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Accepted Article

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To be cited as: Chem. Asian J. 10.1002/asia.201701199

Link to VoR: http://dx.doi.org/10.1002/asia.201701199

A Journal of

ACES Asian Chemical Editorial Society A sister journal of Angewandte Chemie and Chemistry – A European Journal



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

Atsushi Matsumoto, Keisuke Jono, Munetaka Akita, and Michito Yoshizawa*^[a]

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 and hydrophobic 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 Waal 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 MoS_2 nanosheets. Manual grinding and sonication (within total 1 h) of bulk MoS_2 with the V-shaped polyaromatic compounds give rise to MoS_2 nanosheets with lateral sizes of ~150-270 nm and thicknesses of ~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.

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As new dispersants, here we designed V-shaped polyaromatic compounds 1a,b having two anthracene panels and three hydrophilic 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 metallophthalocyanines, through π -stacking interactions 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 and hydrophobic interactions (Figure 1c).^[1,12] In addition, the Vshaped 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.



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.

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

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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 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** (Figure S11 and S13, respectively).^[15]



Figure 2. ^1H NMR spectra (400 MHz, CDCl_3, r.t.) of V-shaped dispersants a) 1a and b) 1b.

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 MoS_2 (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 (14,800 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 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 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).





Figure 3. a) Schematic representation of the exfoliation and dispersion of bulk MoS_2 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 MoS_2 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 MoS_2 with **1a**.

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 (Figure 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 (Figure 4b and S15b). Time-dependent UVvisible analysis revealed that ~80% of the dispersed MoS₂ nanosheets with 1b remains in NMP after being stranded at room temperature for 1 d (Figure S15c). The concentration of MoS₂ nanosheets was estimated to be 0.31 mg/mL 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 hydrophilic side chains showed a lower dispersion ability (0.7fold). 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 (≤ 0.1 -fold) in dispersing MoS₂ nanosheets, 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 (Figure 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 MoS_2 nanocomposites **3a** (from **1a**), **3b** (from **1b**), and **3c** (from **4**)

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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 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.



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 MoS_2 nanosheets with an average height (thickness) of ~7 nm and an average lateral size of ~300 nm (Figure 6a). Under the 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 MoS_2 nanosheets, respectively. $^{\left[19\right]}$ Raman spectra of solids 3a, 3b, and 3c displayed prominent peaks around 380 and 410 cm⁻¹ (Figure 6d,e and S18), which also

formation of thinner, crystalline confirmed the MoS₂ nanosheets.^[20] Powder X-ray diffraction of solid 3b showed broad but typical peaks at 14.2 and 32.6 degrees (Figure S19).



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., λ_{ex} = 532 nm, 0.1 mW) of MoS₂ nanosheets from d) 3a and e) 3b.

 v/cm^{-1}

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 polyaromatic frameworks of 1a,b should effectively interact with the planar surfaces of the MoS₂ nanosheets through both S- π (anthracene) interactions and the hydrophobic effect (Figure 7a).^[12] Non-polyaromatic pentamethylbenzene panels provide only hydrophobic surfaces 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 ($\Phi_{\rm F}$ = 53%) of **1b** in NMP was significantly quenched through the complexation with MoS_2 nanosheets ($\Phi_F = 10\%$; 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 facilely.



Figure 7. a) Optimized structure of the partial framework of a MoS₂ nanosheet interacted 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. Both S- π and hydrophobic 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 novel hetero-layered, inorganic nanosheets is our next target.

Acknowledgements

This work was supported by JSPS KAKENHI, Grant No. JP25104011 and JP26288033, and "Support for Tokyotech Advanced Researchers (STAR)". We thank Dr. Takayuki Arai (JSR Corporation) for the initial synthesis of compounds **5a**,**b** and studies on their host properties. We also thank Dr. Yuka Akimoto and Mr. Yoshiyuki Satoh (Tokyo Institute of Technology) for the FE-SEM analysis.

Keywords: interactions, polyaromatic ring, MoS_2 , dispersion, nanosheets

- a) J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, Germany, 1995; b) J. W. Steed, J. L. Atwood, Supramolecular Chemistry, 2nd ed, Wiley, Chichester, UK, 2009.
- a) X. Huang, Z. Zeng, H. Zhang, Chem. Soc. Rev. 2013, 42, 1934– 1946; b) I. Song, C. Park, H. C. Choi, RSC Adv. 2015, 5, 7495–7514.
- [3] D. W. Johnson, B. P. Dobson, K. S. Coleman, Curr. Opin. Colloid Interface Sci. 2015, 20, 367–382.
- [4] a) R. J. Smith, P. J. King, M. Lotya, C. Wirtz, U. Khan, S. De, A. O'Neill,
 G. S. Duesberg, J. C. Grunlan, G. Moriaty, J. Chen, J. Wang, A. Minett,
 V. Nicolosi, J. N. Coleman, *Adv. Mater.* 2011, *23*, 3944–3948; b) A.
 O'Neill, U. Khan, J. N. Coleman, *Chem. Mater.* 2012, *24*, 2414–2421; c)
 Y. Yao, Z. Lin, Z. Li, X. Song, K.-S. Moona, C.-p. Wong, *J. Mater. Chem.* 2012, *22*, 13494–13499; d) Y. Yao, L. Tolentino, Z. Yang, X.

