Novel pyrene and 8-anilino-1-naphthalenesulfonic acid-MoS₂ intercalates

R. BISSESSUR*, B. D. WAGNER*,
Department of Chemistry, University of Prince Edward Island, Charlottetown, PEI, Canada C1A 4P3
E-mail: rabissessur@upei.ca
E-mail: bwagner@upei.ca

R. BRÜNING
Department of Physics, Mount Allison University, Sackville, New Brunswick, Canada E4L 1E6

Intercalation compounds of pyrene and 8-anilino-1-naphthalenesulfonic acid into MoS₂ have been synthesized and characterized. This was achieved by using the exfoliation/re-stacking properties of LiMoS₂. The degree of intercalation was found to be dependent on the amount of guest species used, the reaction time employed and the method of flocculation. The materials were also characterized by thermogravimetric analysis, four probe electrical conductivity measurements and fluorescence spectroscopy.

1. Introduction

There is significant interest in the properties of luminescent compounds due to their wide range of applications [1]. However, the luminescence quantum yield of many molecules is dramatically decreased, particularly in the solid state, because of competing non-radiative decay pathways [2]. Recently, a wide range of aromatic compounds have been shown to exhibit enhanced fluorescence when incorporated into molecular hosts such as cyclodextrins [3], cucurbiturils [4] and layered structures such as clays [5]. This enhancement in fluorescence can be ascribed to a number of factors [6], including loss of rotational freedom of the molecules and a change in the polarity of the local environment of the probe upon host inclusion. These can result in a decrease in the efficiency of radiationless transitions, and hence an increase in fluorescence, via specific mechanisms. In addition, encapsulation of the organic molecules in these hosts serves as a means of protection from quenching agents such as oxygen and other paramagnetic impurities. Pyrene and 8-anilino-1-naphthalenesulfonic acid (ANS) are two aromatic compounds that have been well studied because of their fluorescence properties. Pyrene exhibits a monomer fluorescence spectrum with well-defined vibronic bands, the relative intensity of which are dependent on the polarity of the medium [7]. Specifically, the intensity ratio of vibronic bands I and III has been shown to be directly correlated to polarity [7], and thus the fluorescence of pyrene has been widely applied as a probe of local polarity [8]. At high concentrations, pyrene exhibits excimer (excited dimer) emission, which is structureless and red-shifted relative to the monomer emission, but which can be used to indicate the interaction of neighbouring pyrene molecules in the system of interest. ANS has also been widely used as a polarity-sensitive probe. In this case, it is the fluorescence quantum yield which is highly polarity sensitive; ANS is nearly non-fluorescent in water, but shows extremely strong fluorescence in non-polar solvents [9]. Dramatic enhancement in the fluorescence of ANS has been observed when encapsulated in cyclodextrins [3b] and cucurbiturils [4].

In this article we report the inclusion of pyrene and ANS into layered molybdenum disulfide (MoS₂). MoS₂ is an interesting layered material because of its extensive use as a hydrodesulfurisation catalyst [10], solid lubricant [11] and potential application as a cathode material in lithium rechargeable batteries [12]. Intercalation compounds of MoS₂ can be achieved by using the exfoliation/re-stacking properties of LiₓMoS₂ [13]. We have exploited this synthetic methodology to intercalate pyrene and ANS into MoS₂, with the goal of using the fluorescence of these polarity-sensitive probes to characterize these materials.

