

Synthesis and characterisation of anthracene-2,6-dithioacetate: a rigid, conjugated molecule for the formation of monolayers on gold.

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Abstract

The synthesis and characterization of a new photoswitchable anthracene compound, anthracene-2,6-dithioacetate, is presented. The compound dimerises in solution upon irradiation with UV light and thin films can be formed on gold surfaces from both the monomer and photodimer.

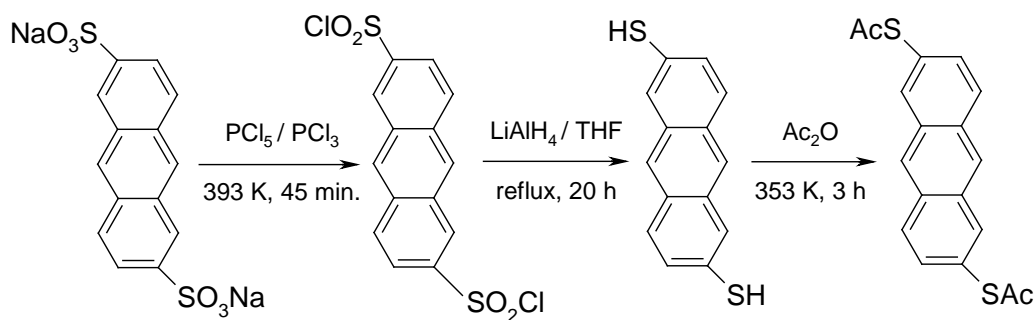
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Dithiols, especially α,ω -dithiols, have recently attracted significant attention in the field of molecular electronics [1-6]. Dithiols may form self-assembled monolayers (SAMs) or thin films on metal surfaces with the advantage of allowing metallic contacts to be made to either end of the molecule [7, 8]. Fully conjugated examples of α,ω -dithiols are scarce but are of interest due to their enhanced molecular conductivity [9]. In this regard, anthracene-containing compounds are attractive as the ring system is fully conjugated and also locked into a planar configuration so that torsion between rings cannot occur, which may affect electronic communication.

In our efforts to access conjugated α,ω -dithiols, we prepared the new compound anthracene-2,6-dithioacetate (Scheme 1). With its rigid, fully conjugated ring system this is a promising but hitherto unexplored molecule in the area of molecular electronics, in particular, in molecular conductivity investigations where the molecule may be connected to metal electrodes via the two available S-linkages. Its ability to photodimerise and switch between fully conjugated and partially conjugated forms, which should affect electronic conduction, makes it an interesting candidate for switchable molecular electronics studies. Furthermore, the formation of SAMs from dithiols can be problematic due to the possibility of double attachment of the molecules. This may be addressed by protecting the thiol groups [10-12] or by the use of rigid molecules [8, 13]. Interestingly, the new compound anthracene-2,6-dithioacetate unifies both of these concepts.

There are few reports of SAMs or thin films incorporating anthracenethiol compounds. SAMs of anthracene-2-thiol can form on gold and silver surfaces [14] and a comprehensive study of anthracene-2-thiol SAMs on gold(111) surfaces was undertaken by Käfer *et al.* [15] where SAM formation was found to be solvent dependent. Fox and Wooten [16] described a photoswitchable anthracene-containing SAM formed by chemisorption of 10-thiododecyl-2-anthryl ether onto a gold(111) surface and we have

recently reported photoswitching experiments using SAMs of anthracene-2-thiol where the photoswitching behaviour was monitored using scanning tunneling microscopy [17]. The $[4\pi + 4\pi]$ photocyclic addition of two anthracene molecules is a well known process [18, 19] with the isolated photodimer first reported by Fritzsche in 1867 [20] and identified as the dimer by Elbs in 1891 [21]. Typically, the photocyclisation reaction occurs upon irradiation at ~ 360 nm and the reverse reaction, dimer to monomer, occurs when using a shorter wavelength or by heating [19].



Scheme 1. Synthesis of anthracene-2,6-dithioacetate.

