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Non-Covalent Synthesis as a New Strategy for Generating Supramolecular Layered Heterostructures

Ram Kumar, Krishnendu Jalani, Subi J. George,* and C. N. R. Rao*

Chemistry and Physics of Materials Unit, Sheikh Saqr Laboratory, International Centre for Materials Science (ICMS), CSIR Centre of Excellence in Chemistry and New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur, Bangalore, India-560064

ABSTRACT: Non-covalent synthesis of stable heterostructures (MoS₂-BN, MoS₂-graphene) of layered materials has been accomplished by a ternary host-guest complex as a hetero-complimentary supramolecular motif. Besides being reversible, this supramolecular strategy to generate heterostructures may find uses in many situations.

INTRODUCTION

Synthesis of heterostructures by the vertical stacking of layered materials is actively being pursued to modulate the functional properties of 2D materials.¹⁻⁴ These novel materials exhibit unique optical, electrical and thermal properties due to synergistic effects and tunable composition of the individual components.5-13 Most 2D heterostructures are prepared by the mechanical assembling of individual monolayers or few-layers of different materials, the resultant materials being stabilized by weak van der Waals forces.¹ Although the van der Waals heterostructures exhibit a plethora of fascinating properties, synthesis of extended stacks with precise sequence and composition of the components remains a challenge. Thus, in an attempt to create stable, multi-component heterostructures, we have investigated a novel class of covalently linked ladder-like materials.14 They have been synthesized by covalently linking different 2D layered materials through organic coupling reaction between surface functional groups. This novel class of materials show interesting properties¹⁵⁻¹⁸ and are different from the van der Waals heterostructures.

The synthetic heterostructures reported so far represent exceptional examples in the family of 2D layered materials and advancement towards higher complexity of heterostructures with multiple components and precise sequences would have to be addressed to explore novel applications. Such a non-covalent synthetic strategy would yield supramolecular heterostructures with selforganizing components and dynamic characteristics which can be reversibly sequenced for various functions. In this manuscript we describe the first successful noncovalent synthesis of heterostructure assemblies of layered 2D sheets. This supramolecular approach facilitates an unprecedented reversible, alternative stacking of layered materials by a solution state self-assembly process.

One of the key requisites for an efficient supramolecular strategy to construct such heterostructures is the use of a hetero-complimentary non-covalent interaction to promote a A-B-A-B kind of assembly rather than self-sorted assemblies of individual components (-A-A-Aor -B-B-B-). For this purpose, the host-guest chemistry of cucurbit[8]uril (CB[8]) is used in the present manuscript, which is known to form ternary complexes with appropriate donor and acceptor molecules with high association constants.¹⁹⁻²⁵ For example, the ternary complex of CB[8], with naphthol donor (D) and viologen acceptor (A) exhibits a high equilibrium association constant in the order of 1012 M-2, which would definitely favor a heteroassembly. In our design strategy we have, therefore, functionalized the electronically dissimilar 2D sheet structures with naphthol and viologen moieties and used this reversible supramolecular motif to interlock the 2D sheets structures to make supramolecular layered heterostructures (Scheme 1).

EXPERIMENTAL SECTION

Reagents and precursors: All the chemicals used in synthesis were of high purity and obtained from commercial sources. DMF was pre-dried before reaction. Carboxylate functionalized graphene was obtained by microwave irradiation following standard procedure.²⁶ Amine functionalized few-layer BN (\approx 1–4 layers) was prepared by mixing boric acid and urea in 1:48 molar ratio and heating in high purity ammonia atmosphere at 900 °C for 5 h.²⁷⁻²⁹

Synthetic procedures for **G-VN**:



Synthesis of G-VN: In a Schlenk flask, 100 mg of carboxylated graphene was added, purged with N2, sealed using septum and to that, 25 mL of dry DMF was added. Uniform dispersion was obtained by sonication for 1 h. To dispersion, N-(3-dimethylaminopropyl)-N'this ethylcarbodiimide hydrochloride (EDC.HCl, 80 mg), 1hydroxybenzotriazole (HOBt, 90 mg), and N,Ndiisopropylethylamine (DIPEA, 1.2 mL) were added under constant stirring. Then 110 mg of compound 2 (synthesis shown below) in dry DMF was injected to the reaction mixture and kept stirring for 24 h. Nitrogen atmosphere was maintained during the reaction. The product was isolated by centrifugation and washed with ethanol four times. The product was dried under vacuum at 65 °C to give 146 mg of the solid product (G-VN).

