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## Supporting Information

## Lamellar Carbon-Aluminosilicate Nanocomposites with Macroscopic Orientation

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### 1. Supplementary Figures S1–S5



**Supplementary Figure S1.** Synthesis of the hexaphenylene amphiphile **1**: *i*) *p*-TsCl, Et<sub>3</sub>N, DCM, r.t.; *ii*) K<sub>2</sub>CO<sub>3</sub>, ethanol/H<sub>2</sub>O, reflux; *iii*) Na<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, dioxane/H<sub>2</sub>O 2:1, reflux.



**Supplementary Figure S2.** GIXD on a sample of a **1**/aluminosilicate film before carbonization (on a bare silicon substrate), confirming the formation of the lamellae. *a*) GIXD pattern of the **1**/aluminosilicate nanocomposite showing in-plane Bragg peaks around  $q_r = 0.48 \text{ nm}^{-1}$ , and *b*) the corresponding GIXD intensity distribution of the (-10) reflection, corresponding to a lamellar periodicity of  $d_L = 13.1 \text{ nm}$ .



**Supplementary Figure S3.** *a*) GIXD 2D pattern and corresponding b) GIXD 1D intensity distributions of 1/aluminosilicate film on an OTS-coated silicon substrate at the rotation angle  $\varphi = \pm 10^{\circ}$  for which no in-plane Bragg peaks were observed.



**Supplementary Figure S4.** *a)* Thermogravimetric analysis (TGA) of the **1**/aluminosilicate nanocomposite in air (blue) and nitrogen (black) atmosphere at a heating rate of 10 K min<sup>-1</sup>, with their corresponding residual masses at 900°C. Degradation of **1**/aluminosilicate nanocomposite in air atmosphere occurred in two steps. According to the mass loss, the first step (maximum decomposition rate at 340°C) was attributed to the poly(ethylene oxide) degradation, whereas the second step (maximum decomposition rate at 610°C) represented the hexaphenylene decomposition. The residual mass of 20% corresponded to the aluminosilicate. When the nanocomposite was heated in nitrogen atmosphere, the residual mass was 46% at 900°C. The comparison allowed us to calculate the weight fractions of 57% carbon and 43% aluminosilicate. *b)* Similarly, TGA of the C/aluminosilicate nanocomposite in air at a heating rate of 10 K min<sup>-1</sup> resulted in a residual mass of 40% at 900 °C, corresponding to the aluminosilicate. Since the poly(ethylene oxide) decomposed below 500°C and the total carbon content of the carbonized films of 32% (relative to the total mass of the organic precursor) corresponded well to the weight fraction of the hexaphenylene carbons (31%), the latter were quantitatively incorporated into the final carbon material.



**Supplementary Figure S5.** *a*) GIXD pattern and *b*) the corresponding GIXD 1D intensity distribution of C/aluminosilicate film on a silicon substrate at the rotation angle  $\varphi = \pm 10^{\circ}$  for which a very weak in-plane Bragg peak was observed.

#### 2. Instrumentation and Methods

**Chemical Analytics.** <sup>1</sup>H and <sup>13</sup>C NMR measurements were carried out at room temperature on a Bruker Avance III 400 spectrometer operating at 400 MHz and 100.57 MHz, respectively, and using CDCl3 as solvent and as the internal standard ( $\delta_{H}$  = 7.26 ppm,  $\delta_{C}$  = 77.00 ppm). Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry (MS) experiments were performed using an Axima-CFRTM plus spectrometer from Schimadzu. CCA (α-cyano-4-hydroxycinnamic acid), DHB (2,5-dihydroxybenzoic acid) or DCTB (trans-2[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile were used as matrices. The number average molar mass  $(M_n)$ , the weight average molar mass  $(M_w)$ , and polydispersity indexes (PDI) of polydisperse compounds were calculated from the MALDI-TOF spectra by slice-wise integration of the individual mass peaks. Thin layer chromatography (TLC) was performed on TLC plates from Merck (silica gel 60 F254) and the products were visualized under UV-light (254 or 366 nm). Products were purified by column chromatography on silica gel 60 from Merck (230–400 mesh).

**Thermogravimetric Analysis (TGA).** Thermogravimetric analyses were performed on a TGA/SDTA 851e Mettler-Toledo (Greifensee, Switzerland). The temperature range of the measurements was 50–900  $^{\circ}$ C in air or nitrogen atmosphere, with a heating rate of 10 K min<sup>-1</sup> and a gas flow of 50 mL min<sup>-1</sup>.

**Polarized Optical Microscopy (POM).** An Olympus BX-60 microscope was used to analyze the orientation of sheared films on glass substrate under crossed polarizers in transmission mode.

