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Synthesis and photophysical properties of a single bond linked tetracene dimer

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ABSTRACT

A tetracene dimer linked directly by a single bond has been successfully prepared by using electron withdrawing groups to improve the stability. The molecular structure of this dimer is characterized by ^{1}H NMR, MALDI-TOF mass spectroscopy, and elemental analysis. The minimized molecular structure and X-ray crystallography reveal that the tetracene subunits of this dimer adopt an orthogonal configuration. Its absorption spectrum differs significantly from that of its monomeric counterpart, suggesting the presence of strong interactions between the two tetracene subunits. The excited state of this dimer is delocalized on both two tetracene subunits, which is significantly different from that of orthogonal anthracene dimers, but similar with that observed for orthogonal pentacene dimer. Most of the excited states of this dimer decay by radioactive channels, which is different from the localized twisted charge transfer state (LTCT) channel of anthracene dimers and the singlet fission (SF) channel of pentacene dimers. The results of this research suggest that similar orthogonal configurations caused different propertied for acene dimers with different conjugation length.

1. Introduction

Recently, acene dimers linked directly by covalent bonds have attracted a lot of research interest, due to the novel photophysical properties induced by the interaction between the acene subunits [1–5]. For example, anthracene dimers show twisted localized charge transfer state (TLCT) upon photoexcitation [6–8], while the pentacene dimers can conduct efficient singlet fission (SF) from the singlet excite states [9–11]. The pentacene dimers are particularly important due to SF is suggested to be able to overcome the Shockley–Queisser theoretical limit of solar energy conversion efficiency for a single junction solar cell by changing one photon into two electrons [12–14]. Based on the significant different properties between the directly linked anthracene dimer and pentacene dimer, tetracene dimer linked directly without any spacer should have different photophysical properties from both of them. However, despite that several tertacene dimers linked by phenyl or xanthene as bridge have been synthesized successfully [15,16], the tetracene dimer linked directly by a covalently bond without any spacer has never been prepared because of its sensitivity towards light and oxygen [15].

Because tetracene compounds are excellent organic semiconductors [17–24], varies teracene compounds were prepared previously. Properties of tetracene compounds can be changed dramatically by the introduction of electron withdrawing groups [25–31], or electron donating groups [32–40]. Among the numerous substituents, cyano group has been proved to be very efficient on improving the stability [26,27]. With this in mind, we assume that introduction of cyano groups into tetracene dimer should be able to improve the stability, and thus the tetracene dimer linked directly with a single covalent bond can be prepared. We first introduced cyano group onto tetracene skeleton to get a stable tetracene monomer, and then coupling this monomer into a single bond linked tetracene dimer (**6**, Scheme 1). The resulted dimer **6** is found to be stable at ambient conditions and can be purified easily. Reliable photophysical measurements can be made on it. To the best of our knowledge, this is the first example of the single bond linked tetracene dimer. Here we present the results.

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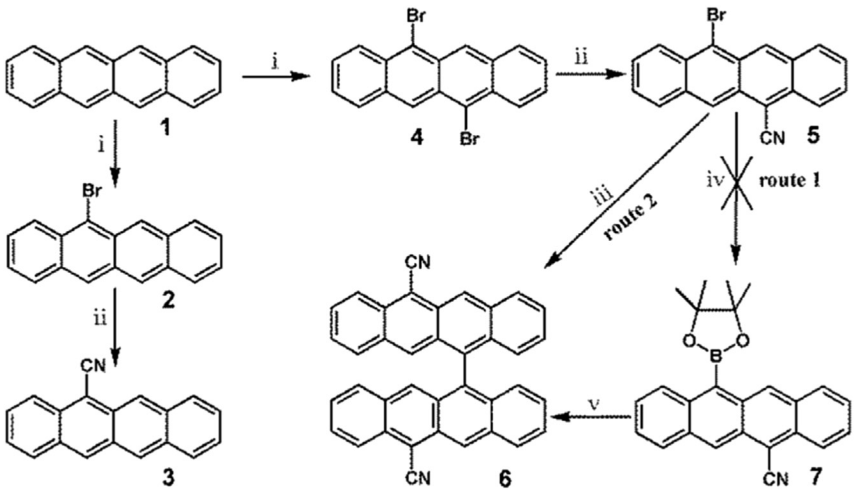

Scheme 1. Synthesis of the compounds. (i) NBS (1 equiv), DMF, $CHCl_3$, 60 °C, 3 h (ii) CuCN (1 equiv), DMF, 150 °C, 10 h (iii) Ni^0-complex, DMF, 70 °C, 32 h. (iv) Pd(dppf)Cl_2, KOAC, bis(pinacolato)diboron, DMF, 100 °C, 12 h. (v)**5**, $Pd_2(dba)_3$, K_2CO_3, Toluene, EtOH, 95 °C, 12 h.