Synthesis of compound **2**: 0.6 g (2 mmol) of compound **1** and 0.61 g (2.98 mmol) of 2-bromoethylamine hydrobromide was mixed together in 40 mL of dry acetonitrile followed by refluxing at 80 °C for 72 h under N2 atmosphere. The product was precipitated out as orange solid which was filtered and washed with acetonitrile to obtain the product in 42% yield. ¹H NMR (400 MHz, D2O): δ = 9.27 (d, *J* = 6.8 Hz, 1H), 9.05 (d, *J* = 6.4 Hz, 2H), 8.68 (d, *J* = 6.8 Hz, 2H), 8.58 (d, *J* = 6.4 Hz, 2H), 5.16 (t, *J* = 6.8 Hz, 2H), 4.54 (s, 3H), 3.84 (t, *J* = 8 Hz, 2H). ¹³C NMR (100 MHz, D2O): δ (ppm) 151.47, 149.47, 146.45, 146.21, 127.71, 126.89, 58.12, 48.53, 39.14. HRMS: m/z, calcd: [C13H17N3]: 215.1412, found: 215.7940, [M]⁺.

Synthetic procedures for **BN-Nap**:



Synthesis of **BN-Nap**: 100 mg of **BN-amine** was added in a Schlenk flask and sealed using septum followed by purging with N2. To that 30 mL of dry DMF was added and sonicated for 1 h to obtain a uniform dispersion of solution. Then N-(3-dimethylaminopropyl)-N'ethylcarbodiimide hydrochloride (EDC.HCl, 80 mg), 1hydroxybenzotriazole (HOBt, 100 mg) and N,N-

diisopropylethylamine (DIPEA, 1.5 mL) was added and stirred for 5 min. Finally 160 mg of naphthol carboxylic acid (4) which was synthesized by following standard procedure,³⁰ was added to that and stirred for 48 h. Nitrogen atmosphere was maintained during the reaction. Obtained product was centrifuged and washed with ethanol to remove DMF. The solid product was further dried at 100 °C under vacuum to give 140 mg final product.

Synthetic procedures for 1T MoS2 and MoS2-Nap:



Synthesis of **1T MoS2**: *n*-BuLi (3.0 mL, 1.6 M in hexane) was added to a suspension of the bulk MoS2 (300 mg) in dry hexane (10 mL) under an inert nitrogen atmosphere. The reaction mixture was heated to reflux for 48 h and then cooled to room temperature. The black precipitate was filtered under a nitrogen atmosphere and washed thoroughly with dry hexane to remove unreacted *n*-BuLi. The black precipitate was immediately added to deionized, degassed cold water (300 mL) and sonicated for 1 h to facilitate exfoliation. The resulting aqueous dispersion was centrifuged at 5000 rpm to remove the non-exfoliated portion as sediments. The aqueous dispersion containing exfoliated MoS2 was collected for the functionalization reaction.

Synthesis of **MoS2-Nap**: 60 ml of exfoliated 1T-MoS2 solution and 600 mg of 2-Bromo-naphthol were mixed with 20 ml of dry DMF in a round bottom flask and kept at stirring for 2 days under N2 atmosphere. The product was precipitated out as black solid which was filtered and washed with ethanol. The obtained product was dried under vacuum at 70 °C.

