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Scheme S-1. Proposed structure of fluorograph*a*ne $(C_1H_xF_{1-x})_n$ where x=0.5. Carbon (black colour), fluorine (green color) and hydrogen (grey color).



Figure S-1. The SEM micrograph and elemental distribution map for fluorograph*a*ne (A - CHF[1h:1bar], B - CHF[24h:5bar], C - CHF[24+24h:5+12bar]) and corresponding EDS spectra.



Figure S-2. The high resolution XPS spectra of C 1s with corresponding fitting.

Table S-1. Quantification of high resolution XPS spectra for C 1s peak.

Sample	C=C	C-C/C-H/C-F	C-0	C=O	C-F	0-C=0	C-F ₂ /π-π*	C-F ₃
CHF[1h:1bar]	26.72	13.98	7.70	4.57	14.72	4.82	14.52	12.98
CHF[24h:5bar]	0.04	10.90	2.20	2.64	19.89	12.89	28.22	23.24
CHF[24+24h:5+12bar]	0.83	14.27	2.60	3.21	32.25	3.10	28.39	15.35



Figure S-3. The high resolution XPS spectra of F 1s with corresponding fitting.



Figure S-4. FT-IR spectra of fluorographane.



Figure S-5. Detail of FT-IR spectra for C-H bond of various fluorographane.



Figure S-6. The Raman spectra of various fluorograph*a*ne. The left graphs show the whole spectrum, while on the right figure show detail of D, G and D' bands.



Figure S-7. The morphology of various fluorograph*a* ne obtained by AFM and corresponding height profiles.



Figure S-8. (I.) Photographs of fluorograph*a*ne samples in water showing high hydrophobic properties (A - CHF[24+24h:5+12bar], B - CHF[24h:5bar], C - CHF[1h:1bar]). (II.) Photographs of of fluorograph*a*ne samples in dimethylsulfoxide show formation stable dispersions in nonaqueous solvent (A - CHF[24+24h:5+12bar], B - CHF[24h:5bar], C - CHF[1h:1bar]).

Experimental section

All fluorine experiments were done on dedicated fluorine line¹ using 20% fluorine in nitrogen (Solvay). Ammonia (99.9995% purity and argon (99.996% purity) was obtained from SIAD, Czech Republic. Graphite oxide (GO) was prepared according to the Hofmann

method from high purity microcrystalline graphite (2-15 μ m, 99.9995%, Alfa Aesar, Germany). Sulfuric acid (98%), nitric acid (68%), potassium chlorate (> 99%), hydrochloric acid (37%), hydrazine hydrate (99%) and *N*,*N*-dimethylformamide (DMF) were obtained from Penta (Czech Republic). Potassium hydrogen phosphate and potassium dihydrogenphosphate were obtained from Lach-Ner (Czech Republic). Potassium was obtained from Sigma-Aldrich, Czech Republic. Deionized water (16.8 Mohm) was used for buffer preparation.

Synthesis of graphite oxide. Concentrated sulfuric acid (87.5 mL) and nitric acid (27 mL) were added to a reaction flask containing a magnetic stir bar. The mixture was then cooled at 0 °C, and graphite (5 g) was added. The mixture was vigorously stirred to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask at 0 °C, potassium chlorate (55 g) was slowly added to the mixture in order to avoid a sudden increase in temperature and a consequent formation of explosive chlorine dioxide gas. Upon the complete dissolution of the potassium chlorate, the reaction flask was loosely capped to allow an escape of the evolved gas and the mixture was continuously vigorously stirred for 96 h at room temperature. When the reaction ended, the mixture was poured into deionized water (3 L) and decanted. The graphite oxide was first redispersed in deionized water until all chloride and sulfate ions were removed. The graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Synthesis of graphane. 1g of HO-GO was dispersed in 1 L of deionized water by ultrasonication (400 W, 60 min) and alkalized by 1M KOH on pH=10. Hydrazine hydrate (10 mL) was added to the suspension and reaction mixture was heated under reflux for 24 hours. Formed chemically reduced graphene (CRG) was separated by suction filtration and dried in vacuum oven at 60 °C for 48 hours. 250 mg of CRG was placed in three neck flask connected with argon and ammonia inlet and glass magnetic stirring bar. To the flask was added 8.2 g of potassium under argon atmosphere and on reaction flask was fitted dry ice condenser. In the reaction flask was condensed about 200 ml of liquid ammonia. Reaction mixture was stirred for 2 hours under ammonia reflux. Subsequently to the reaction mixture was slowly added 2 ml of deionized water to avoid overpressure and explosion. Reaction mixture was stirred for next two hours and unreacted potassium was decomposed by water. Formed graphane was separated from the reaction mixture by suction filtration and repeatedly washed with water. Graphane was dried in vacuum oven for 48 hours at 50 °C.

