
Electronic Supplementary Information (ESI)

Air-stable poly(3,3,3-trifluoropropylsilyne) homo- and copolymers

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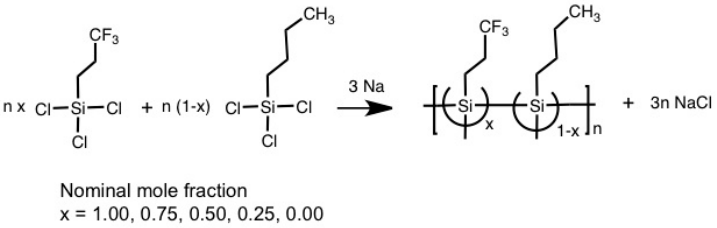
Experimental section

1. Preparation of FSNP, BSNP, and FBSNP

FSNP and **BSNP** were prepared via the Na-mediated condensation of 3,3,3-trifluoropropyltrichlorosilane (**1**, Shin-Etsu) and *n*-butyltrichlorosilane (**2**, Shin-Etsu), respectively, in hot *n*-nonane without crown ether as a co-catalyst under an N_2 atmosphere in accordance with the previously published procedure.[29] **F$_x$B$_{1-x}$SNP** (x = 0.25, 0.50, and 0.75 in which x is the nominal molar fraction of **1**) were produced via Na-mediated co-condensation of **1** and **2** (nominal molar feed ratios: 0.25/0.75, 0.50/0.50, and 0.75/0.25) in a manner similar to that used for the synthesis of **FSNP** and **BSNP**. To avoid contact with air and moisture during the work-up processes, including the preparation, isolation, and sealing of the samples in glass tubes, we typically synthesized **FSNP** in the following manner, as shown in Scheme 1.



Scheme 1. Synthetic scheme for **FSNP** (x = 1.00), **BSNP** (x = 0.00), and **F$_x$B$_{1-x}$SNP** (x = 0.25, 0.50, and 0.75 in a nominal feed fraction of **1** to **2**).

A 20-mL solution of *n*-nonane (Aldrich, dried over 4A molecular sieves) that contained Na (Wako, 2.3 g, 0.10 mol) was placed in a four-necked 100-mL flask and refluxed at 120 °C with vigorous stirring at 800 rpm by a mechanical stirring motor with a glass blade. To this mixture, **1** (5.0 g, 22 mmol) was added dropwise with gentle stirring (800 rpm). After the addition was completed, the reaction mixture was gently stirred at 200 rpm for 2 h and was subsequently allowed to cool to room temperature. The reaction vessel was moved to a glove box that was filled with 99.9% pure N_2 gas.

After 20 mL of THF was added to the reaction mixture and the reaction mixture was subjected to pressured filtration using a fluorinated membrane filter (Whatman, 0.47 μm pore) to remove the NaCl byproduct and unreacted Na, a clear pale-yellow THF/*n*-nonane solution that contained **FSNP** was obtained. Solid samples were yielded by volatilization of the solvents in the glove box. **FBSNP** and **BSNP** were prepared in a similar manner, as outlined in Table S1 in Supporting Information (SI)†. Fourier-transform infrared (FT-IR) signals due to the ν_{as}(Si-O-Si) asymmetric stretching mode at approximately 1000–1100 cm^{-1} and the ν_s(Si-O-Si) symmetric stretching mode at 800 cm^{-1} in fresh **FSNP**, **FBSNP**, and **BSNP** samples were not observed.[45] The isolated yield of these **SNPs** was typically 40–50% when the crude **SNPs** were precipitated into methanol outside of the glove box with no precautions taken against air or moisture exposure. This yield was almost identical to that in a previous report of the synthesis of **SNP** with *n*-hexyl groups that was prepared using Na-K alloy under ultrasound irradiation.[23] When the work-up process in the glove box was employed, not all yields were determined to avoid any contact with contaminants during the weighing of the samples.

2. Preparation of FSNP films

Into a synthetic quartz glass tube (ID 5 mm, OD 7 mm), 40 μL of a THF solution that contained **FSNP**, **SNP**, and **FBSNP** (1 g mL^{-1}) was placed.[29] The samples were manually coated onto the inner wall of the tube and were dried with flowing N_2 gas. The films deposited inside the glass tubes were connected to a two-way vacuum bulb. The tubes were removed from the glove box and sealed outside the box using a vacuum technique and a torch [~0.3 Torr by a rotary pump (ULVAC, Tokyo, Japan) and ~5 × 10^{-5} Torr by a custom-made turbo molecular pump (Torr Science, Kanagawa, Japan)].

