

Polyaromatic Compounds

Side-Chain-Directed Dispersion of MoS₂ Nanosheets by V-Shaped Polyaromatic Compounds

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Abstract: Bulk molybdenum disulfide (MoS₂) itself is virtually insoluble in common organic solvents because of the tight stacks of multiple MoS₂ nanosheets. Here we report that V-shaped polyaromatic compounds with non-ionic side chains can efficiently exfoliate and disperse the inorganic nanosheets. Simple grinding and sonication (less than total 1 h) of MoS₂ powder with the V-shaped compounds gave rise to large MoS₂ nanosheets highly dispersed in NMP through efficient host-guest S- π interactions. DLS and AFM analyses revealed that the lateral sizes (ca. 150–270 nm) and thicknesses (ca. 2–8 nm) of the products depend on the identity of the non-ionic side chains on the V-shaped dispersant.

Rational design of interfacial interactions between organic and inorganic compounds is of importance to create novel supramolecular hybrid materials.^[1] Bulk molybdenum disulfide (MoS₂) is an inorganic solid composed of crystalline MoS₂ nanosheets stacked tightly with each other through van der Waals interactions. The layered compounds display unique conductive characters depending on the thickness and thus promise wide-ranging applications in novel electronic materials.^[2] However, because of the large surfaces of the inorganic nanosheets with strong stacking peculiarity, their facile exfoliating and dispersing methods are still limited, as compared with those for graphene nanosheets.^[3] Sonication, manual grinding, mechanical ball-milling, or their combinations for long hours have proven to be useful for preparing dispersion of MoS₂ nanosheets.^[4] The exfoliation and dispersion of the nanosheets are further facilitated by using ionic additives such as alkali metal ions, sodium cholate, and pyrene derivatives.^[5–7] Nevertheless, host-guest interactions between the organic and inorganic surfaces remain obscure on the molecular level.^[8] The development of a facile and reliable dispersing method based on the novel design of intermolecular interactions is

thus expected to explore the detailed material properties of MoS₂ nanosheets.

Here we report new dispersants **1a** and **1b** composed of a V-shaped polyaromatic framework with non-ionic side chains on the corner (Figure 1a) for facile exfoliation and dispersion of inorganic MoS₂ nanosheets. Manual grinding and sonication (within total 1 h) of bulk MoS₂ with the V-shaped polyaromatic compounds give rise to MoS₂ nanosheets with lateral sizes of \approx 150–270 nm and thicknesses of \approx 2–8 nm highly dispersed in *N*-methylpyrrolidone (NMP). The dimensions of the obtained nanosheets are significantly affected by the character of the side chains on the V-shaped dispersant.

As new dispersants, here we designed V-shaped polyaromatic compounds **1a,b** having two anthracene panels and three methoxy-oligo(ethylene oxide) side chains linked by a benzene ring (Figure 1a,b).^[9] These compounds are non-ionic analogues of ionic compound **2** with two trimethylammonium groups.^[10] In water, the ionic V-shaped compounds can encapsulate various organic compounds, for example, fluorescent dyes, fullerenes, and metallo-phthalocyanines, through π -stacking in-

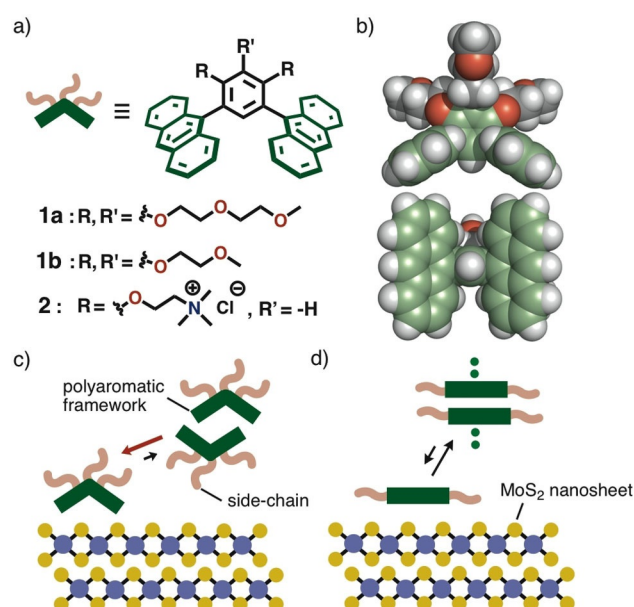


Figure 1. a) Non-ionic V-shaped polyaromatic dispersants **1a** and **1b** designed herein and ionic derivative **2** reported previously. b) The optimized structure of **1b**: side and bottom views.^[9] Hypotheses of interfacial interactions between inorganic MoS₂ nanosheets and c) V-shaped dispersants **1a, b** or d) planar dispersants in solution.