RESULTS AND DISCUSSION

In order to demonstrate this supramolecular design for layered heterostructures, graphene-BN and graphene-MoS₂ hybrids were used. Graphene was functionalized with the viologen acceptor and the BN and MoS₂ sheets with naphthol donors (Scheme 1). 2D sheets functionalized with different organic ligands were synthesized by employing the EDC {1-ethyl-3-(3-dimethylaminopropyl) carbodiimide} coupling reaction (See experimental section for details). Carboxylate functionalized graphene was synthesized by microwave irradiation of graphene in HNO₃/H₂SO₄ mixture and subsequently reacted with amine functionalized viologen to yield viologen functiongraphene (G-VN). BN-amine, synthesized by alized heating boric acid and urea in an ammonia atmosphere, was coupled with naphthol-carboxylic acid to produce naphthol functionalized BN (BN-Nap). Functionalization of MoS₂ was achieved by surface modification strategies

that are reported to enhance its processability and chemical reactivity.³¹ Here 1T-MoS₂ obtained by the lithium intercalation of bulk MoS₂ using *n*-BuLi, are shown to acts as the nucleophile to form C-S bonds by virtue of the excess electrons on its surface. Hence nucleophilic substitution of exfoliated 1T-MoS₂ with a 2-bromo-naphthol derivative yielded the naphthol functionalized MoS₂ (**MoS₂**-**Nap**). These chromophore functionalized 2D sheets and their assemblies were characterized using spectroscopic, microscopic and gravimetric techniques.

The solid state ¹³C-MAS NMR spectrum of **G-VN** showed the characteristic peaks of viologen (Figure S1) wherein the signals at 30.18, 35.38, 62.08 ppm correspond to the sp³ carbons whereas the signals in the range of 120-180 ppm arise from the aromatic carbons.³² Viologen functionalization on graphene was further confirmed by UV-vis absorption and FTIR spectroscopy. The FTIR spectrum of **G-VN** shows the Amide 1 vibrational frequency at 1656 cm⁻¹, with decreased intensity of C=O stretching frequency (1726 cm⁻¹) of the parent carboxylates groups, corroborating a successful EDC coupling reaction (Figure S2b).

Furthermore, the absorption spectrum of 0.0075 wt% aqueous solution of G-VN shows a band at 260 nm corresponding to the viologen chromophore (Figure S2a). The percentage of viologen functionalization on graphene was quantified to be ~15 wt%, from TGA analysis and UV-vis spectrum of G-VN (Figures S2, S3). Viologen functionalization stabilizes the exfoliated graphene sheets as evident from the stable dispersions of G-VN in water and the presence of isolated thin nanosheets in the TEM (Figure S₄). In the case of naphthol functionalized BN sheets (BN-Nap), the UV-vis spectrum shows a broad absorption $(\lambda_{max} = 270 \text{ nm})$ and blue emission $(\lambda_{max} = 358 \text{ nm})$ characteristic of naphthol chromophores (Figure S5). The presence of naphthol chromophores on BN sheets is also evident from the corresponding excitation spectrum (Figure S₅). Further proof for naphthol functionalization was obtained from the FTIR spectrum which clearly shows the appearance of amide vibrational band at 1676 cm⁻¹ in comparison with the parent amine functionalized BN (Figure 1a). TEM imaging of these samples (Figure S6), shows exfoliated folded sheets of BN-Nap.



Scheme 1. Design of supramolecular heterostructures: Schematic illustrations of the ternary supramolecular assembly approach to make layered heterostructures: Acceptor (viologen) modified graphene (G-VN) forms heterostructures with donor (naphthol) modified BN (BN-Nap) and MoS₂ (MoS₂-Nap) in presence of CB[8]. B, C, N, Mo, S in the sheet structures are represented by red, pink, green, pale yellow and blue color spheres, respectively.