Song, W. Zhang, Y. Chen, C.-p. Wong, *Adv. Funct. Mater.* **2013**, *23*, 3577–3583; e) E. P. Nguyen, B. J. Carey, T. Daeneke, J. Z. Ou, K. Latham, S. Zhuiykov, K. Kalantar-Zadeh, *Chem. Mater.* **2015**, *27*, 53–59.

- [5] a) L. Yuwen, H. Yu, X. Yang, J. Zhou, Q. Zhang, Y. Zhang, Z. Luo, S. Su, L. Wang, *Chem. Commun.* **2016**, *52*, 529–532; b) G. S. Bang, K. W. Nam, J. Y. Kim, J. Shin, J. W. Choi, S.-Y. Choi, *ACS Appl. Mater. Interfaces* **2014**, *6*, 7084–7089.
- [6] G. Liu, N. Komatsu, ChemNanoMat 2016, 2, 500–503.
- [7] H. Yang, F. Withers, E. Gebremedhn, E. Lewis, L. Britnell, A. Felten, V. Palermo, S. Haigh, D. Beljonne, C. Casiraghi, 2D Mater. 2014, 1, 011012.
- [8] a) P. Mal, B. Breiner, K. Rissanen, J. R. Nitschke, *Science* 2009, 324, 1697–1699; b) M. Han, J. Hey, W. Kawamura, D. Stalke, M. Shionoya, G. H. Clever, *Inorg. Chem.* 2012, *51*, 9574–9576; c) W. J. Ramsay, F. T. Szczypiński, H. Weissman, T. K. Ronson, M. M. J. Smulders, B. Rybtchinski, J. R. Nitschke, *Angew. Chem. Int. Ed.* 2015, *54*, 5636–5640; d) D. Yang, J. Zhao, L. Yu, X. Lin, W. Zhang, H. Ma, A. Gogoll, Z. Zhang, Y. Wang, X.-J. Yang, B. Wu, *J. Am. Chem. Soc.* 2017, *139*, 5946–5951.
- The optimized structure was obtained by DFT calculations (B3LYP/6-31G* level) by using Spartan'10 (Wavefunction, Inc.).
- [10] K. Kondo, A. Suzuki, M. Akita, M. Yoshizawa, Angew. Chem. Int. Ed. 2013, 52, 2308–2312.
- [11] *Ionic* V-shaped polyaromatic compounds *for organic guests*: a) K. Kondo, M. Akita, T. Nakagawa, Y. Matsuo, M. Yoshizawa, *Chem. Eur. J* **2015**, *21*, 12741–12746; b) Y. Okazawa, K. Kondo, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2015**, *137*, 98–101; c) T. Omagari, A. Suzuki, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2016**, *138*, 499–502; d) K. Kondo, M. Akita, M. Yoshizawa, *Chem. Eur. J.* **2016**, *22*, 1937–1940; e) M. Kishimoto, K. Kondo, M. Akita, M. Yoshizawa, *Chem. Commun.* **2017**, *53*, 1425–1428.
- [12] a) L. M. Salonen, M. Ellermann, F. Diederich, *Angew. Chem. Int. Ed.* 2011, *50*, 4808–4842; b) S. Matsuno, M. Yamashina, Y. Sei, M. Akita, A. Kuzume, K. Yamamoto, M. Yoshizawa, *Nat. Commun.* 2017, *8*, in press (DOI: 10.1038/s41467-017-00605-5); c) Preliminary theoretical calculations (gas phase) indicated the energy of a stacked MoS₂ nanosheet-1b structure (Figure S20a) is 35.2 kcal mol⁻¹ lower than that of the unstacked structure (Figure S20b).^[15] Notably, the dihedral angle between the anthryl groups of 1b (120.0°) is significantly widened (138.6°) upon stack with a MoS₂ nanosheet due to strong intermolecular interactions. The grinding process most probably prompts the intermolecular stacks (Figure 1c).
- [13] a) R. J. Bushby, O. R. Lozman, *Curr. Opin. Colloid Interface Sci.* 2002, 7, 343–354; b) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* 2007, 36, 1902–1929; c) J. K. Klosterman, Y. Yamauchi, M. Fujita, *Chem. Soc. Rev.* 2009, 38, 1714–1725; d) K. Kondo, J. K. Klosterman, M. Yoshizawa, *Chem. Eur. J.* 2017, 23, in press (DOI: 10.1002/chem.201702519).
- a) M. Lee, B.-K. Cho, W.-C. Zin, *Chem. Rev.* 2001, *101*, 3869–3892; b)
 W. Li, Y. Kim, M. Lee, *Nanoscale* 2013, *5*, 7711–7723.
- [15] See the Supporting Information.
- [16] S. Sekiguchi, K. Kondo, Y. Sei, M. Akita, M. Yoshizawa, Angew. Chem. Int. Ed. 2016, 55, 6906–6910.
- [17] The dark green solid obtained from **3b** was gently washed with methanol to remove hydrophilic **1b** to give pure MoS_2 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.*, ~40 mg/mL in NMP after centrifugation at 1,500 rpm)^(4b) because of using high-speed centrifugation (14,800 rpm) for the purification.
- [19] FE-SEM analysis also supported the nanosheet structures of 3a (Figure S22).^[15]
- [20] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, S. Ryu, ACS Nano 2010, 4, 2695–2700.

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