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teractions and the hydrophobic effect.^[11] We therefore hypothesized that the bent polyaromatic framework could efficiently interact with the large surface of an inorganic MoS₂ nanosheet through multiple S- π interactions (Figure 1c).^[1,12] In addition, the V-shaped compound with bulky substituents on the corner might suppress self-stacks through strong π -stacking interactions, in contrast to a planar polyaromatic dispersant (Figure 1d).^[13] The non-ionic and non-coordinative side chains^[14] were also expected to assist in the stabilization of the dispersed MoS₂ nanocomposites in organic solvents without the change of the crystalline nanostructure.

Anthracene-based, new V-shaped dispersant **1a** was synthesized in four steps. Starting from commercially available 1,2,3-trimethoxybenzene, sequential bromination, Negishi coupling, demethylation, and etherification protocols gave rise to **1a** in moderate yield.^[15] The structure and purity were confirmed by NMR spectroscopy, mass spectrometry (MS), and elemental analysis. ¹H NMR spectrum of **1a** showed six aromatic signals (*H*_{a-f}) and ten aliphatic signals (*H*_{g-k} and *H*_{g'-k'}) in the ranges of 7.01–8.45 and 2.77–4.52 ppm, respectively (Figure 2a). In the

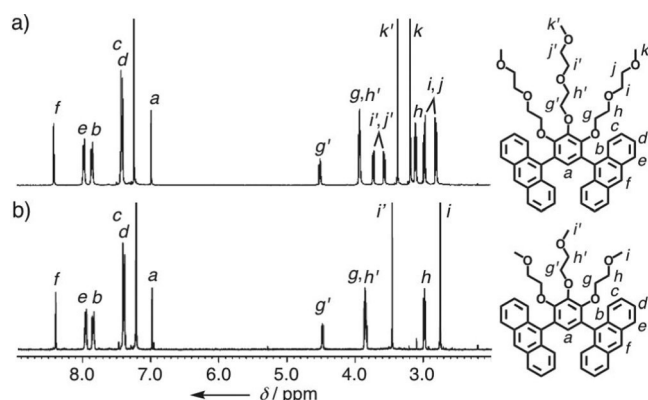


Figure 2. ¹H NMR spectra (400 MHz, CDCl₃, r.t.) of V-shaped dispersants a) **1a** and b) **1b**.

MALDI-TOF MS spectrum, a prominent peak derived from **1a** was observed at *m/z* = 784.39 [*M*]⁺. Analogous compounds **1b** (Figure 2b) and **1c** (Figure S5) were obtained in one step from the precursor of **1a**.^[15] Pentamethylbenzene-based dispersants **5a** and **5b** were also newly prepared in a manner similar to **1a** (Figures S11 and S13, respectively).^[15]

A combination of grinding and sonicating with the dispersants resulted in the formation of MoS₂ nanosheets highly dispersed in NMP. As optimized procedures, a mixture of bulk MoS₂ (1.0 mg) and **1a** (2.2 mg, 2.8 μ mol) was ground for 10 min using an agate mortar and pestle (Figure 3a, right). The resultant solid was sonicated (40 kHz, 150 W) in NMP (1.0 mL) for 30 min to give a dark green solution (**3a**) including MoS₂ nanocomposites. Subsequent high-speed centrifugation (14800 rpm for 10 min) removed suspended MoS₂ solids from the mixture. The UV-visible spectrum of the clear dark green solution displayed broad absorption bands at 610 and 660 nm (Figure 3b), besides prominent absorption bands around 370 nm derived from the anthracene moieties of **1a**. The two