3. Characterization and instrumental measurements

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index ($PDI = M_w/M_n$) of five isolated **SNPs** are given in Table S1. The values of M_n and M_w were evaluated by size-exclusion chromatography (SEC) using a UV–vis photodiode array detector at 40 °C based on a calibration with polystyrene standards on a Shimadzu A10 instrument. The SEC was performed using PLgel 10 µm mixed-B (Varian) as the column and THF as the eluent. The UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer (bandwidth: 1 nm, scanning rate: 100 nm/min, data sampling: 0.5 nm interval). PL and photoluminescence excitation (PLE) spectra in the range of 370 to 900 nm were measured using a JASCO FP-6600 spectrofluorometer (bandwidth: 3 nm for excitation and 2 nm for emission, response time: 1 sec, sensitivity for photomultiplier tube: high, scanning rate: 100 nm/min, data sampling: 1 nm interval) equipped with a housing designed for phosphorescence equipment that was immersed in liquid N_2. FT-NMR spectra (^1H, ^{19}F, and ^{29}Si) were measured with a *JEOL* JNM-LA 400 NMR spectrometer. Chemical shifts were referenced to internal tetramethylsilane and trichlorofluoromethane. FT-IR spectra were obtained on a Horiba FT-730 spectrometer (resolution: 0.5 cm^{-1}, acquisition: 64 scans) by casting a solution of the polymers onto a KBr plate under a N_2 atmosphere. Laser Raman spectra were obtained on a JASCO NRS-2100 (Ar CW-laser 514.5 nm, 10 mW) using the back-scattering mode (acquisition: 50 scans). The polymers were sealed in a glass tube and/or placed onto an Au-coated plate under N_2 atmosphere for measurement. High-resolution transmission electron microscopy (HR-TEM) images were obtained with a JEOL JEM-3100FEF electron microscope (accelerating voltage: 300 kV, bright image mode). X-ray photoelectron spectroscopy (XPS) and analysis was performed on a Kratos Axis 165 (Al-$K\alpha$, 10 mA, 15 kV). Electron energy-loss spectroscopy (EELS) was conducted with a JEOL EM-Z01299TJEC. Specimens for HR-TEM/EELS were prepared by casting a THF solution onto an elastic carbon-film-coated microgrid (Oken-Shoji, Tokyo, Japan). Differential scanning calorimetry (DSC) measurements were conducted on a DSC/TG-DTA 6200 (SII Nanotechnology, Tokyo). Wide-angle X-ray diffraction (WAXD) data were obtained on a Rigaku R-AXIS-IV wide-angle X-ray diffractometer (Ni-filtered Cu$K\alpha$, 45 kV, 50 mW) and were analyzed using the Rigaku automatic X-ray imaging software.

4. Electronic state calculations using Gaussian03[44]

Electronic state calculations of *trans*-perhydrosiladecaline that was partially substituted with TFP and *n*-butyl groups as models of **FSNP** and **BSNP** were employed using the time-dependent (TD)–density function theory (DFT) [Gaussian03 program (B3LYP, 6-31G* basis sets)] running on an Apple iMac (Intel CoreDuo2, 2.0 GHz, 4 GB memory, MacOS ver.10.5.8). For the calculations, the geometries of parent siladecaline were initially optimized at the PM3−MM level of Gaussian03 using standard parameters (default) with an Si–Si bond length of 2.34 Å and an Si-Si-Si bond angle of 111°.

Table S1. Synthetic conditions for **FSNP**, **BSNP** and $\mathbf{F_{x}B_{1\text{-}x}SNP}$.

Polymer	**1 (FSi)**, g	**2 (BSi)**, g	Na, g	*n*-Nonane, mL	M_w[a)]	*PDI* = M_w/M_n[a)]
x = 1.00	5.0	0.0	2.3	20	2.83	1.10
x = 0.75	2.4	1.0	1.6	20	3.95	2.60
x = 0.50	1.0	0.8	0.8	20	5.30	1.22
x = 0.25	0.6	2.4	1.2	20	5.41	1.48
x = 0.00	0.0	2.5	1.0	20	11.8	5.12

[a)] These values were based on a calibration using polystyrene standards.

Table S2. Atomic fractions of **FSi** and **BSi** by ^{1}H NMR and XPS analyses.

FBSNP	Atomic concentration (atomic fraction)	
by nominal fraction	by ^{1}H NMR	by XPS
x = 0.75	0.47	0.50
x = 0.50	0.28	0.25
x = 0.25	0.10	0.12

Table S3. Quantum yield (Φ_F) of **FSNP**, **BSNP** and $\mathbf{F_{0.5}B_{0.5}SNP}$ excited at 366 nm in THF at room temperature.

Polymer	Φ_F / %
x = 1.00	3.0
x = 0.50	1.9
x = 0.00	1.1

[a)] These values were based on a calibration with 9,10-diphenylanthracene and were corrected for refractive index.

Table S4. Thermogravimetric (TG) data of **SNPs** in a stream of N_2 gas with a heating rate of 10 °C min^{-1}.

Polymer	Decomposition /°C		Weight loss /%	
	$T_{\text{d, start}}$	$T_{\text{d, end}}$	□□□	Calc. as elemental Si
x = 1.00	285	563	74	77.6
x = 0.50	320	541	62	73.3
x = 0.00	344	445	46	67.1

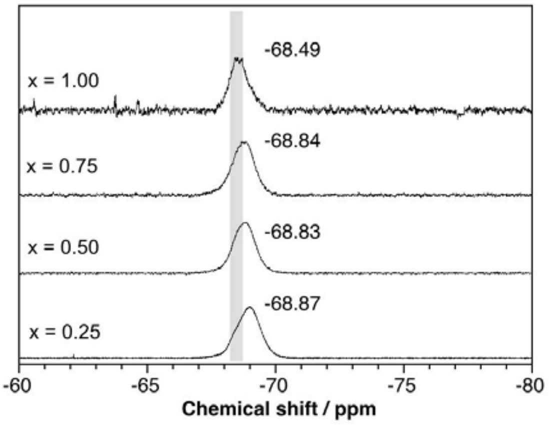


Fig. S1 ^{19}F NMR spectra of **FSNP** and **F$_x$B$_{1-x}$SNPs** (x = 0.25, 0.50, 0.75) in $CDCl_3$ at 25 °C.

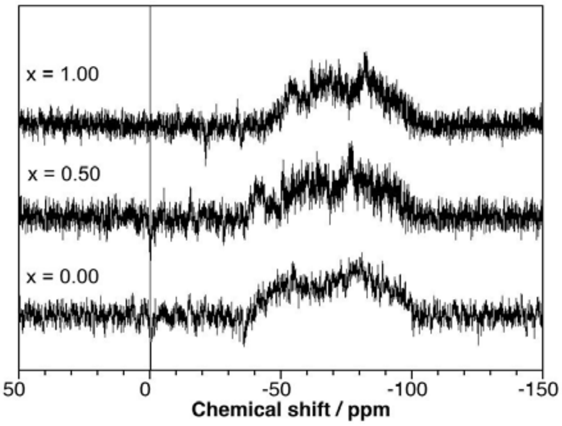


Fig. S2 ^{29}Si NMR spectra of **FSNP**, **F$_x$B$_{1-x}$SNP** (x = 0.50) and **BSNP** in $CDCl_3$ at 25 °C.

