60} (0.36 g, 0.5 mmol), and sarcosine (0.45g, 5 mmol) in dry toluene (200 mL) was refluxed for 48 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue was further purified by column chromatography (SiO_2 100-200 mesh, petroleum ether / CH_2Cl_2 (1:1, *V*/*V*) as eluant). Compound **5** was obtained as brown solid in yield of 35%. Compound **5**: ^1H NMR (600 MHz, $CDCl_3$) δppm: 0.96 (t, 15H, *J* = 6.0Hz, CH_3), 1.45~1.96 (m, 38H, CH_2), 2.77 (s, 3H, NCH_3), 3.99 (t, 2H, *J* = 6.6Hz, OCH_2) , 4.22 (m, 13H, OCH_2 and NCH_2), 4.84 (s, 1H, ArCH), 4.95 (d, 1H, *J* = 9.6 Hz, NCH_2), 6.94 (d, 2H, *J* = 10.8Hz, ArH), 7.67 (br s, 2H, ArH), 7.82 (br s, 6H,

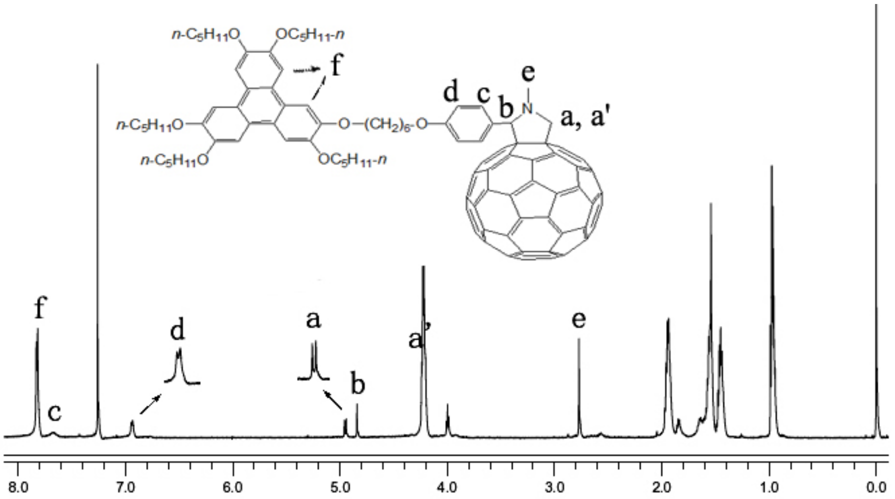

Fig. (2). ^{1}H NMR spectrum of novel discotic C_{60}-triphenylene derivative **5**.

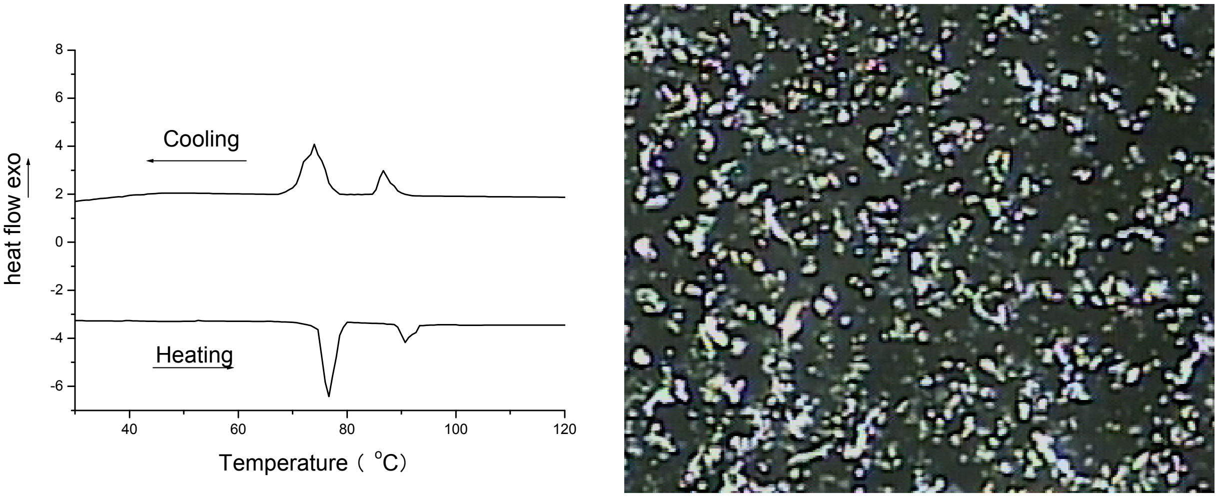

Fig. (3). DSC trace of **5** (scan rate 10°C min^{-1}) and texture of **5** under POM at 85°C (×200).

ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δppm: 14.42, 22.84, 26.26, 26.32, 28.65, 29.38, 29.40, 29.61, 29.71, 40.08, 68.04, 69.06, 69.81, 69.88, 69.94, 69.99, 70.05, 83.27, 107.66, 107.76, 123.93, 123.98, 124.03, 129.01, 135.87, 135.94, 136.65, 136.91, 139.67,139.97, 140.18, 141.64, 141.74, 141.91, 142.06, 142.08, 142.10, 142.19, 142.24, 142.33, 142.39, 142.62, 142.67, 142.75, 143.01, 143.10, 143.23, 144.46, 144.69, 144.78, 145.20, 145.29, 145.34, 145.39, 145.41, 145.48, 145.54, 145.56, 145.62, 145.87, 145.98, 146.00, 146.16, 146.20, 146.22, 146.27, 146.36, 146.38, 146.53, 146.56, 146.91, 147.35, 147.36, 149.25, 149.28. FT-IR (KBr) v / cm^{-1}: 2931, 2858, 1614, 1510, 1433, 1384, 1261, 1170, 1036, 839, 767; MS m/z (%): 1626.48 (M^+, 20). Anal. calcd for $C_{118}H_{83}O_7N$: C 87.11, H 5.14, N 0.86; found C 87.03, H 5.10, N 0.79.

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