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Dual Functionalization of Liquid-Exfoliated Semiconducting 2H-MoS₂ with Lanthanide Complexes Bearing Magnetic and Luminescence Properties

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1. Introduction

2D materials are at the center of intense research for a range of next-generation devices in, for example, energy storage, electronics, and sensing applications, due to their tunable physical, optoelectronic, and chemical properties.[1] These features arise from the anisotropic effects of the materials when thinned toward monolayers.[2] Of particular interest is the use of 2D materials as multimodal platforms for biomedical applications.[3] Most notably, transition metal dichalcogenides (TMDs) are a versatile alternative to the archetypal 2D nanomaterial graphene, with MoS₂, for example, displaying a higher near-infrared absorption compared with graphene oxide, which is attractive for photothermal therapy.[4] Various TMDs and oxides have been employed in multimodal biomedical applications such as MnO₂,[5] TiS₂,[6] and WS₂.[7] However, the majority of TMD multimodal platforms utilize MoS₂ to combine photothermal therapy with drug delivery[8] or use MoS₂/Bi₂S₃ as a dual diagnostic/therapeutic agent.[9]

Direct functionalization of MoS₂ nanosheets is a potentially convenient and controlled route to multimodality. Thioc containing molecules are typical ligands used to functionalize MoS₂ nanosheets via binding to sulfur vacancies in the host lattice.[10] Previous work has functionalized MoS₂ with dimercaptosuccinic-acid-coated Fe₃O₄ nanoparticles for magnetically targeted phototherapy and magnetic resonance imaging (MRI),[11] and disulfide-containing polyethylene glycol to create stable MoS₂ aqueous dispersions for photothermal therapy with drug delivery.[12] In these studies, MoS₂ nanosheets were chemically exfoliated by lithiation to produce the metallic 1T-MoS₂ polymorph, which shows little photoluminescence.[13] In contrast, the bulk 2H-MoS₂ polymorph is a semiconductor with an indirect band gap of 1.2 eV, while the monolayer form has a direct band gap of ≈1.8 eV.[14] Such a tunable band gap has attracted significant research in view of optoelectronic applications compared to graphene, which has no band gap in its native form.[15] Grafting molecules to the surface of such 2H-MoS₂ monolayers are of interest as it allows to modulate the
optical and electronic properties of the semiconductors, due to changes in the electronic structure of MoS2, and to introduce new functionalities. Moreover, binding of mercapto acids to defect sites of 2H-MoS2 was found to improve dispersion of the monolayers in water. [16a] Similarly, reaction of liquid-exfoliated 2D MoS2 with M(OAc)2 salts (M = Ni, Cu, Zn; OAc = acetate) allowed for its dispersion/processing in more conventional laboratory solvents, while furnishing the 2H-polytype of MoS2, which is a semiconductor. [17] Attempts to covalently functionalize 2H-MoS2 with organic molecules featuring thiol groups have given contradictory results. Some studies claim that the thiols bind covalently to the molybdenum ions of 2H-MoS2 at S-atom vacancies, but the Mo–S interaction was not fully investigated. [16b] In other studies, X-ray photoelectron spectroscopy (XPS) provided evidence for the oxidation of organic thiols to disulfides and thus their potential physiadsorption to 2H-MoS2 instead of coordinative linkage. [18] However, binding of dibenzothiophene to S-atom vacancies on small MoS2 clusters was unarguably confirmed by high-resolution scanning tunneling microscopy. [19] In addition, edge sites of 2H-MoS2 nanosheets were recently covalently functionalized with 1,2-dithiolanes. [20]