2. Experimental section

2.1. General methods and materials

^1H NMR spectra were obtained on a spectrometer operating at 300 MHz with chemical shifts reported in ppm (TMS as the internal standard). MALDI-TOF mass spectra were recorded using a Bruker/ultraflex or AXIMA-CFR plus instrument with dithranol as matrix. Elemental analysis was measured on a Vario EL CUBE instruments. The concentrations of all samples in solution used in collecting absorption and fluorescence spectra are 10^{-5} M. The path-length of the cuvette used for collecting absorption and fluorescence spectra is 1 cm. The quartz substrates used for preparation of polymer films were first rinsed with acetone thoroughly and then were immersed in chromic acid lotion for 15 h. After rinsed with doubly distilled water for three times and dried in an oven for overnight, the substrate was ready for film deposition. The polymer films for the absorption and fluorescence spectrum measurements were prepared by dropping a solution of sample (~10^{-5} M in chloroform containing 175 mg mL^{-1} polystyrene or 100 mg mL^{-1} polymethylmethacrylate (PMMA)) onto the surface of the thoroughly cleaned quartz substrate. Then the sample was dried in dark at room temperature under N_2 atmosphere. Absorption spectra were measured on a SHIMADZU UV-2450 spectrophotometer with a wavelength resolution of 0.3 nm. Steady-state fluorescence spectra were measured on FLS920 fluorometer (Edinburgh Instrument). The fluorescence lifetimes were measured by time correlated single photon counting (TCSPC) method on FLS 920 equipped with a picosecond pulsed laser diode (EPL-445) as excitation light source. The absolute fluorescence quantum yields (Φ_F) of the samples were measured with integrating sphere on FLS920. The X-ray diffraction data were collected on an Agilent Xcalibur Eos Gemini diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å) at 296 K.

All chemicals and reagents used in this study were purchased from commercial source and used without purification. 5-bromotetracene (**2**) and 5,11-dibromotetracene (**4**) [41] and 5-cyanotetracene (**3**) [42] were prepared following literature methods.

2.2. Synthesis of compounds

2.2.1. Synthesis of 5-bromo-11-cyanotetracene (*5*)

A mixture of 5,11-dibromotetracene (384 mg, 1 mmol) and CuCN (108 mg, 1.2 mmol) were mixed with 20 ml DMF in a 50 ml round bottom flask. The mixture was stirred under N_2 and refluxed for 24 h. The reaction mixture was cooled to room temperature, and then poured into water. The reaction mixture was extracted with CH_2Cl_2 for three times. The combined CH_2Cl_2 solvent was dried over anhydrous Na_2SO_4 for overnight, and then was removed by rotary evaporation. The solid residue was purified by column chromatography on silica gel with n-hexane/chloroform (1/1) as eluent. After recrystallization from chloroform and methanol, pure product was obtained (60 mg, 18%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.46 (s, 1H), 9.10 (s, 1H), 8.52 (d, $J = 9.0$, 2H), 8.43 (d, $J = 9.0$, 2H), 8.17 (d, $J = 7.8$, 2H), 8.11 (d, $J = 7.9$, 2H), 7.75–7.26 (m, 4H). MS(MALDI-TOF), m/z: 332.89 ($[M]^+$, calcd for $C_{19}H_{10}NBr$, 332.19). Anal. Calcd for $C_{19}H_{10}NBr$: C, 68.70. H, 3.03. N, 4.22. Found: C, 68.81. H, 3.09. N, 4.15.

2.2.2. Synthesis of dimer (*6*)

$NiBr_2$ (66 mg, 0.3 mmol), zinc powder (20 mg, 0.3 mmol) and PPh_3 (triphenylphosphine, 314 mg, 1.2 mmol) were dissolved in 20 ml DMF in a 50 ml flask. The mixture was bubbled with nitrogen for fifteen minutes to remove oxygen. After stirring at 70 °C for 2 h, the colour of the reaction mixture was changed from claybank to reseda, then 5-bromo-11-cyanotetracene (33 mg, 0.1 mmol) was added. The reaction mixture was stirred continuously at 70 °C for another 32 h under nitrogen atmosphere. After cooled to room temperature, the resulting mixture was poured into water and then extracted with CH_2Cl_2 for three times. The combined CH_2Cl_2 layer was dried over anhydrous Na_2SO_4 for overnight, and then the solvent was removed by rotary evaporation. The solid residue was purified by column chromatography on silica gel with n-hexane/chloroform (1/1) as eluent. The target product was obtained after recrystallization (21 mg, 41.7%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.43 (s, 2H), 8.43 (d, $J = 9.0$, 2H), 8.32 (d, $J = 9.0$, 2H), 7.93 (s, 2H), 7.75-7.50 (m, 8H), 7.31-7.18 (t, $J = 7.5$, 2H), 7.07-7.00 (d, $J = 9.0$, 2H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 133.33 132.71 132.17 131.06 130.96 129.65 129.22 128.53 128.45 128.10 128.03 126.29 126.11 125.44 124.92 124.49 124.05 116.78 104.70. MS (MALDI-TOF), m/z: 503.468 ($[M]^+$, calcd for $C_{38}H_{20}N_2$, 504.16). Anal. Calcd for $C_{38}H_{20}N_2$: C, 90.45. H, 4.00. N, 5.55. Found: C, 90.21. H, 4.10. N, 5.69.