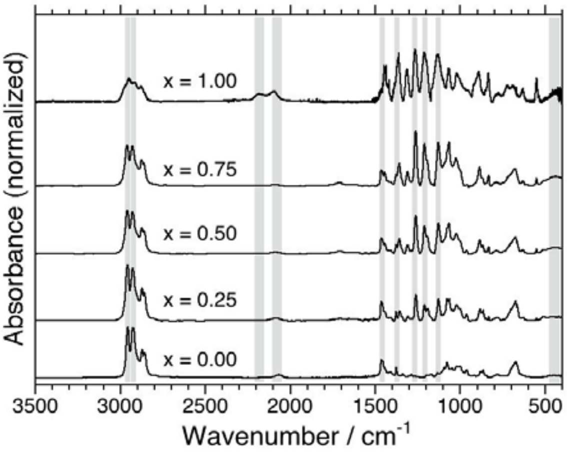


Fig. S3 IR spectra (3500–400 cm^{-1}) of **FSNP**, **F$_x$B$_{1-x}$SNP** (x = 0.25, 0.50, 0.75) and **BSNP** cast onto KBr plates.

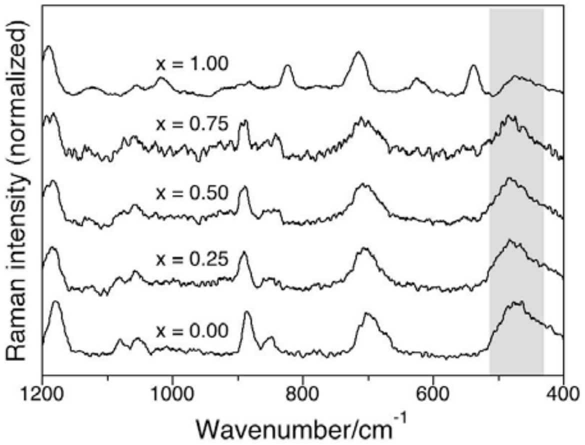


Fig. S4. Raman spectra of **FSNP**, **F_xB_{1-x}SNP** (x = 0.25, 0.50, 0.75) and **BSNP** cast onto Au.

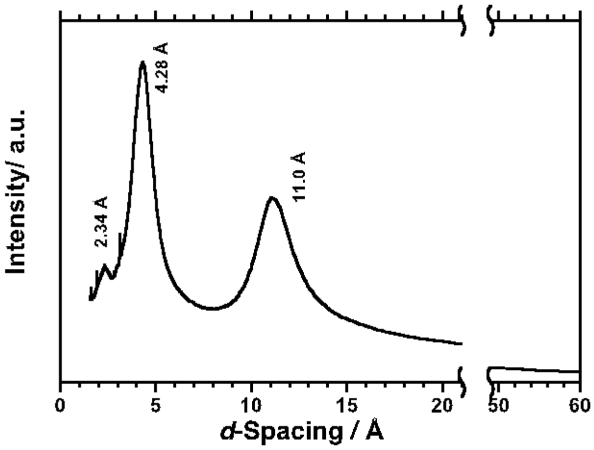


Fig. S5 WAXD data in *d*-spacing of an **FSNP** film in air.

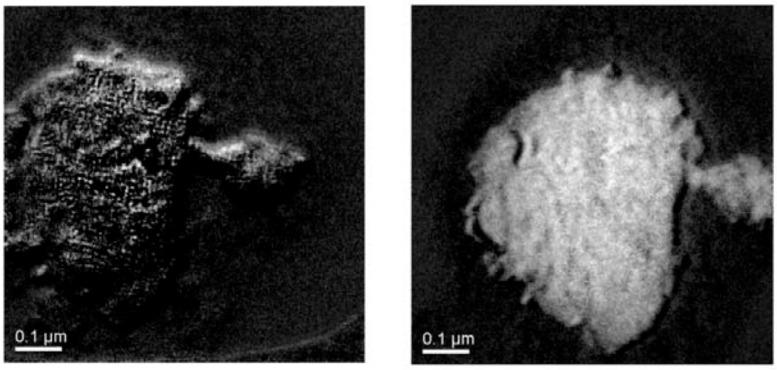


Fig. S6 EELS Si mapping (left) and F mapping (right) images of **FSNP** on a carbon microgrid (scale bar = 0.1 μm).

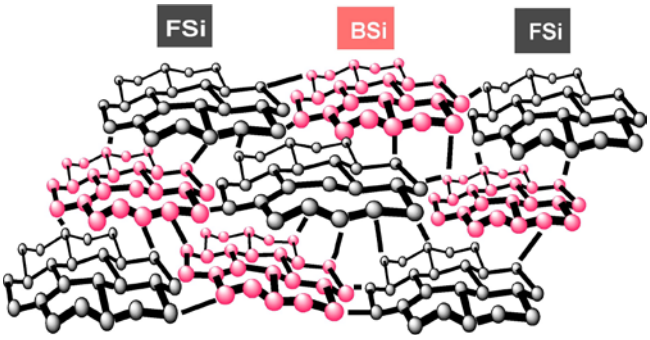


Fig. S7 A proposed structure of **FBSNP** with domain-like segregation (gray and magenta are trifluoropropylsilane and n-butylsilane moieties, respectively).

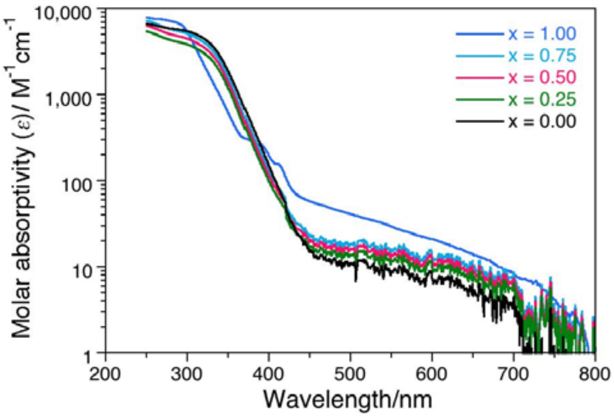


Fig. S8 Semi-log UV–vis absorption spectra of **FSNP**, **BSNP** and **F_xB_{1-x}SNP** (x = 0.25, 0.50, 0.75) in THF at 25 °C.

