## **Supporting Information**

# Dynamic Tungsten Diselenide Nanomaterials: Supramolecular Assembly-Induced Structural Transition over Exfoliated Two-Dimensional Nanosheets

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#### **Experimental Section**

#### Materials

Adenine, chloroform, dimethylformamide, potassium tert-butoxide, hexane, poly(propylene glycol) diacrylate (average molecular weight, 800 g/mol; degree of polymerization, 14) and other chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA) and used without further purification.

#### Characterization methods

Rigaku Ultima IV wide-angle X-ray diffraction (WXRD; Rigaku, Tokyo, Japan) patterns were analyzed using a Bruker phase diffractometer (Cu K $\alpha$ ,  $\lambda = 1.54056$  Å with a nickel monochromatic at 40 kV). Differential scanning calorimetric (DSC) curves were acquired with a PerkinElmer-DSC 4000 instrument for thermal properties analysis. Raman spectra were obtained 200 to 1600 cm<sup>-1</sup> at 25 °C using a laser Raman spectrometer (Model CRM 2000; WITec Inc., Ulm, Germany). Ultraviolet-visible (UV-Vis) spectroscopy data were obtained using a UV-Vis spectrophotometer (Jasco V-550 type, Tokyo, Japan). Fluorescence spectra were recorded using a 1 cm-path quartz cell on a Jasco FP-8300 spectrophotometer equipped with xenon lamp at a slit width of 10 nm. An excitation wavelength of 420 nm was used and fluorescence emission was monitored in the range of 420-900 nm. Field emission scanning electron sicroscopy (FE-SEM; JSM-6500F, JEOL, Japan) and high-resolution transmission electron microscopy (HRTEM, H-7000; Hitachi, Tokyo, Japan) were carried out to analyze sample morphology and microstructure. Variable-temperature Fourier transform infrared (VT-FTIR) measurements were performed with a PerkinElmer Spectrum Two system (PerkinElmer, Buckinghamshire, UK) at a wave number range of 600–4000 cm<sup>-1</sup>. The chemical shifts and elemental

components of the samples were verified via X-ray photoelectron spectroscopy (XPS, British VG Scientific ESCALAB 250 with an Al K  $\alpha$  source; Sussex, UK). The thicknesses and morphology of exfoliated WSe<sub>2</sub> nanosheets were analyzed using an atomic force microscope (NX10, AFM Park Systems, Suwon, South Korea). Small angle X-ray scattering (SAXS) data were generated using the BL17A1 wiggler beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Each samples was sealed in polyimide film (Kapton, 12 µm-thickness) and analyzed at 25 °C using an X-ray photon of wavelength 0.113 nm and beam diameter of 1.0 mm (*q*-range: 5-100 Å<sup>-1</sup>).



**Fig. S1**: Magnified XRD peaks extracted from **Fig. 2a** for A-PPG, WSe<sub>2</sub> and WSe<sub>2</sub>/A-PPG composites.



**Fig. S2**: High-resolution XPS spectra of **(a)** N 1s and **(b)** O 1s for A-PPG and WSe<sub>2</sub>/A-PPG composites and **(c)** Se 3d for WSe<sub>2</sub> and 50/50 WSe<sub>2</sub>/A-PPG composites.



Fig. S3: DLS analyses of (a) A-PPG and (b) 50/50 WSe<sub>2/</sub>A-PPG composite in THF.



Fig. S4: AFM images of the 50/50 WSe<sub>2</sub>/A-PPG composite. (a) Step height was determined from the AFM images of the WSe<sub>2</sub> nanosheets shown in panel (b).



**Fig. S5**: DSC curves of A-PPG, WSe<sub>2</sub> and WSe<sub>2</sub>/A-PPG composites for the first cooling/second heating process.

	Second heating scan				First cooling scan			
Sample	$\frac{T_{\rm mo}^{1}}{(^{\rm o}{\rm C})}$	$T_{\rm mf}^{l}$ (°C)	$T_{\rm m}^{-1}$ (°C)	$\Delta H_{\rm m}^{-1}$ (J/g)	$T_{\rm co}^2$ (°C)	$T_{\rm cf}^2$ (°C)	$T_{\rm c}^2$ (°C)	$\Delta H_{\rm c}^2$ (J/g)
A-PPG	90.37	101.53	96.47	248.38	41.25	37.02	39.64	215.60
10/90 WSe <sub>2</sub> /A- PPG	86.21	101.75	96.70	203.67	44.33	35.55	40.68	175.52
30/70 WSe <sub>2</sub> /A- PPG	84.96	97.543	90.67	173.15	43.45	31.70	37.74	133.76
50/50 WSe <sub>2</sub> /A- PPG	102.88	109.01	109.48	80.84	43.93	36.20	40.18	79.45

**Table S1.** Thermal properties for the second heating and first cooling cycles based on DSC curves.

<sup>1.</sup> Melting point ( $T_{\rm m}$ ), onset melting point ( $T_{\rm mo}$ ), final melting point ( $T_{\rm mf}$ ), and melting enthalpy ( $\Delta H_{\rm m}$ ).