Reaction of commercially available anthracene-2,6-disulfonic acid with phosphorus pentachloride over 45 minutes yielded anthracene-2,6-disulfonyl chloride in 80 % yield. If the reaction was allowed to proceed for two hours, a significant amount of 9,10-dihydroanthracene-2,6-disulfonyl chloride (~ 15 %) was obtained, which was unable to be separated from the anthracene-2,6-disulfonyl chloride using silica column chromatography. Using LiAlH₄, the disulfonyl chloride compound was reduced to anthracene-2,6-dithiol, which has been previously reported but with limited characterization data [22]. We found anthracene-2,6-dithiol to be insoluble in all common laboratory solvents with the notable exception of dimethylsulfoxide (DMSO). When

mixed with DMSO, it formed a bright orange-coloured solution that faded to yellow with time. ^1H NMR experiments performed using DMSO-d_6 indicated the dissolved compound was anthracene-2,6-disulfonic acid. The ability of DMSO to oxidize thiols to sulfonic acids has previously been reported by Lowe [23]. However, using neat acetic anhydride, the insoluble anthracene-2,6-dithiol was converted to anthracene-2,6-dithioacetate in 59 % yield, and is reasonably soluble in dichloromethane and chloroform. In terms of molecular electronics applications, the inclusion of the terminal thioacetate groups is useful for three reasons; firstly, they aid in the solubility of the compound, second, they protect the thiol groups from oxidation and hence improve the stability of the molecule, and third, these groups are readily removed when forming SAMs on gold either by addition of base or directly by contact with the gold surface [24].

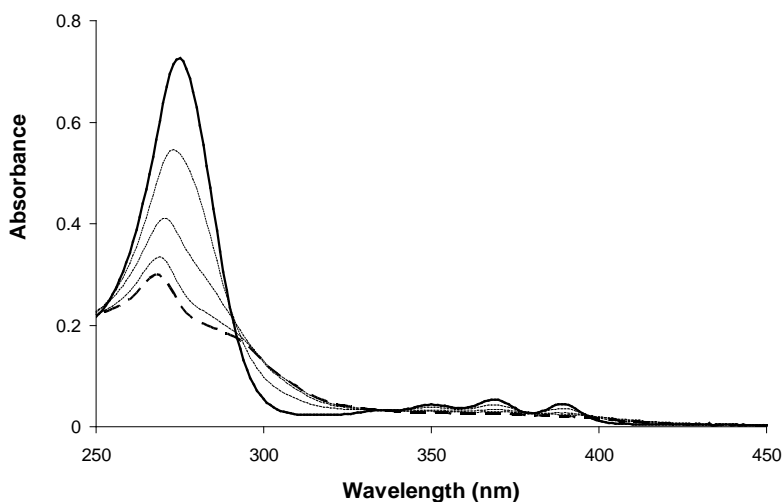


Figure 1. UV-visible absorption spectra of anthracene-2,6-dithioacetate (solid line) showing spectroscopic changes upon irradiation with 365 nm light (dashed lines).

The UV-visible spectrum of anthracene-2,6-dithioacetate in dichloromethane is shown in Figure 1 (solid line). The spectrum has a strong β absorption band with λ_{max} at 275 nm and a broad p band from 325 to 410 nm with maxima at 354, 369 and 390 nm. Figure 1 also shows UV-visible absorption spectra recorded over time for a solution of anthracene-2,6-dithioacetate irradiated with 365 nm light (dashed line). The well-documented anthracene photodimerisation process (see Figure 2) was monitored by the decrease in absorbance of the characteristic monomer band at 275 nm and an accompanying increase in absorbance at 263 nm assigned to the photodimer. At 365 nm, the dimer does not absorb significantly and reverse dimer-to-monomer reaction is minimal [25]. The isosbestic point of the spectra at ~ 294 nm is not particularly clean indicating that the dimerisation reaction occurs with some side reactions. We note that two photodimer products are possible with 2,6-substituted anthracenes (with identical substituents) however no attempt was made to separate them in this work. Interestingly, the photocycloaddition also proceeds under irradiation with 254 nm light. UV-visible spectra of solutions of the dimer stored at room temperature (away from light) reveal that even after 50 h, the dimer does not revert back to the monomer.