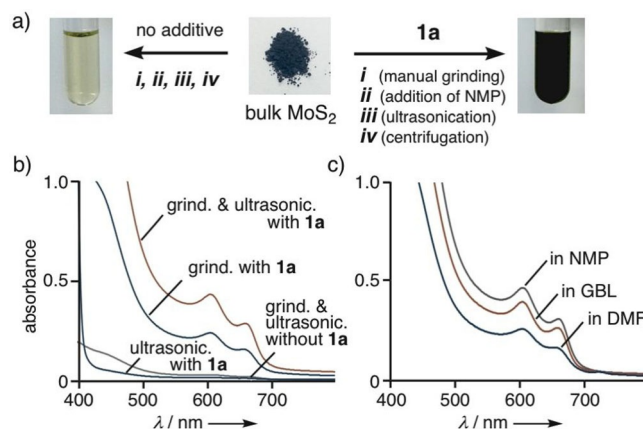


Figure 3. a) Schematic representation of the exfoliation and dispersion of bulk MoS₂ with/without V-shaped compound **1a**. b) UV-visible spectra (r.t.) of NMP solutions after grinding (10 min) and/or ultrasonication (30 min) of bulk MoS₂ with/without **1a**. c) UV-visible spectra (r.t.) of NMP, GBL, and DMF solutions after grinding (10 min) and ultrasonication (30 min) of bulk MoS₂ with **1a**.

peaks arise from stacked MoS₂ nanosheets providing the original crystalline structure. A clear Tyndall effect was also observed in the NMP solution (Figure S21a), suggesting the presence of 10² nm-sized particles. In contrast, the same protocol in the absence of **1a** gave a clear pale yellow solution (Figure 3a, left) showing no absorption band corresponding to the MoS₂ nanosheets (Figure 3b). Only grinding (for 10 min) or sonicating (for 30 min) with **1a** is less or not effective in dispersing the nanosheets in NMP (Figure 3b). In addition, NMP proved a solvent better than γ -butyrolactone (GBL) and *N,N*-dimethylformamide (DMF) for the MoS₂ dispersion under the optimized conditions (Figure 3c).

Both the non-ionic side chains and polyaromatic rings on dispersant **1a** are essential for the preparation of highly dispersed MoS₂ nanosheets. By using the optimized procedures for **1a** (10 min manual grinding and 30 min ultrasonication), we estimated the dispersion abilities of various V-shaped compounds **1b–d**, **2**, **4**, and **5a,b** (Figures 1a and 4a) toward bulk MoS₂ in NMP. Treatment with V-shaped compound **1b** bearing shorter 2-methoxyethoxy groups afforded a dispersed MoS₂ solution (**3b**) with a higher concentration (1.3-fold) as compared with that with **1a** (Figures 4b and S15b). Time-dependent UV-visible analysis revealed that \approx 80% of the dispersed MoS₂ nanosheets with **1b** remains in NMP after being stranded at room temperature for 1 day (Figure S15c). The concentration of MoS₂ nanosheets was estimated to be 0.31 mg mL⁻¹ from the amount of the recovered MoS₂ nanosheets, which was isolated from **3b** by vacuum freeze-drying followed by washing with methanol.^[17,18]

As compared with **1a**, similar dispersant **1c** with longer side chains showed a lower dispersion ability (0.7-fold). These findings imply that long side chains suppress the exfoliation process of bulk MoS₂. V-shaped compounds **1d** with two 2-methoxyethoxy groups and **2** with two trimethylammonium groups were less effective (\leq 0.1-fold) in dispersing MoS₂ nano-

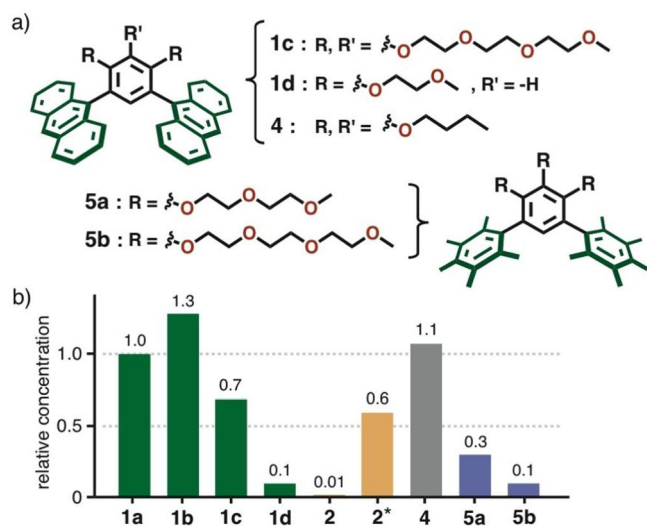


Figure 4. a) V-shaped compounds 1c–d, 4, and 5a–b studied herein. b) Relative concentrations of dispersed MoS₂ nanosheets in NMP (r.t.) by using compounds 1a–d, 2, 4, and 5a–b under the optimized conditions (10 min manual grinding and 30 min ultrasonication). Asterisk: H₂O is used as solvent instead of NMP.