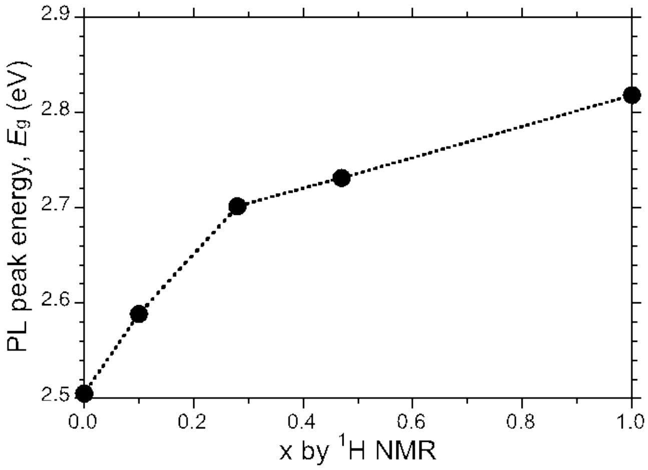


Fig. S9 PL peak energy (in eV) of five **SNPs** in THF excited at 360 nm at 25 °C as a function of the FSi fraction (x) in **SNPs** evaluated by ^{1}H NMR (taken from Table 1). For x = 0, a shorter PL peak wavelength at 495 nm was adopted.

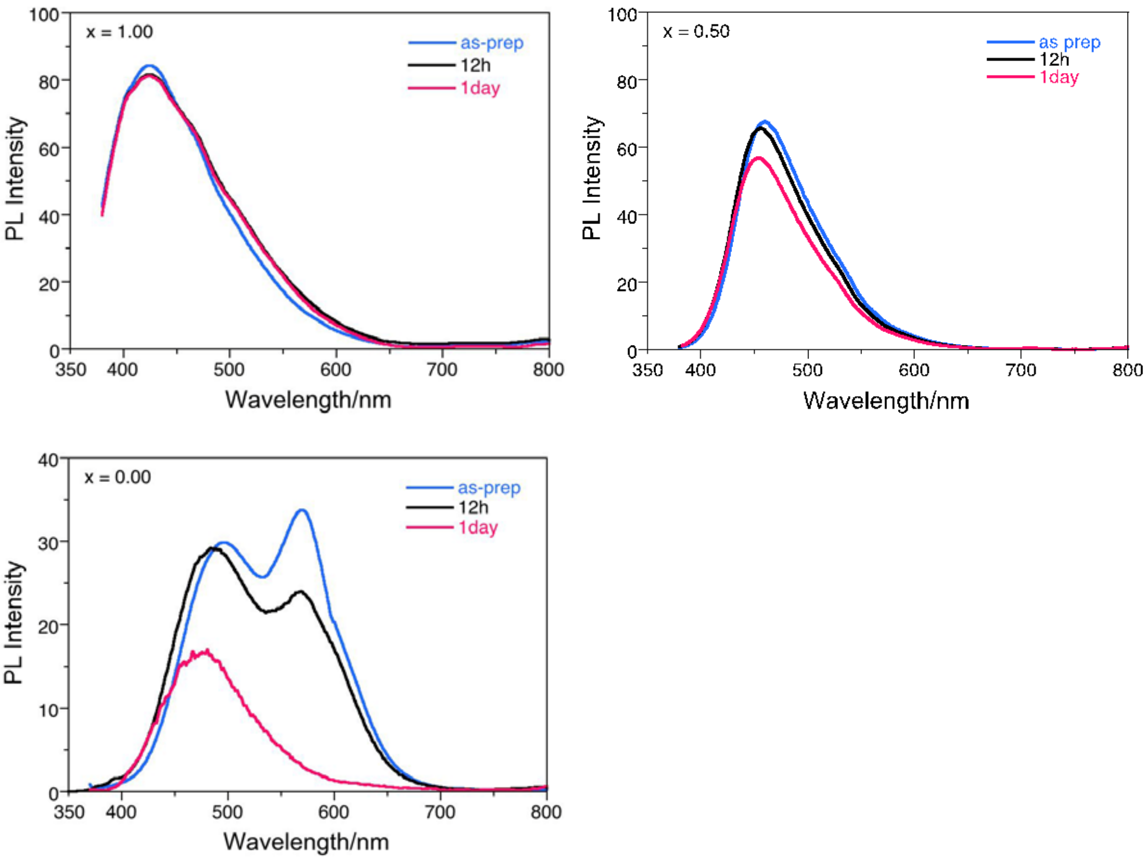


Fig. S10 Changes in the PL spectra of **FSNP**, **$B_{0.5}S_{0.5}NP$** and **BSNP** in a THF–water (90/10 (v/v)) solution after storage for various times.