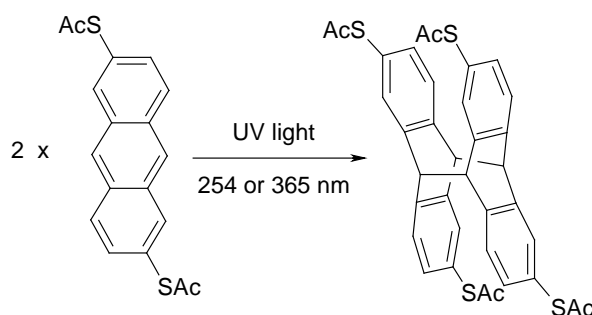


Figure 2. The photodimerisation reaction of anthracene-2,6-dithioacetate (one isomer shown).

Investigations were undertaken to confirm the ability of 2,6-anthracenedithioacetate to form thin films on gold using scanning tunnelling microscopy (STM). Monolayer films on gold(111) surfaces were prepared by immersion of clean gold substrates in 1 mM dichloromethane solutions of anthracene-2,6-dithioacetate. The addition of a base such as ammonium hydroxide, which is able to cleave the protecting acetyl group, was found to be unhelpful as the deprotected compound rapidly precipitated from solution. Representative STM images of thin-films formed from anthracene-2,6-dithioacetate are shown in Figure 3. Long range ordering is not apparent although some small domains of ordered molecules are present. Line profile measurements indicate that the spacings associated with the molecules are ~ 2 nm x ~ 1.5 nm. This is significantly greater than the spacing reported for the upright phase of 2-anthracenethiol of ~ 1.25 nm x ~ 1 nm [15].

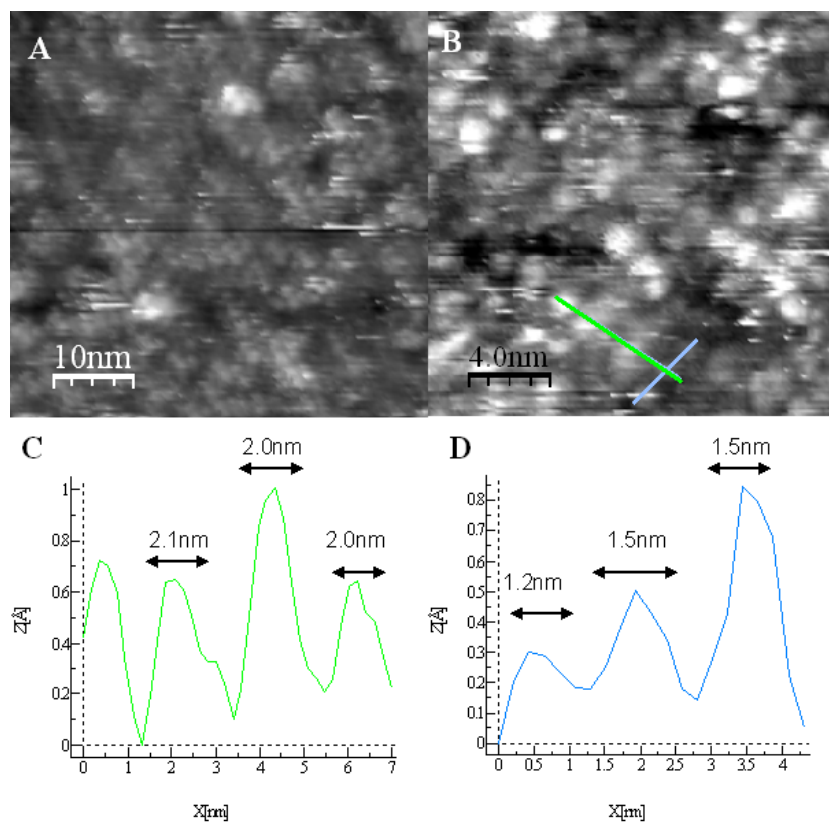


Figure 3 (A) STM image of a monolayer formed from anthracene-2,6-dithioacetate on Au(111). (B) Higher magnification image. (C & D) Line profile data taken from the range shown in panel B.

