Enhanced Stability of Rubrene against Oxidation by Partial and Complete Fluorination

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I. CYCLIC VOLTAMMETRY

At potentials above 0.5 V, a second chemically irreversible oxidation wave located at around +1.0 V is observed for RUB (Fig. S1a). In the backward scan a weak reduction signal at $\sim +0.7$ V appears. We attribute this peak to the reduction of products formed in follow up reactions that are coupled to the second oxidation. At higher scan rates ($v \geq 1000$ mV s$^{-1}$) the peak current of the signal at +0.7 V decreases and the second oxidation becomes chemically reversible (Fig. S1b). Thus, the follow up reactions seem to be slow and within the time scale of the cyclic voltammetric experiment.

For F$_{14}$-RUB the electron transfer reaction at $-2.15$ V becomes chemically reversible for scan rates $v \geq 500$ mV s$^{-1}$ (Fig. S2). Nevertheless, the corresponding peak current of the re-oxidation peak in the backward scan remains low. We observe a weak oxidation wave at around $-1.2$ V which indicates products from follow up reactions that are coupled to the second reduction.

Figure S1. Anodic cyclic voltammograms of RUB ($c = 2.6$ mM) in 0.1 M NBu$_4$PF$_6$/CH$_2$Cl$_2$ at Pt recorded with different scan rates in a potential window of $-0.34$ to $+1.26$ V. (a) black line = 100 mV s$^{-1}$. (b) black line = 500 mV s$^{-1}$, red line = 1000 mV s$^{-1}$, blue line = 2000 mV s$^{-1}$ and green line = 5000 mV s$^{-1}$. The voltammograms are not background corrected.

Figure S2. Cathodic cyclic voltammograms of F$_{14}$-RUB ($c = 1.4$ mM) in 0.1 M NBu$_4$PF$_6$/CH$_2$Cl$_2$ at Pt recorded in a potential window of $-0.35$ to $-2.45$ V with different scan rates. Black line = 100 mV s$^{-1}$, red line = 200 mV s$^{-1}$, blue line = 500 mV s$^{-1}$ and green line = 1000 mV s$^{-1}$. The voltammograms are not background corrected.
II. NEXAFS

For the unsubstituted rubrene it has been observed that the molecules exhibit significant twist in the gas phase and in amorphous thin films, while the backbone is planarized in the crystalline phase\textsuperscript{1,2}. As reported recently, in contrast to RUB for PF-RUB thin film phases with both planar and twisted tetracene backbone are possible\textsuperscript{3}. Hence PF-RUB molecules in twisted $D_2$ and planar $C_{2v}$ symmetries have been considered for the NEXAFS computations. However, as it turns out the spectra of the two different isomers with planar and twisted backbone are virtually identical (Fig. S3). In addition, a visualization of all contributing NEXAFS resonances combined with the origin of their respective excitation centers (either tetracene backbone or phenyl rings) is presented in this figure as vertical bars.

Figure S3. Computed NEXAFS spectra of PF-RUB for twisted and planar configuration of the tetracene backbone (visualized in bottom panel). In the top panel additionally all individual resonances of the spectrum computed for the planar geometry are presented (black: excitation center in the tetracene backbone, red: in the phenyl rings)