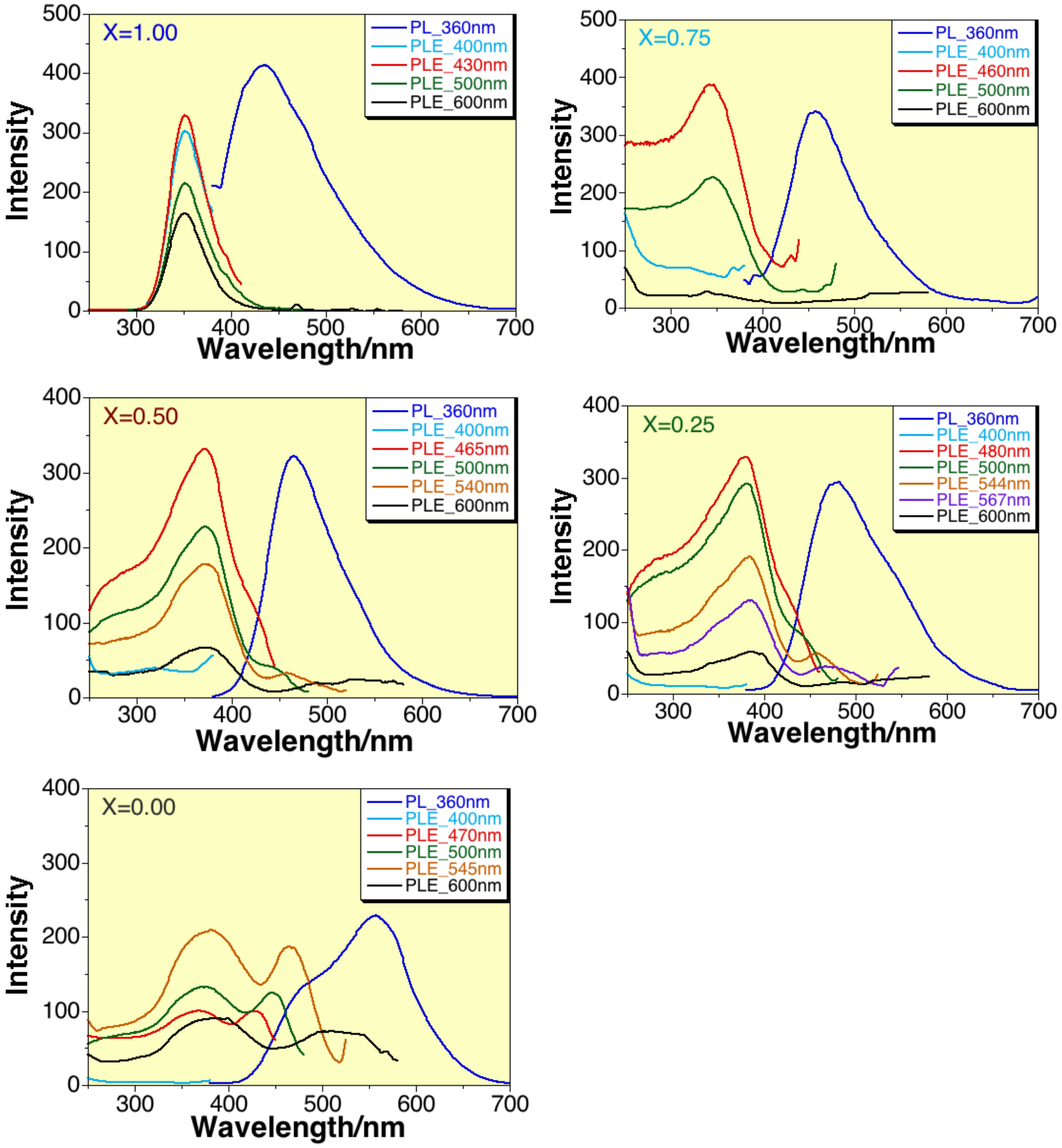


Fig. S11 PLE spectra (excited at 360 nm) of thin films of **FSNP**, **SNP** and **F$_x$B$_{1-x}$SNP** (x = 0.25, 0.50, 0.75) under vacuum at 77 K.