The formation of monolayer films directly from anthracene photodimers has not been previously reported in the literature. Figure 4 shows STM images of monolayers formed by irradiating a dichloromethane solution of anthracene-2,6-dithioacetate (1 mM) with UV light followed by immersion of a clean gold substrate. The images are substantially different to those shown in Figure 3. Significantly more ordering is apparent with the molecules forming row-like structures that span several nanometers. Line profile data

reveal spacings between features of $\sim 4 \text{ nm} \times 2.5 \text{ nm}$, but do not give any insight into the molecular binding geometry. The monolayer is quite stable with no structural change observed two weeks after the initial formation. Interestingly, neither the monomer nor dimer monolayer films could be converted to the other by irradiation with UV light.

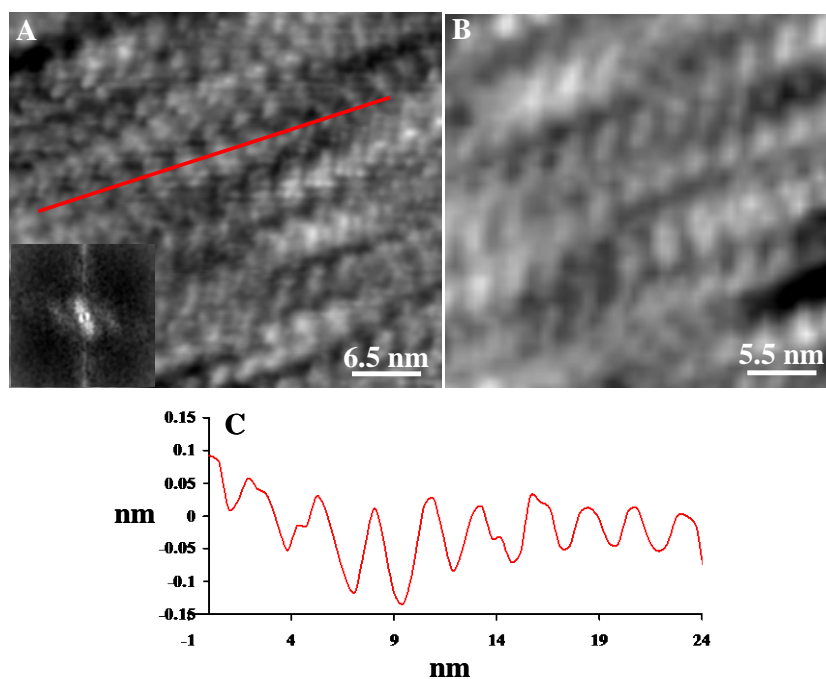


Figure 4. (A) STM image of a monolayer formed from the photodimer on Au(111). Inset: Fourier transform data. (B) Filtered image showing molecular ordering. (C) Line profile data taken from image (A).

In conclusion, we have synthesized and characterized the new compound anthracene-2,6-dithioacetate, which photodimerises upon irradiation with 365 or 254 nm light. Preliminary investigations indicate that monolayer films on gold (111) formed from the monomer have different surface structures compared with those of the photodimer. These initial results suggest that this molecule is a promising candidate for further molecular electronics investigations.

Experimental

Physical measurements.

¹H NMR spectra were recorded using a BVT 3000 Bruker Spectrospin instrument operating at 300.13 MHz. Spectra are referenced internally to residual protic solvent (CDCl₃, δ 7.26). UV-visible spectra were recorded using an Agilent 8453 UV-Visible spectrophotometer with ethanol as solvent. Electrospray ionization mass spectra (ESI-MS) were recorded using a Perkin-Elmer SCIEX API300 Triple Quadrupole Mass Spectrometer. The general conditions were: ion spray voltage = 5000V, drying gas temperature = 50 °C, orifice voltage = 30V, ring voltage = 340V, and injection via syringe pump. Spectra were averaged over 10 scans. Elemental microanalyses were carried out by the Microanalytical Service Unit at the Research School of Chemistry, Australian National University.