sheets in NMP, which suggests the importance of multiple non-ionic side chains. Compound 4 with three butoxy groups,^[16] whose lengths are comparable to those of the side chains on 1b, also gave a highly dispersed MoS₂ solution (1.1-fold) through the optimized protocols (Figures 4b and S15b). In contrast, dispersion abilities of new compounds 5a and 5b^[15] bearing two small aromatic rings, 2,3,4,5,6-pentamethylbenzene panels, were lower (≤ 0.3 -fold) than that of 1a under the same conditions. These results indicate that V-shaped polyaromatic frameworks can effectively interact with the surface of MoS₂ nanosheets in NMP. Interestingly, an aqueous dispersion of MoS₂ nanosheets with a moderate concentration (0.6-fold) was obtained by using ionic polyaromatic compound 2 (Figure 4b).

The lateral sizes and thicknesses of the obtained MoS₂ nanocomposites 3a (from 1a), 3b (from 1b), and 3c (from 4) were evaluated by dynamic light scattering (DLS) and atomic force microscopy (AFM) analyses. DLS chart of the dark green solution of 3a in NMP revealed the existence of nanoparticles with average lateral sizes of ≈ 270 nm (Figure 5a). On the other hand, the dark green NMP solutions of 3b and 3c showed DLS peaks with average lateral sizes of ≈ 150 and ≈ 160 nm, respectively (Figure 5b, c).

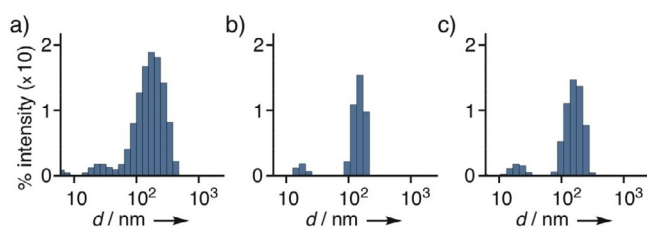


Figure 5. DLS charts (NMP, r.t.) of MoS₂ nanocomposites a) 3a (from 1a), b) 3b (from 1b), and c) 3c (from 4).

The thicknesses of the nanoparticles were revealed by AFM study. After the evaporation of the solvent by vacuum freeze-drying, the methanol solution of 3a was cast on a mica surface. AFM analysis of the surface exhibited clear images of thin MoS₂ nanosheets with an average height (thickness) of ≈ 7 nm and an average lateral size of ≈ 300 nm (Figure 6a). Under the

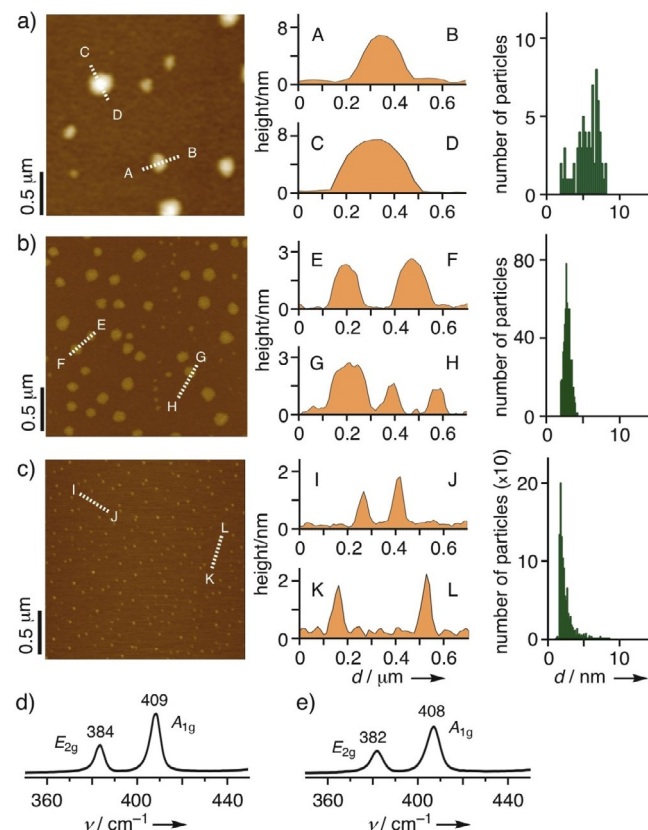


Figure 6. AFM images (dry, mica, r.t.; left), the selected height profiles (center), and the height distributions (right) of the samples obtained from a) 3a (from 1a), b) 3b (from 1b), and c) 3c (from 4). Raman spectra (solid, r.t., $\lambda_{\text{ex}} = 532$ nm, 0.1 mW) of MoS₂ nanosheets from d) 3a and e) 3b.