Functionalization of 2H-MoS2 nanosheets with lanthanide complexes is attractive due to the varied luminescent and paramagnetic elements the rare earths possess. For example, Gd3+ with seven unpaired electrons and a slow magnetic relaxation is used as a 1T MRI contrast agent, while Eu3+ and Tb3+ have narrow emission bands for optical imaging and long photoluminescence lifetimes (in the millisecond timescale). [21] The latter is useful for biological imaging as signals can be gated to avoid organic fluorescence from proteins and DNA, which occur on the nanosecond timescale. Nanoparticles have been used as platforms for binding lanthanides, [22] with one example anchoring both Eu and Gd simultaneously onto a silica nanoparticle surface, [23] building on previous work by Lewis et al. who used gold nanoparticles as a scaffold for the assembly of lanthanide(III) complexes. [24] In comparison, there are few examples that exist of nanosheets as platforms for lanthanide complexes. Graphene has been functionalized with either Gd(III) or Tb(III) complexes, [25] and with EuO3 nanoparticles. [26] Recently, MoS2 was exfoliated using cysteamine, and reacted with DTPA-dianhydride (DTPA = diethlenetriaminepentaacetic acid) to form a Gd(III) chelate. [27] However, the MoS2 nanosheets agglomerated during exfoliation with cysteamine to form large spheres, eventually forming a core–shell-like structure when reacted with Gd3+. Additionally, the functionalization of MoS2 with cysteamine caused a phase transition from the 2H-MoS2 to the 1T-MoS2 phase.

In this paper, we demonstrate that it is possible to covalently functionalize atomically thin 2H-MoS2 nanosheets simultaneously with Eu(III) and Gd(III) complexes to form a novel 2D luminescent and paramagnetic multimodal material (Scheme 1). The 2D structure of the MoS2 nanosheets was maintained post-functionalization, and we demonstrate that they exhibit sensitized luminescence from Eu3+ as well as the paramagnetism of Gd3+.

2. Results and Discussion

MoS2 nanosheets were prepared from bulk MoS2 powder exfoliated in 2-propanol as previously described by Backes et al. [27] The dispersions were analyzed using atomic force microscopy (AFM) (Figure 1). Low-resolution AFM scans revealed a limited number of larger sheets (N = 21) with a mean 30 nm height and 182 nm diameter (Figure 1a) and a unimodal distribution. High-resolution scans (Figure 1b,c) revealed the majority of sheet heights as 1.45 ± 0.43 nm (N = 1715) (Figure 1d), indicative of a bilayer structure (one sheet is ≈0.7 nm). [28] The ligand N,N′-bis(p-thiophenylamido) diethlenetriamine-N,N′,N′-triacetic (H3L) was prepared as previously described by Lewis et al. [24b] (through a condensation reaction between 4-aminothiophenol and DTPA-bis(anhydride), and was reacted with GdCl3·6H2O or EuCl3·6H2O to afford GdL and EuL, respectively. For functionalization of nanosheets, a 5 mL MoS2 dispersion (2-propyl alcohol, 0.25 mg mL−1) was mixed with 5 mL of a methanolic solution of EuL (20 μmol) or 5 mL EuL/GdL solution (in methanol, 10 μmol of each complex) and sonicated for 3 h. The hybrid material was isolated and washed with methanol through three rounds of centrifugation. The final pellet was resuspended in methanol to form a stable colloid for further characterization.

The optical properties of MoS2@LnL were investigated in detail. UV–vis absorption spectra of MoS2@LnL show a peak at 269 nm, which is not present in the as-synthesized MoS2 nanosheets, and is assigned to the π–π* transitions of the thiophenylamide groups of the grafted EuL and GdL (Figure 2a). [24a] The shift of the 266 nm peak for EuL to 269 nm for the functionalized MoS2@LnL material could potentially reflect the different chemical environment of the thiophenylamide group once grafted to the MoS2 surface. Importantly, the well-defined absorption peaks of MoS2 at 618 and 677 nm, ascribed to the A and B direct exciton transitions, [29] are only present in the 2H-MoS2 phase, and are indeed absent in the 1T-MoS2 phase. [13,18a] MoS2@EuL and MoS2@EuL/GdL show similar absorbance maxima at 615 and 676 nm. Hence, we conclude that the 2H-MoS2 does not undergo a phase change during functionalization as others have reported. [18b,27]