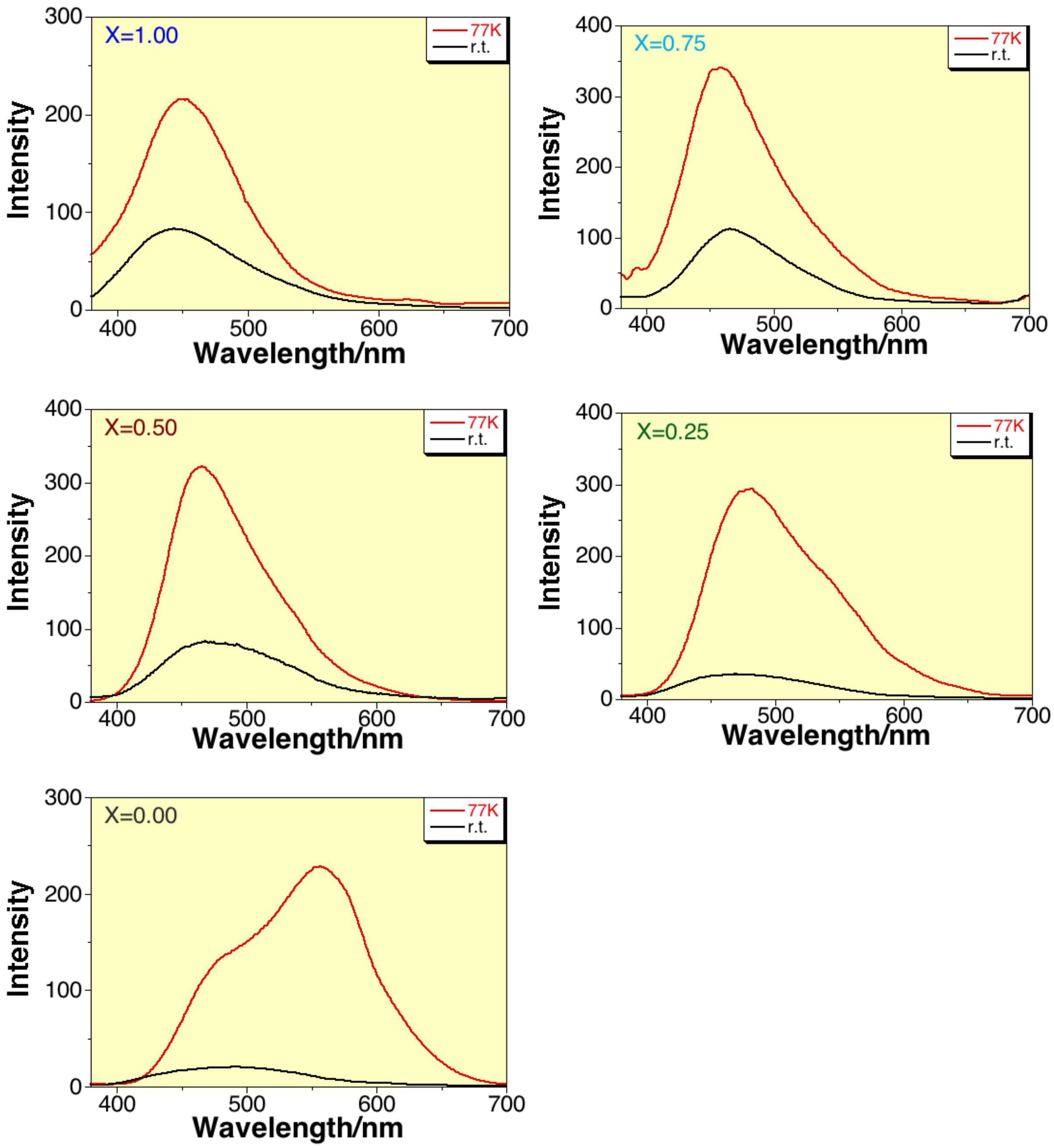


Fig. S12 PL spectra (excited at 360 nm) of thin films of **FSNP**, **BSNP** and **F**$_x$**B**$_{1-x}$**SNP** (x = 0.25, 0.50, 0.75) under vacuum at 77 K and at room temperature.

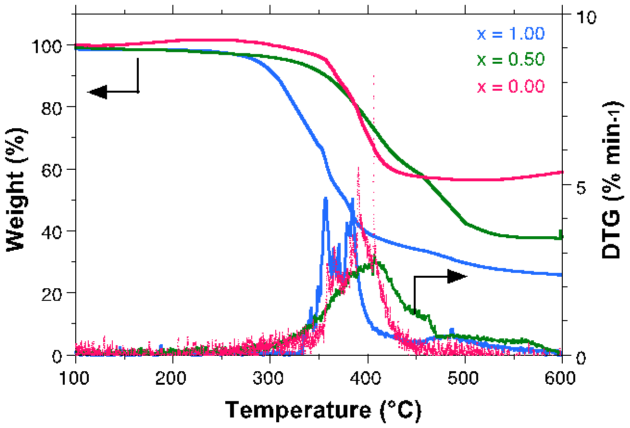


Fig. S13 Thermogravimetric (TG) and differential TG (DTG) charts of **FSNP**, **BSNP** and **$F_{0.5}B_{0.5}$SNP** under an N_2 atmosphere with heating rate of 10 °C min^{-1}.

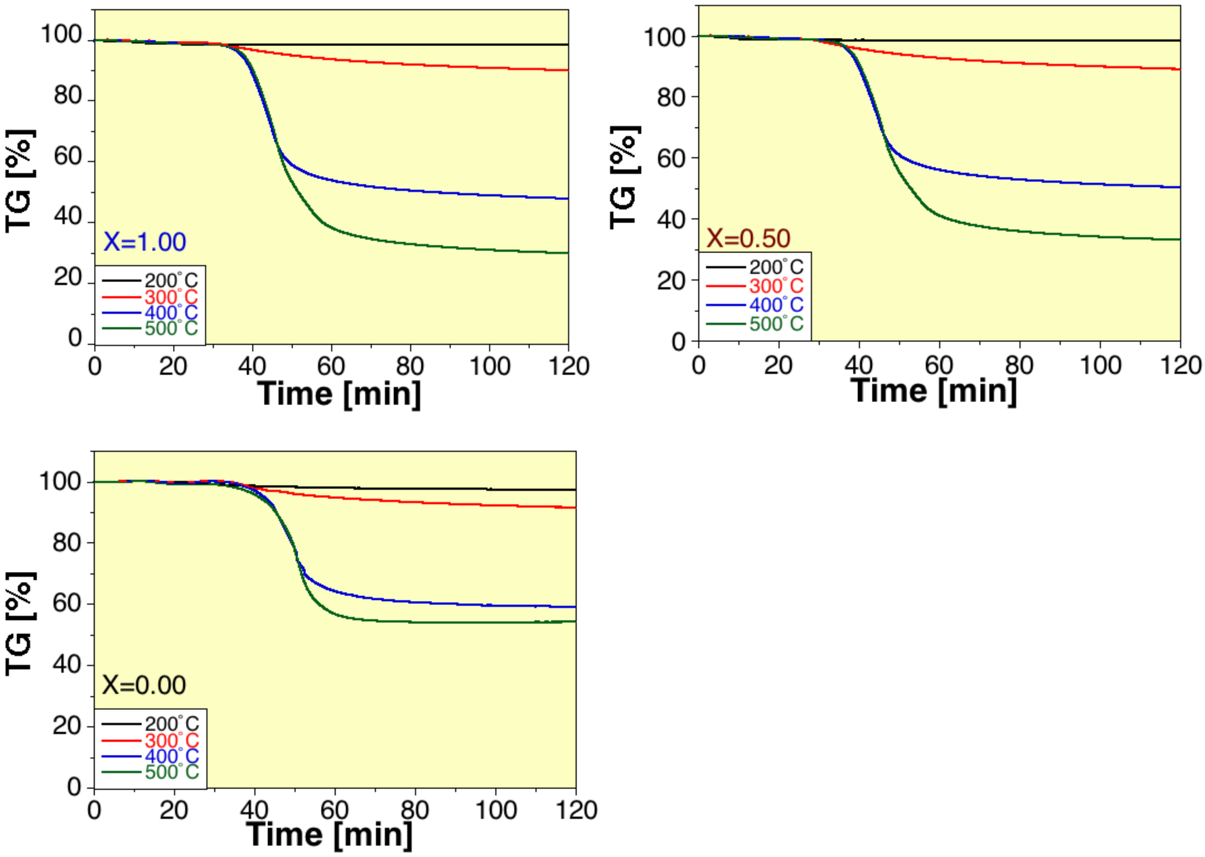


Fig. S14 TG and ITG curves of polymer (sample amount: ca. 1 mg in N2).