**Polarized UV/vis Spectroscopy.** Polarized UV/vis spectroscopy of sheared films on fused glass substrates was carried out on a Jasco V-670 (Gotha, German) using the polarizer accessory.

Atomic Force Microscopy (AFM). The samples were analyzed in tapping mode using an Asylum Research Cypher instrument at room temperature in air. Cantilevers (HQ:NSC15/AIBS,  $\mu$ masch<sup>R</sup>) with a resonance frequency on average of  $f_0$  = 325 kHz and

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k = 40 N/m were used. Scan rates between 0.5 and 2 Hz were applied; the image resolution was 512 × 512 pixels. The lamellar periodicities of the samples were estimated based on the FFT of the line profile obtained from the refined AFM height images.

Transmission Electron Microscopy (TEM). Top-view Transmission electron microscopy images were recorded in bright field mode on a Philips CM12 (Philips, Eindhoven, Netherlands) electron microscope operated at 100 kV. An FEI Tecnai Osiris S/TEM machine with high brightness Schottky field emission gun (X-FEG) operated at 200 kV was used for cross-sectional scanning and conventional transmission electron microscopy imaging. Conventional bright-field TEM images were acquired digitally on a 11 Megapixel Gatan ORIUS<sup>™</sup> CCD camera. High-angle annular dark-filed (HAADF) scanning transmission electron microscopy (STEM) images with 1024 × 1024 pixels were recorded using the Tecnai Imaging and Analysis (TIA)<sup>™</sup>. The cross-sectional specimens were prepared by mechanical polishing (1/aluminosilicate on an OTS-coated silicon substrate. Film samples with a thickness below 100 nm appropriate for top view TEM imaging were prepared on OTS-coated silicon substrates, transferred onto a copper grid (200 µm mesh) by a lift-off technique, and then coated with an approximately 10 nm thick layer of evaporated amorphous carbon. A 25 wt% aqueous solution of poly(acrylic acid) (PAA, Acros Organics,  $M_w = 250'000 \text{ g mol}^{-1}$ ) was placed onto the specimen, in order to produce an at least 0.5 mm thick layer of PAA. The PAA solution was left to dry for 2–4 h until it became glassy and stiff. Mechanical peeling (e.g., with the tweezers) was used to detach the PAA together with the intact carbon-coated film specimen from the silicon substrate. It was then placed onto a pool of deionized water with the PAA side on the water surface. The water dissolved the PAA, leaving a floating sample of the carbon-coated film specimen that was caught with a copper TEM grid.

**Grazing Incidence X-ray Diffraction (GIXD).** GIXD measurements on samples before carbonization were performed at the Harvard/BNL diffractometer at the beamline X22B, NSLS, BNL, NY, USA, with 8.16 keV X-rays using a CCD detector. The grazing angle of incidence was set to  $= 0.21^{\circ}$ , i.e., just below the critical angle of the silicon substrate,

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 $_{c}$  = 0.22°, which corresponds to  $q_{c}$  = 0.032 Å<sup>-1</sup>. GIXD experiments for samples after carbonization were performed at the beamline ID10 at the European Synchrotron Radiation Facility in Grenoble using 22.0 keV X-rays and a Pilatus 300K detector. The grazing angle = 0.080° ( $_{c}$  = 0.082°). Hence, the incidence waves experience total external reflection, and only the evanescent wave probes the sample. In this configuration, the scattered intensity by the surface was maximized, whereas the bulk scattering was reduced. Scanning Electron Microscopy (SEM). SEM images were recorded on a Zeiss Merlin FE-SEM (Zeiss, Göttingen, Germany) equipped with a Gemini IITM column operation between 1.0 and 2.0 keV with a probe current of 100–500 pA. We used the (on axis) in-lens and the high efficiency secondary electron (HE-SE2) detectors of the Gemini II column (beam booster) for imaging of the carbon nanocomposite film on silicon substrate.

**Raman Spectroscopy.** Wavelength-dependent Raman spectra were recorded on a custommade Raman microscope. The pump was provided by the monochromated output of a tunable Argon-Krypton ion gas laser set at 1.0 mW whenever the output power allowed it. For the 457.9 nm and 476.5 nm lines, the maximal output power of 450 and 780 μW was used, respectively. Laser light and Raman scattered light were focused on the sample and collected in backscattering geometry by a 0.75 NA glass-corrected objective. The scattered light was analyzed using a Princeton Instrument Acton Trivista 500 triple-stage spectrometer. The two first spectrometer stages operate in subtractive mode to filter out the pump light. The Raman signal was then dispersed by the third spectrometer stage using a 1350 lines/mm grating on a back-illuminated CCD (Princeton Instrument PyLON eXcelon). The integration time was set to 60 s and accumulated three times.

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