Steady-state emission spectra and luminescence lifetimes were recorded for both MoS2@EuL and MoS2@EuL/GdL (Figure 2b). The luminescence lifetimes of the 5D0 → 7F2 transition at ∼613 nm of Eu3+ were similar for both MoS2@LnL adducts and comparable to the value of 0.8 ms reported for...
EuL\textsuperscript{[24b]} This indicates that no quenching pathways are introduced by attaching the Eu(III) complex to the surface of the MoS\textsubscript{2} nanosheets and that the lanthanide ion most likely preserves its coordination environment. Steady-state emission spectra ($\lambda_{\text{exc}} = 270$ nm) showed the $5D_0 \rightarrow 7F_J$ ($J = 0, 1, 2, 3, 4$) emission lines of Eu\textsuperscript{3+} to be present in both MoS\textsubscript{2}@EuL and MoS\textsubscript{2}@EuL/GdL samples, indicating that the presence of Gd\textsuperscript{3+} does not alter Eu\textsuperscript{3+} emission (Figure 2c).\textsuperscript{[30]} These results are significant as they demonstrate that the desired luminescence characteristics of the Eu\textsuperscript{3+} ions (i.e., sharp line-like emission with long lifetimes, compared with organic luminophores) are retained after binding. As the excitation wavelength (266 nm) is commensurate with the $\pi - \pi^*$ transition of the ligand, this is further evidence that the structural integrity of the complex is not compromised upon binding to MoS\textsubscript{2}, and indeed the population of the lanthanide excited state proceeds through the triplet state of the ligand, as observed previously by Lewis et al.\textsuperscript{[24a]}

Figure 3 shows that the Mo, Eu, and Gd signals are spatially colocalized, confirming that EuL and GdL are associated with the MoS\textsubscript{2} nanosheet surface (see Figure S2 in the Supporting Information for a line-scan profile).

We note an increase in Eu and Gd signal intensity at the edge of the MoS\textsubscript{2} (Figure S2, Supporting Information), possibly due to preferential binding of thiolated ligands to MoS\textsubscript{2} edge sites, as described by others.\textsuperscript{[10,31]} In HAADF-STEM images of MoS\textsubscript{2}@EuL, Mo and Eu signals also colocalize (Figure S3, Supporting Information). EDX sum spectra from imaging demonstrated the expected ratio of Mo:S (1:2), with Eu and Gd at a level of 0.5 $\pm$ 0.2 at\% and 0.5 $\pm$ 0.2 at\% (i.e., $\sim$1:1), respectively, in MoS\textsubscript{2}@EuL/GdL; and Eu at 0.5 $\pm$ 0.1 at\% in MoS\textsubscript{2}@EuL (see Table S1 for tabulated results, including inductively coupled plasma mass spectrometry (ICP-MS), and Figure S4 in the Supporting Information for 1D-EDX spectrum).

To investigate the nature of the thiol–MoS\textsubscript{2} interaction, XPS was performed. Recently McDonald and co-workers investigated this interaction on MoS\textsubscript{2} nanosheets functionalized with cysteine, and while the free thiol (S-H) peak was absent in the Fourier transform-infrared red spectrum, XPS showed clear evidence that a disulfide cystine formed during the functionalization process.\textsuperscript{[18a]} Figure 4 shows the XPS spectra of Mo 3d, Eu 3d, and S 2p core levels. The binding energy of Mo and S in MoS\textsubscript{2}@EuL is consistent with crystalline $2H$-MoS\textsubscript{2}, with Mo$^{4+}$ 3d$^{5/2}$ and Mo$^{4+}$ 3d$^{3/2}$ doublets observed at 229.2 and 232.4 eV, respectively, S 2s appears at 226.4 eV.\textsuperscript{[12a]} The S 2s peak of EuL is at a higher binding energy of 227.7 eV, indicative of the
different chemical environment compared to the bound thiol (S-Mo). A limited Mo \( ^{6+} \) (MoO\(_3\)) component was also observed at 235.64 and 232.55 eV in MoS\(_2\)@EuL, possibly due to a small amount of surface oxidation or dangling edge sites. Eu \( ^{3+} \) 3d\(_{5/2}\) peaks appeared in both MoS\(_2\)@EuL and EuL at 1135 eV, with both samples showing characteristic multiplet split Eu\(^{3+}\) 3d\(_{5/2}\) peaks at 1143 and 1125 eV.\(^{[32]}\) Importantly, the S2p doublet peaks shifted from 164.7 and 163.5 eV for EuL, which has unbound SH groups, to 163.4 and 162.1 eV in MoS\(_2\)@EuL, in agreement with existence of thiolate–Mo bonds.\(^{[32]}\) A similar trend was reported by Tagmatarchis and co-workers for surface functionalization of exfoliated 2H-MoS\(_2\) with 1,2-dithiolane bearing an ethylene glycol alkyl chain with a pyrene moiety, concluding that the 2Sp XPS peaks of functionalized MoS\(_2\) and bulk MoS\(_2\) were comparable.\(^{[20]}\) There was no indication of a free thiol component or a disulfide component in the XPS spectrum of MoS\(_2\)@EuL. Fourier-transform infrared (FT-IR) spectroscopy of MoS\(_2\)@LnL showed no S–H stretch, which further confirms the absence of a thiol component (Figure S5, Supporting Information). We note that the distance between the two pendant sulfur groups of LnL is 0.6–0.7 nm,\(^{[34]}\) which is \( \approx 2a \) of the MoS\(_2\) crystal (\( \approx 0.6 \) nm) and is commensurate with binding.\(^{[35]}\) The inductively coupled plasma optical emission spectrometry (ICP-OES) results presented in the Supporting Information suggest that the actual stoichiometric formula of the material produced is MoS\(_{1.73}\) Ln\(_{0.02}\).