2. Experimental

Pyrene (99%) and ANS (97%) (Fig. 1) were purchased from Aldrich and were used without any further purification. LiₓMoS₂ was prepared by reacting MoS₂ (99%, Aldrich) with 3 equivalents of n-BuLi (2.5 M solution in hexanes) in a dry box (Equation 1). The concentration of n-BuLi was adjusted to 1 M by adding dry pentane...
and the reaction mixture was allowed to stir for at least 2 days at room temperature. The product was filtered off in the dry box, washed with pentane and then dried under suction. Elemental analysis of the product confirmed its stoichiometry to be LiMoS₂. The prepared LiMoS₂ was stored in the dry box until future use.

\[
\text{MoS}_2 + n\text{-BuLi} \rightarrow \text{LiMoS}_2 + 1/2\text{Bu-Bu} \quad (1)
\]

Reaction of LiMoS₂ with water resulted in the formation of single layers of MoS₂ as described by Equation 2. In a typical reaction, water (20 mL) was added to LiMoS₂ (200 mg, 1.20 mmol) and the suspension sonicated for 2 h. This procedure resulted in complete exfoliation of the MoS₂ layers.

\[
\text{LiMoS}_2 + \text{H}_2\text{O} \rightarrow (\text{MoS}_2)_{\text{single layers}} + \text{LiOH} + 1/2\text{H}_2 \quad (2)
\]

A solution of pyrene in CH₂Cl₂ or ANS dissolved in ethanol was then added to the single layers and the reaction mixture was allowed to stir at room temperature for days. In some of the preparations concentrated hydrochloric acid was added after 2 days of stirring. The stirring was then further continued for several days. The reaction mixtures were then filtered off and washed thoroughly with water to remove LiOH, followed by ethanol or CH₂Cl₂ to remove excess guest species (G). This experimental procedure led to the formation of sandwiched compounds of MoS₂ as described by Equation 3.

\[
(\text{MoS}_2)_{\text{single layers}} + xG \rightarrow (G)_x\text{MoS}_2 \quad (3)
\]

Powder X-ray diffraction (XRD) was run on a diffractometer equipped with a graphite monochromator and an analyzer crystal was used, along with a scintillation detector. Cu Kα radiation (\(\lambda = 1.542 \text{ Å}\)) was utilized and the data collection was carried out at 22 °C. Samples were run under vacuum with a scan range of 3 to 100 degrees. In order to minimize scattering from materials other than the samples in the XRD measurements, the powdered samples were placed on a single crystal silicon substrate with the surface cut parallel to the (510) plane [supplied by The Gem Dugout, State College, PA].

Thermogravimetric analyses (TGA) were performed on a Mettler Toledo Star system using a heating rate of 10°C/min.

Electrical conductivities were measured on pressed pellets of the samples by using the conventional four probe technique. The diameter of the pellets were either 0.68 cm or 1.27 cm.

Fluorescence spectra were measured on a Photon Technology International LS-100 luminescence spectrometer using front-face emission from the solid samples. This was achieved using a 1 cm² solid aluminum support (the same size as a standard fluorescence cuvette used for solution work) which had been machined at a 45° angle to the excitation and emission paths of the spectrometer and painted flat black. The powder samples were directly adhered to this support using double-sided adhesive tape. The excitation wavelength used was 310 nm (pyrene) and 340 nm (ANS).

### 3. Results and discussion

Powder X-ray diffraction shows that we have formed genuine intercalation compounds (Fig. 2). Intercalation was found to be complete since no pristine MoS₂ phase can be observed. However, we found that the degree of intercalation depended on the amount of pyrene used in the reaction as well as on the reaction time (Table I). An increase in interlayer spacing from 1.29 Å to 1.89 Å was observed by merely increasing the reaction time for an additional 12 h. The smaller interlayer spacing values observed for these short reaction times are attributed to the phenomenon of staging similar to those observed for graphite intercalation compounds [14]. Similar trends have also been observed for the intercalation of naphthalene in MoS₂ [15]. The addition of concentrated hydrochloric acid after two days, followed by continued stirring for many days resulted in a product with a larger interlayer spacing. The maximum interlayer spacing value observed is 10.28 Å, corresponding to an inter-layer expansion of 4.13 Å (Table I). This is consistent with having the pyrene molecule lying co-planar with respect to the disulfide sheets (Fig. 3). A similar effect was observed for the ANS-MoS₂ system, showing a maximum interlayer spacing value of 11.34 Å.