

## Supplementary Information

for

# Applications of Some EPR Methods to the Investigation of the Radical Species Produced by the Reactions of Hydroxyl Radicals with PEFC-Related Fluorinated Organic Acids

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### **Energy diagram for the 1:2:1 triplet signal and the effect of non-Boltzmann distribution of the spin states on TR-EPR spectra**

In the usual EPR spectra, the carbon radicals having  $\bullet\text{CH}_2$ - structure provide 1:2:1 triplet signal as shown in [Figure S1\(a\)](#). The three peaks in the spectrum are assigned to the transitions from  $m_s = -1/2$  to  $m_s = +1/2$  in the electron spin states which are modified by the coupled nuclear spin states of  $M_I = -1, 0,$  and  $+1$  for the peaks L, C, and H in the EPR spectra, respectively. The EPR signal intensity is proportional to the difference between the populations of two electron spin states, which is caused by the Boltzmann distribution of electron spins under the magnetic field in the thermal equilibrium. The thermal equilibrium could be achieved in the spin relaxation time  $T_1$  from the non-Boltzmann distribution which corresponds to random orientation of the electron-spin magnetization. In the non-thermalized state, the population difference of electron spin states coupled with each nuclear spin state is changed as shown in [Figure S1\(b\)](#). As the result, the emission signal can be seen for  $M_I = -1$ , and no signal is observed for  $M_I = 0$ . Thus, the ratio of the signal intensities in the TR-EPR spectra become -1:0:1 before the thermal equilibrium.