Further evidence of 2H-MoS\(_2\) thiolation comes from Raman spectroscopy; the E\(_{2g}\) and A\(_{1g}\) modes of MoS\(_2\)@LnL were shifted by 3 cm\(^{-1}\) to higher wavenumbers, compared to the as-synthesized MoS\(_2\) nanosheets (Figure S6, Supporting Information). A similar shift in MoS\(_2\) Raman modes was reported by Cho et al. after passivating mechanically exfoliated MoS\(_2\) with alkanethiols.\(^{[36]}\)

The paramagnetism of solid state MoS\(_2\)@EuL/GdL and GdL was confirmed using Q-band electron paramagnetic resonance (EPR) spectroscopy at 298 K (Figure 5). The EPR spectrum
of the GdL complex showed a single resonance peak due to Gd$^{3+}$ with $S = 7/2$, $g = 1.99$, and a negligible zero-field splitting (zfs) term. MoS$_2$@EuL/GdL showed a similar resonance peak, thus confirming the paramagnetism of the hybrid material. The broader EPR signal may result from small distortions in the coordination geometry of the Gd$^{3+}$ ion upon grafting to MoS$_2$. Indeed, the EPR spectrum of MoS$_2$@EuL/GdL requires zfs terms of 1575 and 100 MHz (Figure S7, Supporting Information). Unfunctionalized MoS$_2$ does not show a broad signal but only a weak sharp resonance at $g = 2.00$. A similar resonance peak was observed by others in $2H$-MoS$_2$ nanosheets, and was attributed to sulfur vacancies. Additional resonance peaks, such as those found in $1T$-MoS$_2$ ($g = 1.93$), are absent, which further confirms the purity of the $2H$-MoS$_2$ phase. Furthermore, MoS$_2$@EuL/GdL showed a relatively strong paramagnetic response in comparison to unfunctionalized $2H$-MoS$_2$ (Figure S8, Supporting Information), consistent with the presence of paramagnetic Gd$^{3+}$.

3. Conclusions

In conclusion, liquid exfoliated $2H$-MoS$_2$ nanosheets were covalently functionalized simultaneously with Eu$^{III}$ and Gd$^{III}$ complexes, with the luminescent and paramagnetic properties of the respective lanthanides being maintained post functionalization, in addition to the semiconductor $2H$-MoS$_2$ nanosheet phase. These results represent the first example of preformed lanthanide complexes being covalently linked to $2H$-MoS$_2$ nanosheet surfaces, and offer a broad approach to synthesizing transition metal chalcogenide nanosheets with molecular functionality that draw from the varied luminescent and paramagnetic properties the rare earths possess. Furthermore, this approach can be applied to bind lanthanide single-molecule magnets and even molecular spin qubits to the surface of semiconducting 2D TMDs, allowing fabrication of devices that will exploit their peculiar magnetic bistability and/or quantum properties.

4. Experimental Section

**General:** All materials and chemicals were purchased from Sigma-Aldrich, and used as received.

**Preparation of H$_2$L and LnL ($Ln = Gd$ or Eu):** N,N'-Bis[2-thiophenyl(aminocarbonyl)]diethylene-triamine-N,N',N''-triacetic acid (H$_2$L) was synthesized through a previously reported procedure. H$_2$L was then reacted with Gd$^{3+}$ or Eu$^{3+}$ ions to form the respective complexes, LnL ($Ln = Gd$ or Eu).