Synthesis

Preparation of anthracene-2,6-disulfonyl chloride [26]. Anthracene-2,6-disulfonic acid disodium salt (2.5g, 6.54mmol) and phosphorus pentachloride (5g 24mmol) were heated with stirring to 120 °C. The mixture formed a paste and a reflux condenser was added and phosphorus trichloride (5.0 ml, 33 mmol) was added and the mixture heated at reflux for 45 minutes with stirring. After cooling to room temperature, the reaction was quenched by drop-wise of water (caution: strongly exothermic reaction). Once the reaction had subsided, water (25 mL) was added and the precipitated product was collected by filtration. The crude product was dissolved in dichloromethane (400ml) and filtered through a plug of anhydrous sodium sulfate. The solvent was removed using a rotary evaporator to yield 2.1g (80%) of anthracene-2,6-disulfonyl chloride as a bright yellow powder. ¹H NMR (300MHz, CHCl₃): δ 8.86 (s, J_{HH} = 1.9 Hz 2H, H_{1,5}), 8.81 (s, 2H, H_{9,10}), 8.33 (d, J_{HH} = 9.0 Hz, 2H, H_{4,8}), 8.05 (dd, J_{HH} = 7.2 Hz, 2H, H_{3,7}).

Preparation of anthracene-2,6-dithiol. Lithium aluminium hydride (405 mg, 10.7 mmol) was added to a flame dried round bottom flask together with dry THF (130 ml) and cooled to 0 °C with stirring. Anthracene-2,6-disulfonyl chloride (500mg 1.3mmol) in dry THF (25 ml) was added over half an hour with the temperature maintained at 0 °C. The solution was then heated at reflux for 20h. After this time, the mixture was allowed to cool to room temperature and quenched with aqueous HCl (10 M). The mixture was filtered and the solvent removed under vacuum. The crude product was suspended in ethyl acetate and washed with brine. The ethyl acetate was removed under vacuum and the crude product was suspended in methanol. The insoluble product was filtered and additionally washed with dichloromethane, acetone and finally diethyl ether to give 105 mg (33 %) of crude anthracene-2,6-dithiol, which was characterized by conversion to the dithioacetate (below).

Preparation of anthracene-2,6-dithioacetate. Acetic anhydride (2 ml, 18mmol) was added to crude anthracene-2,6-dithiol (100 mg, 0.4 mmol) and stirred under nitrogen gas. The mixture was heated to 80-85°C for 3h. After cooling to room temperature, the product was dissolved in dichloromethane and washed with bicarbonate solution and then brine. The dichloromethane solution was then passed through a sodium sulfate plug and the resulting crude product was purified using silica column chromatography using dichloromethane as eluant. The pure product was dried under vacuum at room temperature. Yield: 80 mg (59 %). ¹H NMR (300MHz, CHCl₃): δ 8.412 (s, 2H, H_{9,10}), 8.121 (s, 2H, H_{1,5}), 8.02 (d, J_{HH} = 8.7 Hz, 2H, H_{4,8}), 7.43 (dd, J_{HH} = 10.5 Hz, 2H, H_{3,7}) ¹³C NMR (300MHz, CHCl₃): δ 194 (CO), 162 (aromatic-S), 134, 131, 130, 129, 126, 125 (aromatic), 30 (CH₃). UV-vis (EtOH, λ_{max}, nm [ε, × 10³ M⁻¹cm⁻¹]): 275 [104], 350 [5.23], 360 [7.26], 389 [6.12]. MS: *m/z* 327 ([M + H], 55). Anal. Calcd. for C₁₈H₁₄O₂S₂: C, 66.23; H, 4.23. Found: C, 66.07; H, 4.33.

Thin films.

Thin films were formed by immersion of a gold(111) substrate in a vial containing a degassed 1mM dichloromethane solution of the compound. The vial was filled with argon gas and sealed for a period of 72-96 hours. The gold substrate was then washed extensively with dichloromethane and dried under a stream of nitrogen gas. The substrate was fixed to an STM stub using silver epoxy. For thin-films formed from the photodimer, the solution was irradiated with 254 nm light (Minerallight Multiband lamp, Pathtech Model UV GL-55) for a period of 5 minutes prior to immersion of the gold substrate. STM images were obtained using a Nanosurf Easyscan instrument running Nanosurf acquisition software. Pt/Ir (80/20) 0.25-0.2mm tips were used and sharpened with mechanical cutting. Images were processed using freeware WSxM [27]. FFT was used to filter some images, as indicated in figure captions. Measurement of features in images is taken across the base of the feature. Size dimensions shown are typical of those from a number of analysed images.

Acknowledgments

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