Surface functionalization of nanoporous carbons with fluoralkyl groups

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Synthetic setup

In recent years, fluorine-containing carbons have been of considerable interest. The most promising fields of their applications are lithium battery electrodes and supercapacitors. Fluorination can also significantly affect the properties of the surface layer of the material, increasing its hydrophobicity and conductivity, which are important. Known methods of fluorination operate with potentially dangerous and toxic compounds: elemental fluorine, BrF_3, ClF_3, XeF_2, and the plasma of CF_4, CF_3I, and SF_6. Fluorination of carbon materials at high temperatures by fluorine-containing hydrocarbons (CHF) is a promising alternative as it requires no special treatment conditions, chemically aggressive and toxic substances and can be carried out using standard chemical equipment.

Nanoporous activated carbon BAU obtained by carbonization/activation of birch wood was used as the model carbon. The specific surface area (S_{BET}) of BAU is 508 m^2/g, and the total pore volume (V_{tot}) of 0.39 cm^3/g (Table 1). Fluoroalkylation of BAU with 1,1,1,2-tetrafluoroethane (F4) and pentafluoroethane (F5) was carried out at 400, 500, 600, 700, and 800 °C in a stream of fluorinating agent diluted in argon.
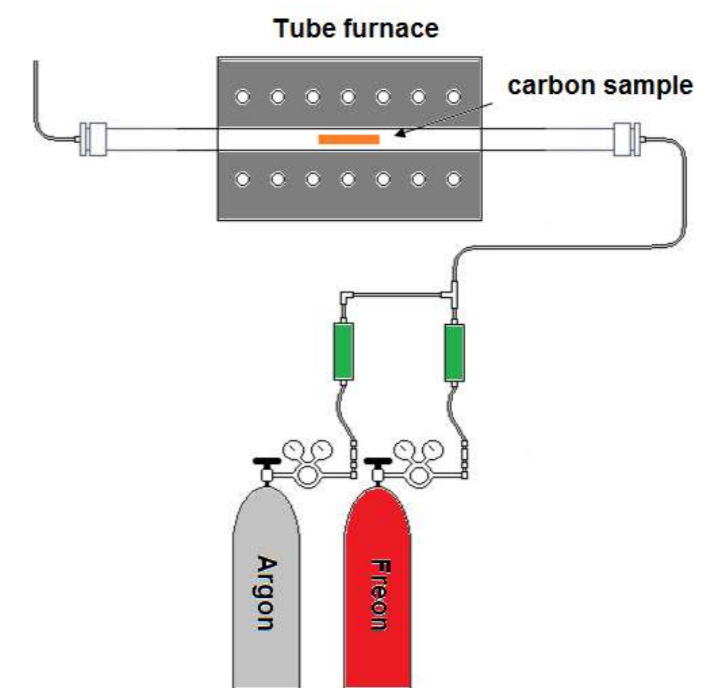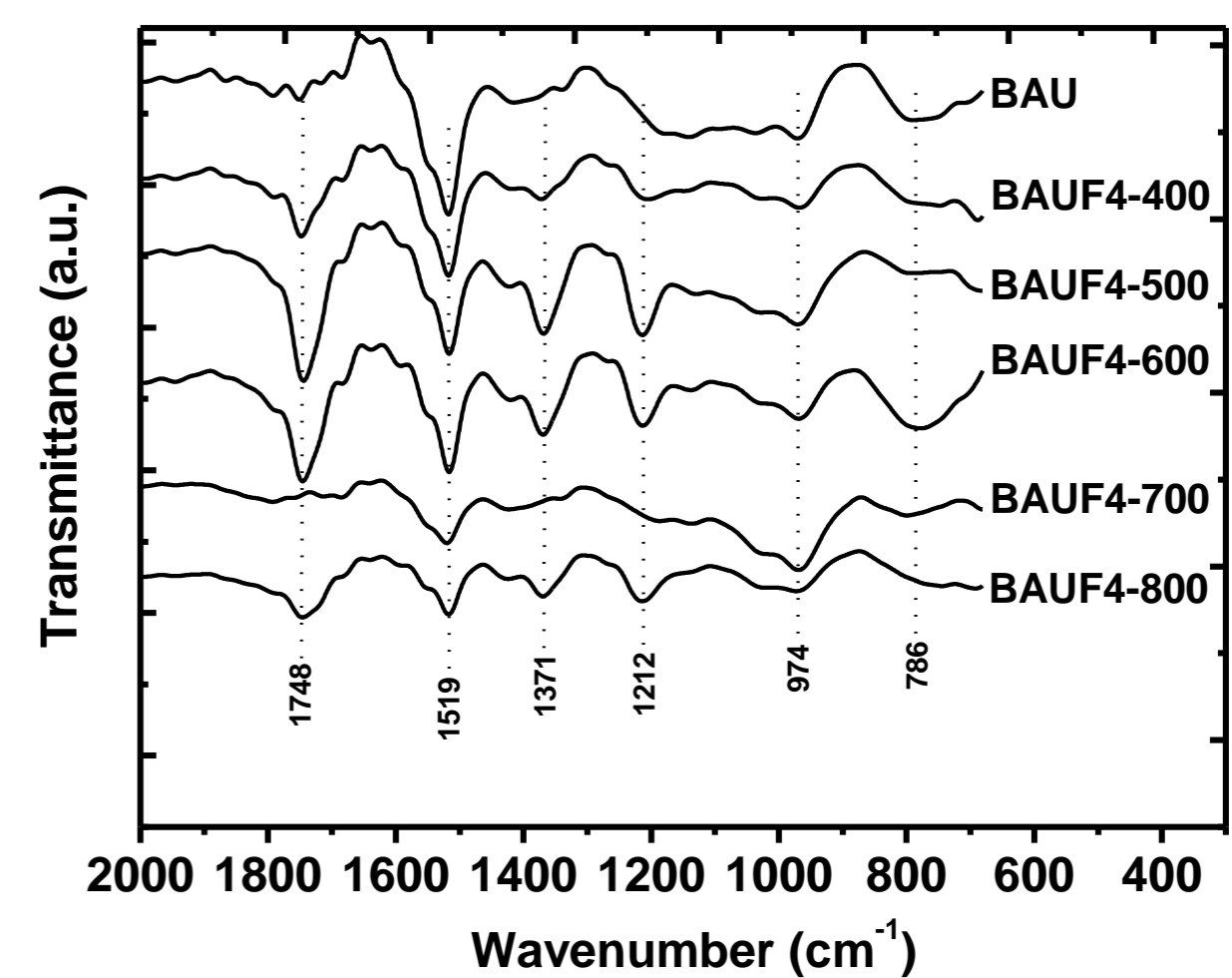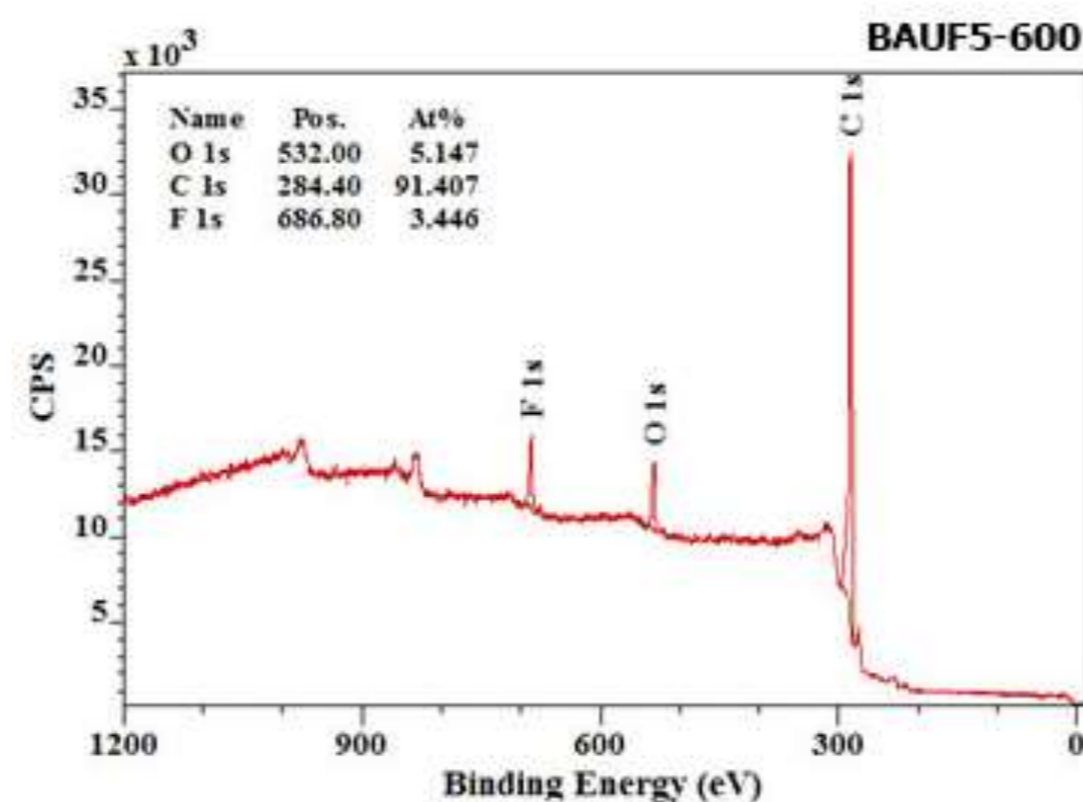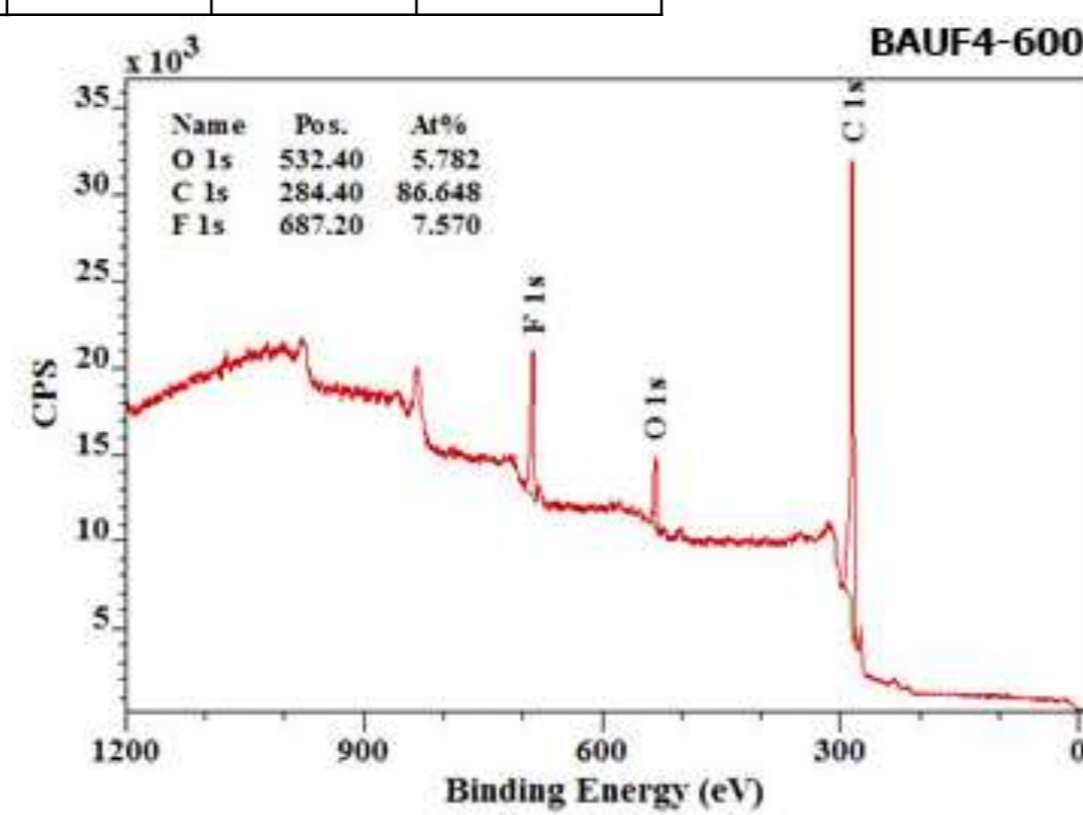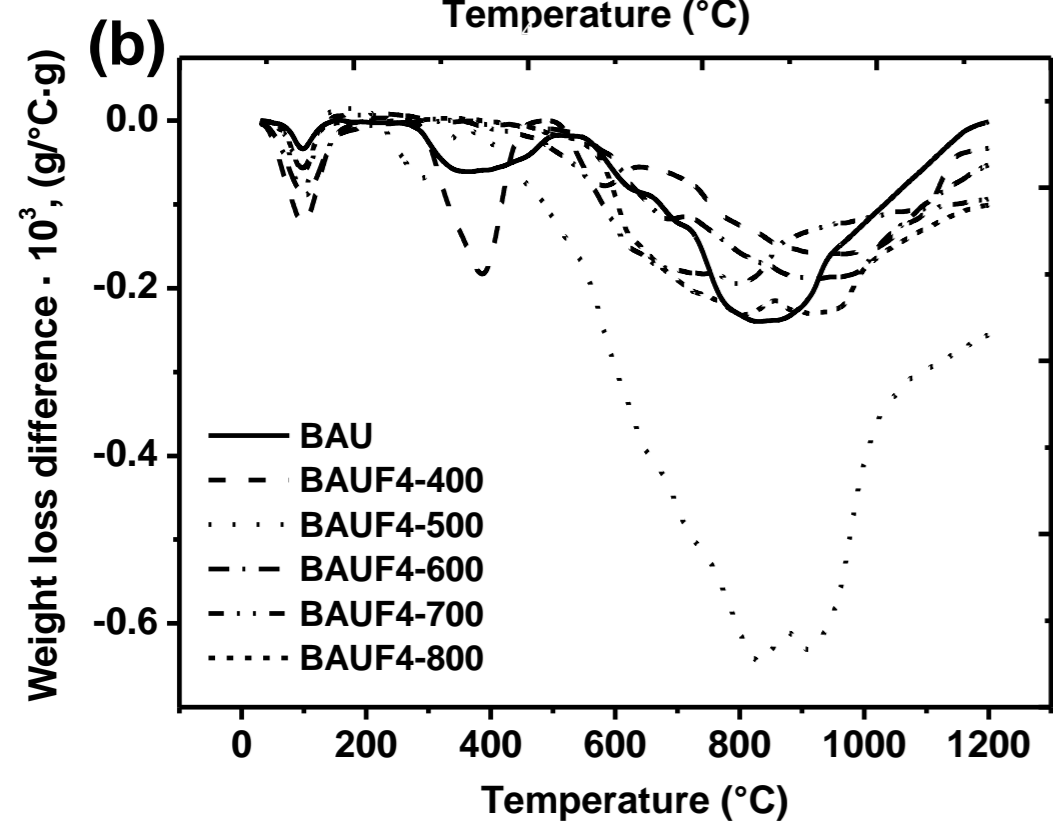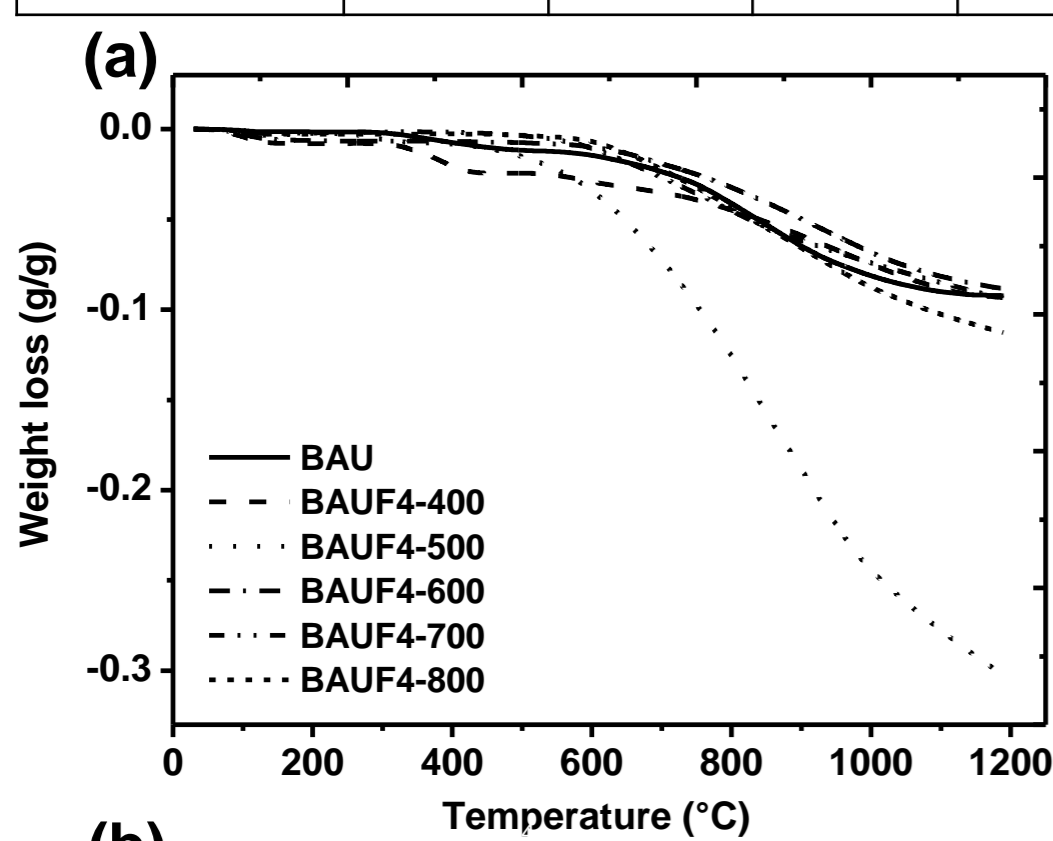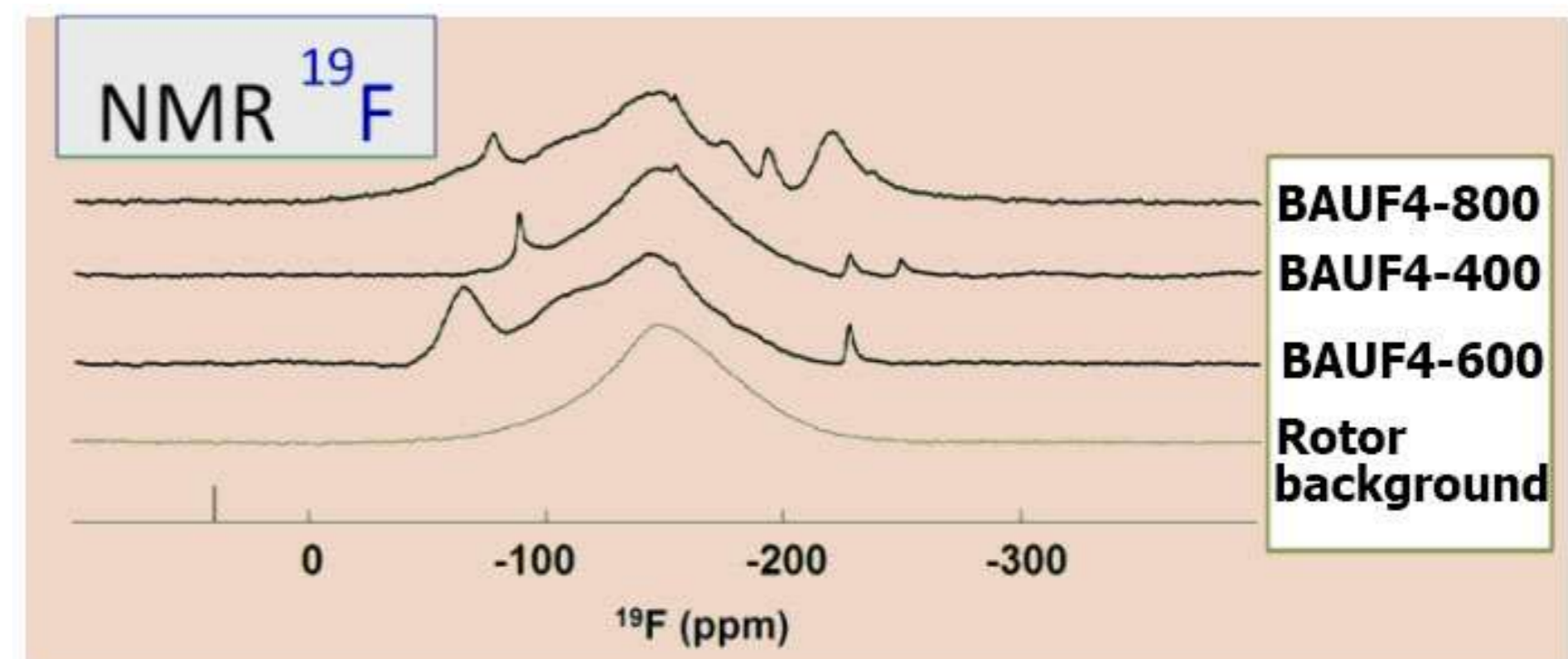
Characterization of fluoralkylated carbons

Table 1. C.A. data and texture characteristics of BAUF4

Sample	Texture						C.A.
	S_{BET}, m^2/g	S_{micro}, m^2/g	S_{ext}, m^2/g	V_{tot}, cm^3/g	V_{micro}, cm^3/g	$^aV_{meso}$, cm^3/g	C_F, mmol/g
BAU	508	383	125	0.39	0.21	0.18	–
BAUF4-400	677	527	150	0.43	0.23	0.20	0.17
BAUF4-500	403	306	97	0.29	0.15	0.14	0.42
BAUF4-600	194	119	75	0.13	0.05	0.08	1.86
BAUF4-700	135	90	45	0.11	0.04	0.07	1.64
BAUF4-800	85	55	30	0.08	0.02	0.06	1.44

TG/DTG profiles, XPS, ATR and 19F MAS NMR spectra for selected BAUF4 and BAUF5 samples.