Since the functionalization of MoS₂ was achieved by the nucleophilic substitution with bromo-naphthol ligand, the presence of C-S vibrational stretching at 615 cm⁻¹ in FTIR spectrum (Figure 1b) and absence of Br signal in XPS measurements (Figure S8) confirms the presence of naphthol chromophores on the MoS₂-Nap sheets. Further the TGA analysis of **MoS₂-Nap** suggests 8 wt% of naphthol functionalization on MoS₂ (Figure S9). TEM imaging of these functionalized nanosheets showed fewlayer sheets with interlayer distances ranging from 0.76 nm to 0.93 nm, reiterating the functionalization with naphthol groups (Figure S10).



Figure 1. Comparison of the FTIR spectra of the precursors boron nitride (BN), Naphthol-carboxylic acid (4) and the naphthol functionalized BN (**BN-Nap**), showing the disappearance of the C=O bond stretching vibration and the appearance of amide bond vibration, b) Proof of Naphthol functionalization with MoS2. Infrared spectra of the **Nap-Br** and **MoS2-Nap** showing the disappearance of C-Br bond vibration and appearance of the C-S bond stretching vibration.

After synthesizing and characterizing various chromophore functionalized 2D sheets, we proceeded to generate supramolecular 2D heterostructures. Thus, we carried out the co-assembly of viologen appended graphene sheets with the naphthol functionalized BN or MoS₂, in the presence of CB[8] (Scheme 1). We envisage that the hetero-ternary supramolecular inclusion complex of viologen and naphthol with CB[8] would drive the alternative stacking of these 2D sheets to yield the supramolecular heterostructures. In a typical co-assembly procedure, the individual components were added to water and sonicated for few hours to make well-dispersed aqueous solution of exfoliated sheets which would increase the efficiency of ternary complexation. Ternary complex formation was probed by changes in the spectroscopic properties, the resultant heterostructures being characterized by X-ray diffraction and other microscopic techniques. The UV-vis spectrum of the G-VN:BN-Nap hybrids in presence of CB[8] showed a weak charge-transfer (CT) band at 480 nm, characteristic of the viologen-naphthol interaction, suggesting the formation of ternary complex (Figure 2a). Quenching of naphthol emission in the coassembled solution was taken to indicate the participation of **BN-Nap** in ternary complex formation (Figure S11). In the case of G-VN:MoS₂-Nap hybrids, probing this CT absorption was difficult due to the overlapping band originated from MoS₂ (Figure 2b). However, a de-convoluted absorption spectrum of the resulting hybrid by subtracting the contributions from individual components reveal a weak broad CT band absorption in the 470-500 nm region (Figure S12). Scattering in the UV-vis spectra after co-assembly (Figure S11, S12) in both the cases suggests the formation of an extended assembly in solution which starts precipitating over time. This was also evident from the photographs of the co-assembled solutions (insets of Figure 2a and 2b) showing the formation of precipitates (vial ii) within 2 hours of mixing the individual components.

The supramolecular co-assembly process in solution could be probed via the zeta potential measurements. G-VN sheets showed a negative zeta potential because of the presence of surface carboxylate anions in presence of water.33 Small percentage of cationic viologen groups on graphene surface is not sufficient to overcome the negative charges of carboxylate anions and eventually shows a negative zeta potential of -18 eV. On the other hand, **BN-Nap** in water shows a negative zeta potential of -25 eV, due to the presence of negatively charged oxygencontaining groups (B-O-H, N-O-H) on BN surface. MoS₂-Nap having surface negative charge reveals a negative zeta potential of -24 eV. Upon co-assembly with CB[8], both G-VN:BN-Nap (-3 eV) and G-VN:MoS₂ (-9.45 eV) showed significant decrease in the zeta potential values suggesting the formation of an extended layered heterostructures (Figure 2c, Figure S13).

Decisive evidence of an extended assembly of supramolecular heterostructures is provided by the Dynamic Light Scattering (DLS) experiments, which show significant increase in the size of the co-assembled hybrids compared to the individual components. The number average size data depict larger assemblies for **G-VN:BN-Nap** (1000 nm) and **G-VN:MoS₂-Nap** (900 nm), compared to the lower sizes for individual 2D sheets (Figure 2e,f).

