

## Electron-transfer-induced transformation of trifluoromethylfullerenes electrochemical, ESR and theoretical studies

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Fullerenes and their derivatives in neutral and anionic states show a variety of physical properties making these compounds as prospective organic semi-, superconductors and ferromagnets.<sup>1</sup> Electrochemical studies of fullerene derivatives make possible to reveal the reduction potentials, electrochemical gaps and chemical transformation due to electronic transfer. Electrochemical behavior of trifluoromethylfullerenes  $C_{70}(CF_3)_n$ ,  $n=2-20$  can be separated to reversible (for the majority, up to four electrochemically reversible single-electron reductions)) and irreversible. Irreversible reductions are due to chemical transformations: dimerization ( $C_{1-p^7mp}-C_{70}(CF_3)_{10}$ )<sup>2</sup> or the leaving of the  $CF_3$  group in the case of skew-pentagon-pyramid patterns of  $CF_3$  addends<sup>3,4</sup>. For example, major isomer of  $C_{70}(CF_3)_{12}$  and *spp*- $C_{70}(CF_3)_{16}$  isomer display *ECE* mechanism during reduction yielding  $C_{70}(CF_3)_{11}^-$  and  $C_{70}(CF_3)_{15}^-$  anions correspondingly. Furthermore, oxidation of  $C_{70}(CF_3)_{15}^-$  is electrochemically reversible process at moderate voltammetric scan rates evidencing relatively high stability of the respective radicals  $C_{70}(CF_3)_{15}^\cdot$ . Thus, the electron-transfer-induced detachment of  $CF_3$  group is a promising approach to synthesis of novel fullerene derivatives and fullerene-based stable radicals.

Here we report novel isomer  $p^9mp-C_{70}(CF_3)_{12}$ , its structure, proved by  $^{19}F$  and  $^{19}F-^{19}F$  COSY NMR spectroscopy and interesting results of CVA studies, which is similar to  $C_{1-p^7mp}-C_{70}(CF_3)_{10}$ . According to cyclic voltammetry studies, new  $C_{70}(CF_3)_{12}$  exhibits two reduction process at  $-1.05$  (irreversible) and  $-1.68$  and oxidation process at  $-0.43$  V vs  $Fc^{0/+}$  at moderate scan rates. The electrochemical reversibility of the first reduction step can be achieved at the scan rate of more than  $20\text{ V s}^{-1}$ . The process has been assigned to recombination of anion-radical species yielding  $[C_{70}(CF_3)_{12}]_2^{2-}$ . ESR spectroscopy of chemically generated  $p^7-C_{70}(CF_3)_8^\cdot$  and  $p^7mp-C_{70}(CF_3)_{10}^\cdot$  and  $p^9mp-C_{70}(CF_3)_{12}^\cdot$  reveals unresolved singlet signals for all studied anionic compounds with typical *g*-values of 2.002 and line widths of 1 G. Bond energy between fullerene cage in dianionic dimers of  $[C_{70}(CF_3)_8]_2^{2-}$ ,  $[C_{70}(CF_3)_{10}]_2^{2-}$  and  $[C_{70}(CF_3)_{12}]_2^{2-}$  were estimated as  $-31$ ,  $+54$ ,  $+47\text{ kJ mol}^{-1}$  according to DFT calculation.

### References

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