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Figure 4. High-resolution XPS spectra of MoS$_2$@EuL (top) and EuL (bottom) for a) Mo3d and S2s; b) Eu3d; and c) S2p regions.
Preparation of MoS2@Lnl (L = Gd or Eu): MoS2 nanosheets were prepared by the exfoliation of bulk MoS2 powder in 2-propanol alcohol as previously reported by Backes et al.11 100 mL of 2H-MoS2 powder in isopropyl alcohol (20 mg mL\(^{-1}\)) was aliquoted into 10 mL glass vials, which were then placed in a sonicator bath (37 kHz, 30% power) for 24 h (Scheme S1, Supporting Information). The solution was centrifuged at 1500 rpm for 45 min in 2 x 50 mL falcon tubes. The top 35 mL of each tube was carefully aliquoted and stored for further characterization. The final concentration of the MoS2 suspension was 0.25 mg mL\(^{-1}\). 5 mL MoS2 suspension in isopropyl alcohol (0.25 mg mL\(^{-1}\)) was mixed with EuL (5 mL methanol, 20 µmol) or EuL/GdL (5 mL methanol, 10 µmol each) and sonicated (37 kHz, 30% power, room temperature (RT)) for 3 h. The hybrid material was isolated and washed with methanol through three rounds of centrifugation (10 000 rpm). Then, the final pellet was responded in methanol (3 mL).

Characterization Techniques: High resolution TEM imaging, HAADF-STEM imaging, and EDX imaging were performed using a probe side aberration corrected FEI Titan G2 80-200 S/TEM “ChemiSTEM” instrument operating at 200 kV. EDX spectra and STEM images were analyzed using Bruker Esprit software. STEM images were analyzed using Gatan Digital Micrograph software. Samples were prepared by dripping dilute nanoparticle solution onto a carbon-coated copper grid. EDX quantification was performed with the Bruker Esprit software using the Cliff–Lorimer approach and with no absorption correction. ICP-MS measurements were performed at the University of Manchester School of Earth, Atmospheric and Environmental Sciences. Raman spectroscopy was performed using a Renishaw RM system 1000 Raman spectrometer with a 514 nm laser. AFM measurements were performed using a Bruker Multimode 8 instrument with a silicon-nitride tip. EPR spectra were recorded in continuous-wave mode with a Bruker EMX 300 EPR spectrometer operating at a microwave frequency of 34 GHz (Q-band) at 298 K. Simulations were performed using EasySpin software with MATLAB.42 Magnetic studies were performed using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7-tesla magnet. Hysteresis curves were recorded at 2 K by cycling the magnetic field between (7 T) and (−7 T) fields (sequence used: (0) → (7 T) → (−7 T) → (7 T)). UV–vis absorption spectra were collected using a double beam UV-1800 Shimadzu UV–vis spectrophotometer between 200 and 900 nm. Samples were measured in quartz cuvettes with a path length of 1 cm, and pure solvent was used as a blank. Phospholinescence (PL) emission spectra were collected using a GILDEN Photonics fluoroSENS spectrophotometer at a 270 nm excitation wavelength, with a 1 nm resolution. Quantum yields were measured using Bruker Esprit software. The final concentration of the NlL complex was 0.25 mg mL\(^{-1}\) and sonicated (37 kHz, 30% power) for 24 h (Scheme S1, Supporting Information). The solution was centrifuged at 1500 rpm for 45 min in 2 x 50 mL falcon tubes. The top 35 mL of each tube was carefully aliquoted and stored for further characterization. The final concentration of the MoS2 suspension was 0.25 mg mL\(^{-1}\). 5 mL MoS2 suspension in isopropyl alcohol (0.25 mg mL\(^{-1}\)) was mixed with EuL (5 mL methanol, 20 µmol) or EuL/GdL (5 mL methanol, 10 µmol each) and sonicated (37 kHz, 30% power, room temperature (RT)) for 3 h. The hybrid material was isolated and washed with methanol through three rounds of centrifugation (10 000 rpm). Then, the final pellet was responded in methanol (3 mL).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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