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Figure 2. a) Absorption spectrum showing the charge-transfer (CT) band at $\lambda_{max} = 480$ nm after mixing **BN-Nap** and **G-VN** in presence of CB[8]. b) Absorption spectrum of **MoS₂-Nap:G-VN**:CB[8] ternary assembly and the de-convoluted spectrum to show the CT band of the ternary complex. Inset of a) and b) shows the photographs of the vials with various components, i. **BN-Nap:G-VN**, ii. **BN-Nap:G-VN**:CB[8], iii. **BN-Nap:G-VN**:CB[8]:ADA, with CB[8]:ADA ratio as 1:5. c) Bar diagram showing the zeta potential changes for the reversible assembly of **G-VN** with **BN-Nap** and **MoS₂-Nap** in presence of CB[8] and adamantyl amine (ADA). d) Schematics for the reversible assembly of **G-VN** with **BN-Nap** and **MoS₂-Nap** in presence of CB[8] and ADA. e) and f) are the corresponding Dynamic Light Scattering (DLS) data showing the formation of extended heterostructures in presence of CB[8] and its reversible assembly with ADA. ([**BN-Nap**] = 0.0075 wt%, [**G-VN**] = 0.0075 wt%, [**MoS₂-Nap**] = 0.0075 wt%, CB[8] = 10⁻⁴ M, H₂O).

Thermogravimetric analysis (TGA) of the **G-VN:BN-Nap** heterostructures in presence of CB[8] showed exceptional stability as the weight loss is observed at higher temperature (400 °C) compared to the individual components, **G-VN** (200 °C) and **BN-Nap** (150 °C), suggesting an extensive crosslinking and chelation of the 2D sheets preventing the collapse of the scaffold (Figure S14).

A unique advantage of non-covalent interactions is their reversible nature, which can be exploited to impart dynamic property to resultant supramolecular materials. We have further examined the reversibility of these novel supramolecular heterostructures formed via ternary host-guest complexation, by introducing a competitive guest molecule into the system (Figure 2d). Adamentylamine (ADA) was used as a competitive guest molecule, as they are known to form a strong 1:1 inclusion complex with CB[8] (K_a ~ 10¹¹ M⁻¹).³⁴⁻³⁵ Thus competitive replacement of naphthol and viologen components by ADA should result in the dis-assembly of the supramolecular heterostructures. Interestingly both supramolecular heterostructures showed significant decrease in the size and increase in the negative surface charge (Figure 2c-f), on addition of 5 eq. ADA with respect to CB[8], thus supporting an unprecedented reversible stacking of 2Dheterostructures. Formation of layered heterostructures was also investigated using powder X-ray diffraction

(PXRD) patterns of the precipitates of G-VN:BN-Nap:CB[8] and G-VN:MoS,-Nap:CB[8], dried under vacuum. The XRD data of G-VN:BN-Nap assembly showed the appearance of a new reflection at $2\theta = 5.4^{\circ}$ (d = 1.63 nm) corresponding to the interlayer distance between the G-VN and BN-Nap sheets. A similar reflection at low angle regions was observed for G-VN:MoS₂-Nap assembly at $2\theta = 4.48^{\circ}$ (d = 1.96 nm) corresponding to the interlayer spacing between MoS₂-Nap and G-VN. Interestingly, the broad reflection at $2\theta \sim 25^{\circ}$ corresponding to a *d* spacing of 0.34 nm, observed in the **BN-Nap** and G-VN XRD pattern, characteristic of van der Waals layered structures, disappeared in the co-assembled materials suggesting an alternatively stacked heterostructure (Figure 3).