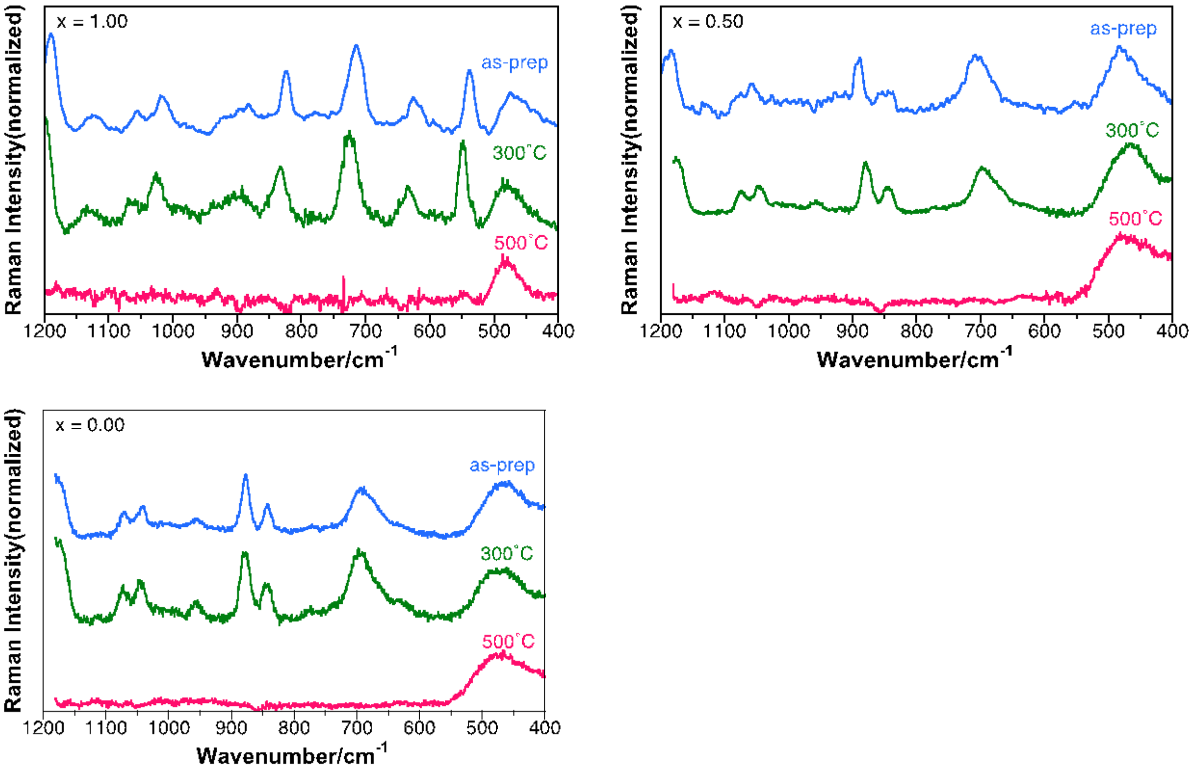


Fig. S15 Raman spectra of **FSNP**, **BSNP** and **$F_{0.5}B_{0.5}$SNP** pyrolyzed at 300 and 500 °C for 90 min under an N_2 atmosphere.