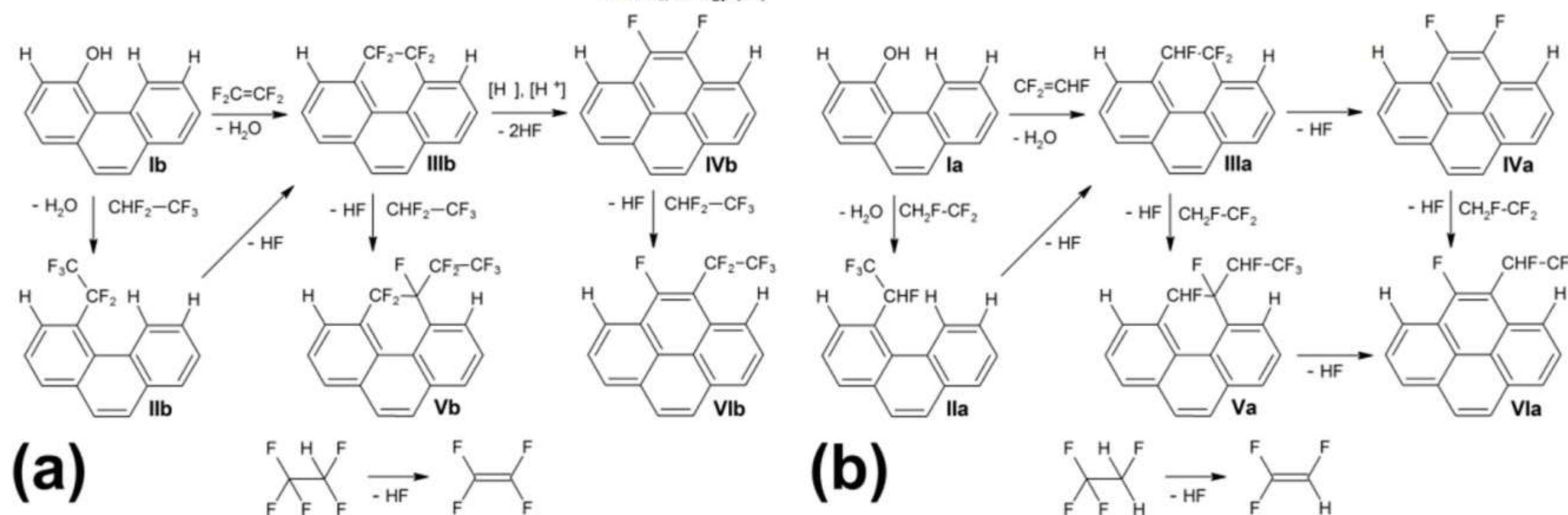
Schema of pyrolytic addition of C_2HF_5 (a) and $C_2H_2F_4$ (b), catalytic hydrogenolysis and cyclization.

Conclusion. We have demonstrated the temperature-differentiated addition of the F-containing groups by treating BAU with CHF. The treatment at 400 and 500 °C caused the formation of the carbon solids containing fluorine. This fluorine includes in the fluoroalkyl groups, and it can be added in small amounts at 400 °C. At 600 °C, the fluorine content is maximal over the studied range of the treatment temperature. Almost all this fluorine is in a semi-ionic form. This form is like that of the fluorine attached by the treatment of the carbon surface with elemental fluorine. When increasing the treatment temperature up to 800 °C, the fluorine-enriched matrix once again can attach the fluoroalkyl groups, "so-called" covalent fluorine. Further studies (starting from these interesting results) are currently underway aimed at tuning the treatment temperature to regulate the physicochemical parameters by changing the chemical nature of the grafted groups. Both CHF and products of the fluorine addition to the carbon matrix can form long-lived CF_2 biradicals at high temperatures. By migrating (laterally) across the damaged surface of the carbon matrix, they can interact with the conjugated π system and the surface radicals. By forming cross-links, they can bind individual graphene-like layers. In this way, the compaction and layer ordering can reduce the BET surface area at the expanse of the advanced microporosity. In contrast to known fluorinated materials, here we reported fluoroalkylated ones. They are potential precursors for obtaining sulfur-containing functional materials by replacing the semi-ionic fluorine for the sulfur-containing groups.