Characterization of the heterostructures was carried out with various microscopic techniques. TEM and FESEM imaging of **G-VN:BN-Nap** heterostructures showed extended structures formed by the multi-layer stacking of 2D sheets (Figure S15 and S16). Detailed TEM analysis of **G-VN:MoS₂-Nap** heterostructures show an interlayer spacing in the range of 1.5 to 2.0 nm, as evident from the corresponding histogram profiles (insets, Figure 4a and 4b). This observation is consistent with the XRD results and confirms the formation of alternate heterostructures.



Figure 3. PXRD spectra for the **BN-Nap:G-VN:**CB[8] and **MoS₂-Nap:G-VN:**CB[8] supramolecular heterostructures along with their individual components (**BN-Nap**, **G-VN**, **MoS₂-Nap**). New peaks at $2\theta = 5.4^{\circ}$ (1.63 nm) for the **BN-Nap:G-VN** hybrid and at $2\theta = 4.48^{\circ}$ (1.96 nm) for **MoS₂-Nap:G-VN** hybrid compared to **BN-Nap**, **G-VN** and **MoS₂-Nap** confirms the presence of alternately stacked heterostructures. The schematics adjacent to the each PXRD spectrum suggest the corresponding species.



Figure 4. a), b) are the TEM images for the MoS_2 -Nap and G-VN layered heterostructures showing the heterostructure interlayer separation ranging from 1.5 nm to 2 nm. Insets show the histogram profile corresponding to the interlayer distance as marked by arrow heads in the image.

Elemental mapping of the **G-VN:BN-Nap:**CB[8] assembly using energy-dispersive X-ray analysis (EDAX) shows uniform distribution of B, N, C and O, confirming the homogeneous nature of the heterostructures (Figure 5). Electron energy-loss spectra (EELS) of the **G-VN:BN-Nap** heterostructures was recorded to identify the atomic composition (Figure S17). The spectra show the characteristic K-shell ionized edges of B, C, N, O at 193.3, 298, 409.7, 543 eV, respectively. The K-shell ionization edge at 193.3 eV is due to the transition of B is electron to the π^*

antibonding orbitals, associated with planar bonding and sp² hybridization of boron. The signals in the 200–216 eV range are due to the 1s $\rightarrow \sigma^*$ transition of boron. The peak at 402.5 eV is assigned to 1s $\rightarrow \pi^*$ transition of N, whereas peaks at 409 and 416 eV are due to 1s $\rightarrow \sigma^*$ transition of BN. The C K shell ionization edge has bands at 286 and 298 eV corresponding to 1s $\rightarrow \pi^*$ and 1s $\rightarrow \sigma^*$ transitions of graphene. The O K shell ionization is also observed at 543 eV due to oxygen containing functional groups in the heterostructures. EDAX and EELS analyses of **G**-**VN:MoS₂-Nap** heterostructures in the presence of CB[8] also reveal uniform distribution of Mo, S, C, O and N confirming the homogeneous nature of the heterostructures (Figures S19-S20).



Figure 5. a) FESEM image of the **BN-Nap:G-VN** supramolecular heterostructures and the corresponding, b) elemental mapping, B (yellow), C (red), N (green) and O (cyan). c) Energy dispersive X-ray (EDAX) analysis of **BN-Nap:G-VN** hybrids showing the presence of B, C, N, O signals.

CONCLUSIONS

In conclusion, we have shown that a non-covalent synthetic design as a new strategy for the reversible construction of layered heterostructures of 2D materials. A perfectly alternate stacking of 2D nano-sheets in these novel supramolecular layered heterostructures have been achieved by the use of a hetero-complementary host-guest interaction with very high association constant. This supramolecular strategy has been demonstrated with the heterostructures of graphene with boron nitride and MoS₂, which were fully characterized by various techniques. We believe that the supramolecular strategy presented here can be extended to the synthesis of novel heterostructures with multiple components and programmed sequences.

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ASSOCIATED CONTENT

Supporting Information

Spectroscopic studies, characterization and Supporting Figures.

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AUTHOR INFORMATION

Corresponding Author

*<u>Email: cnrrao@jncasr.ac.in;</u> *<u>Email: george@jncasr.ac.in</u>

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