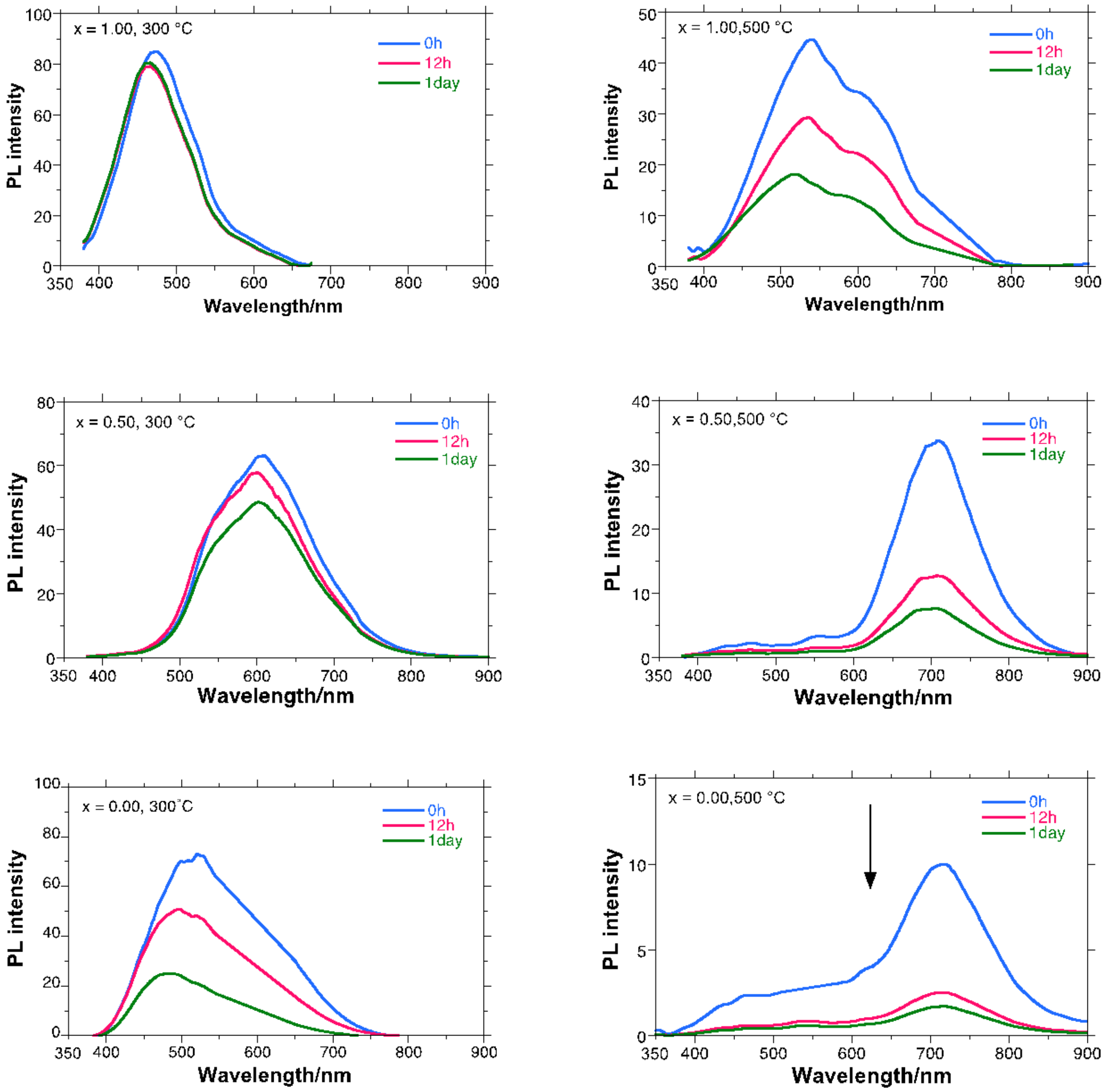
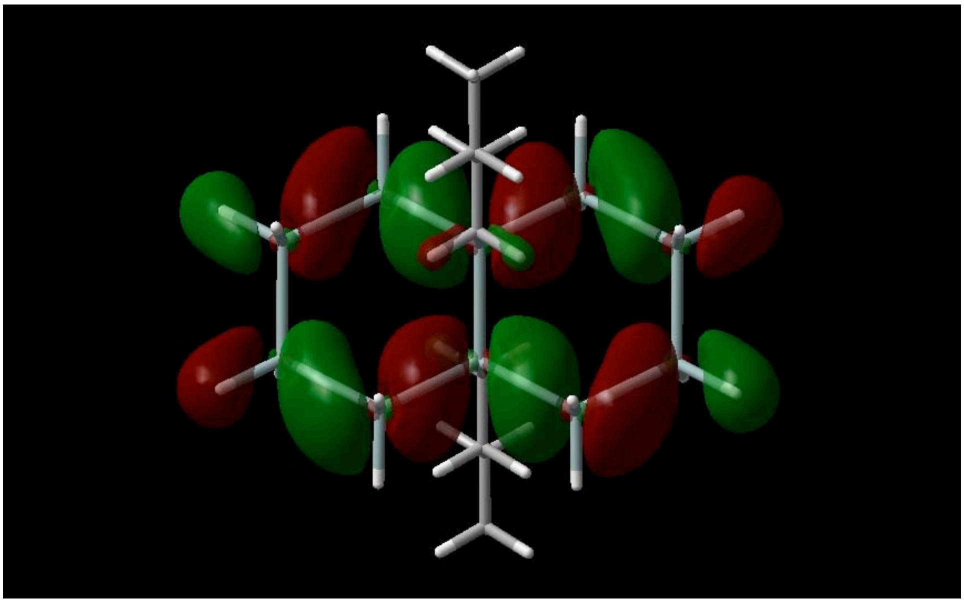


Fig. S16 Changes in the PL spectra of pyrolyzed **SNP** films in THF–water (90/10 (v/v)) solution after storage for various times. The samples are **FSNP**, **$F_{0.5}B_{0.5}$SNP** and **BSNP**. The samples were pyrolyzed at 300 and 500 °C for 90 min under vacuum (5×10^{-5} Torr).



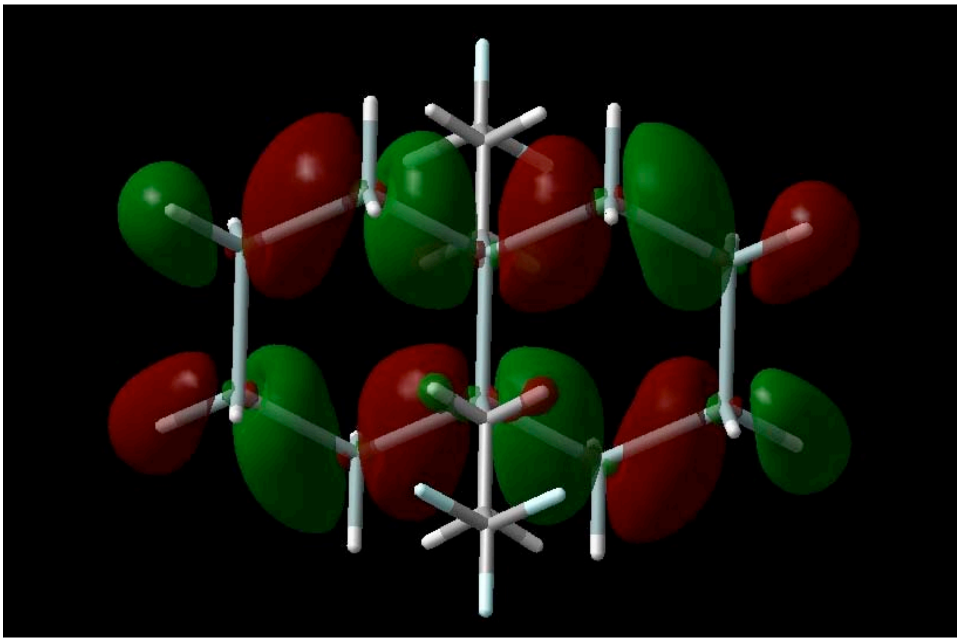


Fig. S17 The first HOMO of (top) **3** and (bottom) **4**.