Fluoration of graphane. Fluoration was performed using fluorine/nitrogen mixture (20 vol.% F₂) in Monel autoclave with Teflon liner. To the autoclave was charged with 100 mg of graphane, evacuated and fluorine/nitrogen mixture was introduced. The reaction pressure was in the range of 1 bar up to 12 bar and reaction time from 1 hour up to 48 hours. For the sample CHF [1h:1bar] the reaction conditions were 1bar/1hour, for CHF[24h:5bar] 5.2bar/24 hours and for CHF[24+24h:5+12bar] 5.2bar/24hours and subsequently reactor

was evacuated and repeatedly pressurized to 12bar for 24 hours. Afterwards the gas was removed under vacuum, the autoclave was filled by nitrogen (1 bar) and opened.

An inVia Raman microscope (Renishaw, England) with a CCD detector was used for Raman spectroscopy in backscattering geometry. A Nd-YAG laser (532 nm, 50 mW) with 50x magnification objective was used for measurements. Instrument calibration was performed with a silicon reference which gives a peak centre at 520 cm⁻¹ and a resolution of less than 1 cm⁻¹. In order to avoid radiation damage, laser power output used for this measurement was kept in a range of 0.5 mW to 25 mW. Prior to measurements, the samples were suspended in isopropanol (concentration 1 mg/ml) and ultrasonicated for 5 minutes. Then the suspension was deposited on a small piece of silicon wafer and dried.

Combustible elemental analysis (CHNS-O) was performed with a PE 2400 Series II CHNS/O Analyzer (Perkin Elmer, USA). In CHN operating mode, the most robust and interference free mode, the instrument employs a classical combustion principle to convert the sample elements to simple gases (CO₂, H₂O and N₂). The PE 2400 analyzer automatically performs combustion, reduction, homogenization, separation and detection of the gases. An MX5 (Mettler Toledo) microbalance was used for precise sample weighing (1.5 – 2.5 mg per single sample analysis). The accuracy of CHN determination is better than 0.30 abs.% Internal calibration was performed using N-phenyl urea. The fluorine concentration measurement the sample was combusted using Schöniger method and the combustion products were absorbed in water. The concentration of fluorine ions was subsequently measured using ion selective electrode.

High resolution X-ray photoelectron spectroscopy (XPS) was performed on an ESCAProbeP (Omicron Nanotechnology Ltd, Germany) spectrometer equipped with a monochromatic aluminum X-ray radiation source (1486.7 eV). A wide-scan survey with subsequent high-resolution scans of the C 1s core level and F 1s core level was performed. The relative sensitivity factors were used in the evaluation of the carbon-to-oxygen (C/O) ratios and elemental composition (C, O and F) from the survey spectra. Samples were drop casted from a suspension in isopropanol (2 mg/ml) on a conductive carrier made from gold evaporated on silicon wafer.

For the measurement of atomic force microscopy (AFM) images, the samples were suspended in isopropanol (1 mg/ml) and ultrasonicated for 15 minutes (75 W). After sedimentation, the suspension of fluorographane was dropped on a freshly cleaved mica substrate. These measurements were carried out on an Ntegra Spectra from NT-MDT. The surface scans were performed in a tapping (semi-contact) mode. Cantilevers with a strain constant of 1.5 kN.m⁻¹ equipped with a standard silicon tip with curvature radius lower than 10 nm was used for all measurements.

Fluorographane was investigated by scanning electron microscopy (SEM) using a Tescan Lyra dual beam microscope with an FEG electron source with an accelerating voltage

of 15 kV. Elemental composition and mapping were performed using an energy dispersive spectroscopy (EDS) analyzer (X-MaxN) with a 20 mm² SDD detector (Oxford instruments) and AZtecEnergy software. To conduct the measurements, the samples were placed on a carbon conductive tape. Transmission electron microscopy using scanning transmission electron (STEM) detector was performed on a Tescan Lyra dual beam microscope. 30 kV accelerating voltage was used for observations. A suspension of fluorograph*a*ne with isopropanol (1 mg/ml) was ultrasonicated for 15 minutes (75 W) before use. The bright field modes were used for imaging.

Surface area was measured by a sorption analyser Coulter SA 3100 (Backman Coulter). The samples were outgassed for 6 hours at 100 °C under high vacuum (VALUE) prior to the sorption experiments. The reason for such low temperature is to avoid degradation and further decomposition of oxygen functionalities, present mainly in CRG, on fluorographane. A TCD nitrogen cooled (77 K) detector was used for the evaluation of the results using a BET and Kelvin equations.

The contact angle was measured using See System E from Advex Instruments (Czech Republic). On the silicon wafer coated with fluorographane was drop casted water (1 μ L) and the measurement of contact angle was subsequently performed at ambient conditions.

^[1] M. Valášek, F. Šembera, M. J. Hughes, I. Stibor, Z. Janoušek and J. Michl, Efficient Preparation of Fluorine Compounds, ed. H. W. Roesky, 2012, John Wiley & Sons, Hoboken, NJ, p. 22.