similar conditions, AFM images of the samples obtained from 3b and 3c also showed the formation of MoS₂ nanosheets with average thicknesses of ≈ 3 nm (Figure 6b) and ≈ 2 nm (Figure 6c), respectively. The observed thicknesses indicate that the products from 3a, 3b, and 3c are composed of ≈ 13 , ≈ 4 , and ≈ 3 layers of single MoS₂ nanosheets, respectively.^[19] Raman spectra of solids 3a, 3b, and 3c displayed prominent peaks around 380 and 410 cm⁻¹ (Figures 6d,e and S18), which also confirmed the formation of thinner, crystalline MoS₂ nanosheets.^[20] Powder X-ray diffraction of solid 3b showed broad but typical peaks at 14.2 and 32.6 degrees (Figure S19).

The present studies demonstrate that grinding with compound 1a is essential for facile dispersion of MoS₂ nanosheets from the bulk powder. In addition, the concentration of the dispersed nanosheets can be enhanced by 1.8 times by the sonication of the resultant mixtures in NMP. Although the detailed three-dimensional structures of the obtained MoS₂ nanosheet-dispersant composites are still unclear, the V-shaped pol-

aromatic frameworks of **1a**, **b** should effectively interact with the planar surfaces of the MoS₂ nanosheets through host-guest S- π (anthracene) interactions (Figure 7a).^[12] Non-polyaromatic pentamethylbenzene panels provide only van der Waals interactions so that compounds **5a**, **b** show very low dispersion abilities toward MoS₂ nanosheets. Fluorescence analysis of the nanocomposites also supported the presence of such intermolecular host-guest interactions. Strong anthracene emission (Φ_F = 53 %) of **1b** in NMP was significantly quenched through the complexation with MoS₂ nanosheets (Φ_F = 10 %; Figure 7b). The side chains themselves are ineffective in dispersing MoS₂ nanosheets in NMP and thereby the combination of the rigid and bent polyaromatic framework and the non-ionic, flexible side chains is of importance to disperse the nanosheets facily.

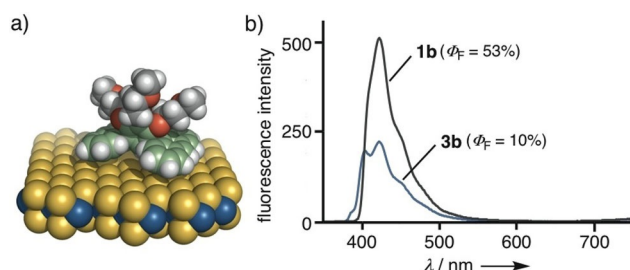


Figure 7. a) Optimized structure of the partial framework of a MoS₂ nanosheet interacting with dispersant **1b**. b) Fluorescence spectra (NMP, λ_{ex} = 369 nm, r.t., 0.44 mM based on **1b**) of dispersant **1b** and MoS₂ nanocomposite **3b**.

In conclusion, we have revealed that V-shaped polyaromatic compounds bearing three non-ionic side chains (i.e., 2-methoxyethoxy groups) act as new dispersants for inorganic MoS₂ nanosheets in NMP. The V-shaped dispersants newly designed in this work are readily synthesized in four-step reactions. Manual grinding and sonication (within total 1 h) of bulk MoS₂ in the presence of the dispersant afford highly dispersed MoS₂ nanosheets. Notably, the lateral sizes and thicknesses of the obtained nanosheets depend on the identity of the side chains on the V-shaped dispersant. Multiple S- π (polyaromatic ring) interactions are essential for the formation of the highly dispersed nanosheets. With the aid of the present facile and reliable method, the dispersion of other layered inorganic compounds (e.g., WS₂ and h-BN nanosheets) for the preparation of hetero-layered, inorganic nanosheets is our next target.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: dispersions • MoS₂ • nanostructures • noncovalent interactions • polyaromatic rings

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- [17] The dark green solid obtained from **3b** was gently washed with methanol to remove hydrophilic **1b** to give pure MoS₂ nanosheets (0.31 mg), which show no emission derived from fluorescent **1b**.
- [18] The rotational speed of centrifugation greatly affects the concentration of MoS₂ nanosheets in solution. The concentration of the present product is lower than that of previously reported samples (e.g., $\approx 40 \text{ mg mL}^{-1}$ in NMP after centrifugation at 1,500 rpm)^[4b] because of using high-speed centrifugation (14,800 rpm) for the purification.
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