<sup>2.</sup> Crystallization point ( $T_c$ ), onset crystallization point ( $T_{co}$ ), final crystallization point ( $T_{cf}$ ), and crystallization enthalpy ( $\Delta H_c$ ).



**Fig. S6**: Five-cycle DSC heating/cooling scans for A-PPG and 10/90 WSe<sub>2</sub>/A-PPG composite under nitrogen flow.

DSC measurements were performed using a PerkinElmer-DSC 4000 analyzer to study the phase transition behavior for each phase change material and WSe<sub>2</sub>. **Fig. S5** and **Table S1** demonstrate the DSC thermal curves for A-PPG, WSe<sub>2</sub> and the WSe<sub>2</sub>/A-PPG composites. A-PPG had a heat of fusion ( $\Delta H$ ) of 248.4 J/g and melting point ( $T_m$ ) of 96.5 °C, whereas WSe<sub>2</sub> did not show any phase transition behavior over a wide temperature range. Surprisingly, the melting points of WSe<sub>2</sub>/A-PPG composites with various *wt%* ratios were similar to pristine A-PPG (96.5 °C) and the observed  $\Delta H$  values gradually increased with the amount of A-PPG, suggesting introduction of WSe<sub>2</sub> into the A-PPG matrix did not affect the phase behavior of A-PPG. In addition, validation tests by multicycle DSC (Fig. S6) further confirmed the excellent phase transition behavior and thermoreversible stability of the WSe<sub>2</sub>/A-PPG composites, indicating attachment of the adenine molecules to the chain end of PPG offers the potential to achieve temperatureresponsive phase-change composites with higher thermal stability and that the presence of exfoliated WSe<sub>2</sub> may assist disordered-ordered transition in the matrix phase.<sup>36</sup>



Fig. S7: VT-FTIR spectra of 50/50 WSe<sub>2</sub>/A-PPG composite at various temperatures.

VT-FTIR was carried out to validate the DSC results and investigate the relationship between hydrogen bonding interactions and thermodynamic phase transitions. Fig. S7 illustrates the VT-FTIR spectra of 50/50 WSe<sub>2</sub>/A-PPG composite from 25 °C to 120 °C. The two stretching vibration peaks of hydrogen bonded N–H at 3111 cm<sup>-1</sup> and 3285 cm<sup>-1</sup> were observed in the higher wavenumber region (2800–3600 cm<sup>-1</sup>) at 25 °C, and shifted to a higher wavenumber (cm<sup>-1</sup>) as temperature increased to 120 °C. In addition, a free amine N-H stretching vibration appeared at around 3491 cm<sup>-1</sup> at 120 °C.<sup>S1</sup> In the lower wavenumber region of 1500-1800 cm<sup>-1</sup> at 25 °C, three characteristic peaks were present at 1595 cm<sup>-1</sup>, 1664 cm<sup>-1</sup> and 1723 cm<sup>-1</sup> ascribed to C=N stretching vibrations ( $V_{C=N}$ ), hydrogen-bonded C-N stretching (V<sub>C-N</sub>) and semi-crystalline ester-carbonyl C=O stretching vibrations (V<sub>C=0</sub>), respectively.<sup>S2</sup> The first two amine peaks shifted to lower wave number peaks at 1592 and 1635 cm<sup>-1</sup>, but the ester-carbonyl peak at 1723 cm<sup>-1</sup> shifted to a higher wavenumber (1733 cm<sup>-1</sup>) at 120 °C, suggesting destruction of the hydrogen-bonded conformation as temperature increased up to 120 °C.<sup>S3</sup> Generally, during heating and melting, the hydrogen-bonded dimers between adenine groups were disturbed and weakened successively, and an order-disorder transition from a semicrystalline solid to the liquid state occurred. However, when the temperature was reduced to 30 °C, the spectrum spontaneously reverted to the original semi-crystalline pattern, indicating WSe<sub>2</sub>/A-PPG contains stable thermoreversible hydrogen bond interactions in the bulk state (Fig. S7). In addition, these results further demonstrate the exfoliated WSe<sub>2</sub> nanosheets do not affect hydrogen bond reversibility as temperature varies and also promote the formation of contractile and extended lamellar structures on the surface of the 1T- and 2H-WSe<sub>2</sub> phases, respectively.



Fig. S8: TGA curves for A-PPG containing different mass fractions of WSe<sub>2</sub>.



Fig. S9: <sup>1</sup>H-NMR spectra of A-PPG in deuterated chloroform (CDCl<sub>3</sub>) at various concentrations at 25  $^{\circ}$ C.



Fig. S10: A typical Benesi–Hildebrand plot of A-PPG self-complex in CDCl<sub>3</sub> at 25 °C.

The association constant ( $K_a$ ) of A-PPG as determined by <sup>1</sup>H-NMR titration method (**Fig. S9**) and calculated from the slope of the plot (**Fig. S10**) was 1.2 M<sup>-1</sup>, which is consistent with  $K_a$  values reported in previous works (ca. <5 M<sup>-1</sup> in CDCl<sub>3</sub>).<sup>S4-S6</sup>

### References

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