Three Mechanisms of Room Temperature Dynamic Nuclear Polarization occur simultaneously in Ionic Liquid

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Supplementary Information

The following information is related to an example of a fitting procedure that was done to extract the contribution of different DNP mechanisms to the DNP profile. The main idea is based on the assumption that EPR spectra which are obtained independently by, e.g. CW EPR, can be used to reproduce DNP spectra shape (see eq. 1-3 of the primary text).

In order to obtain numerical parameters to reproduce the lineshape $g(\omega)$ in the DNP spectra fitting procedure, the fitting of EPR spectra of nitroxide was performed using the pseudo-Voigitian function:

$$g(\omega) = \sum_{i=1}^{3} A_i \left[m_i \frac{2}{\pi} \frac{\delta_i}{4(\omega - \omega_{ci})^2 + \delta_i^2} + (1 - m_i) \frac{\sqrt{4\ln 2}}{\sqrt{\pi}\delta_i} e^{-\frac{4\ln 2}{\delta_i^2}(\omega - \omega_{ci})^2} \right] \quad \text{(S1)}$$

where A, m, δ, and ω_c are area, the relative weight of Lorentzian contribution, linewidth (FWHM), and centre of the peak, respectively.

As a result, fitting of EPR lineshape, obtained from CW EPR of nitroxide in ionic liquid at 303 K containing three hyperfine lines, is presented in Figure S1. Fitting parameters are presented in Table 1.

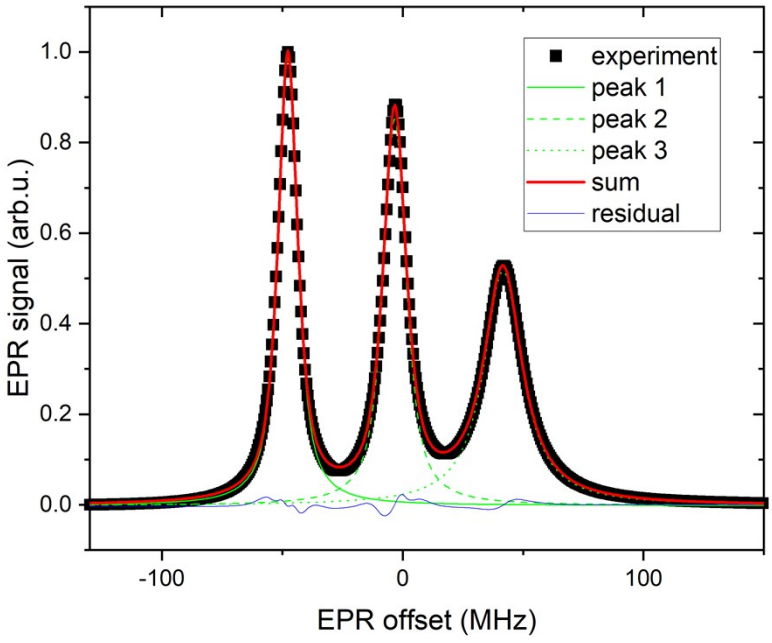

Figure S1. EPR lineshape obtained from CW EPR experiment. The lines present the fitting using a pseudo-Voigitian function (see equation S1). The corresponding fitting parameters are presented in the Table S1

Table S1. Fitting parameters using eq (1-3) and data presented in Figure S1. The standard error of the fits does not exceed 1 %

Parameter	Peak 1	Peak 2	Peak 3
A , arb.u.	14.0	14.1	15.5
m	0.84	0.83	0.98
δ^*, MHz	9.7	11.3	19.2
ω_c, MHz	-47.7	-3.3	41.6

*in order to implement additional broadening of DNP spectra in comparison with EPR lineshape parameter w_i (i=1..3) was considered as an additional fitting parameter with a prefactor *B* similar for all three peaks $\delta_i^{`} = B\delta_i^{`}$

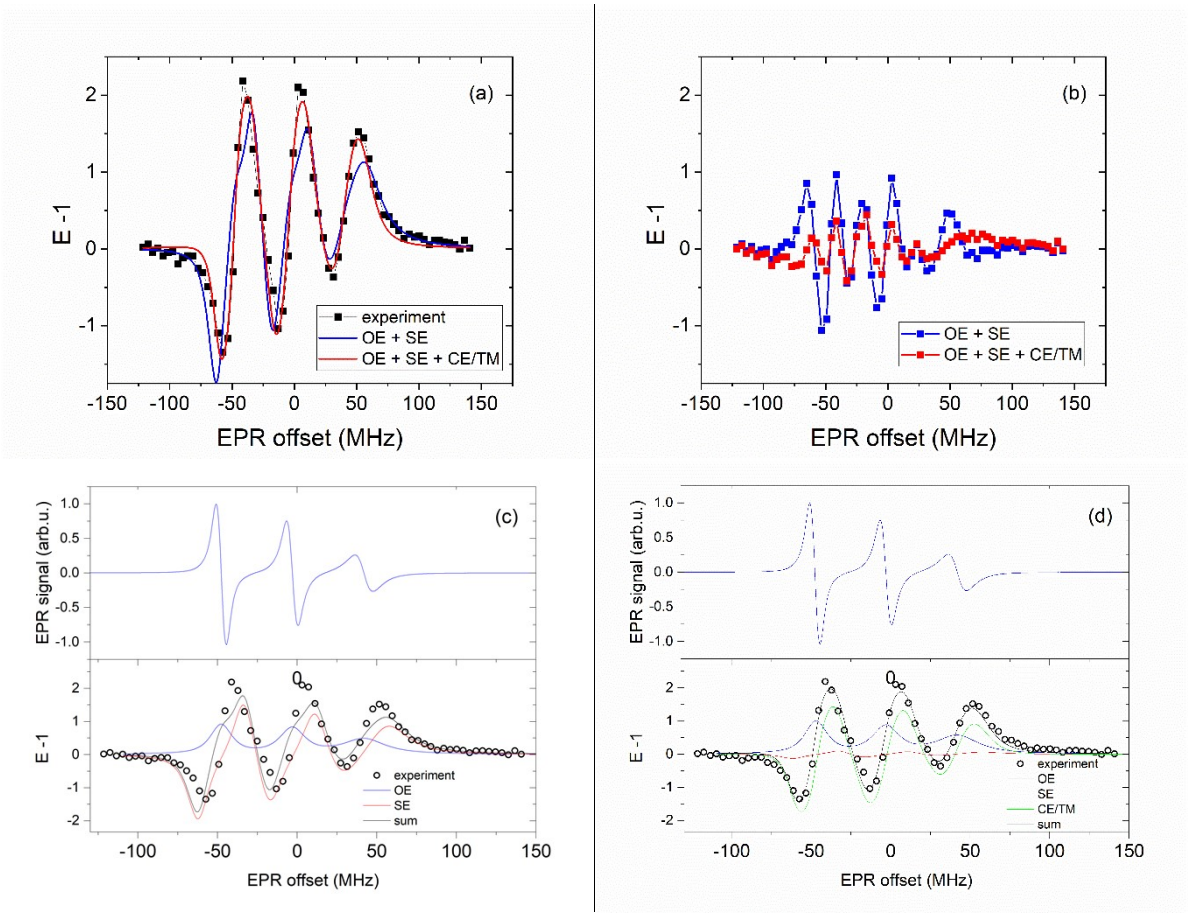

Figure S2. (a) Comparison of fittings using three mechanisms (OE, SE, and CE/TM) and only two, OE and SE, with corresponding residuals (b). The bottom figures (c and d) present CW EPR spectra and separated contributions for two (c) and three (d) mechanisms models, respectively.

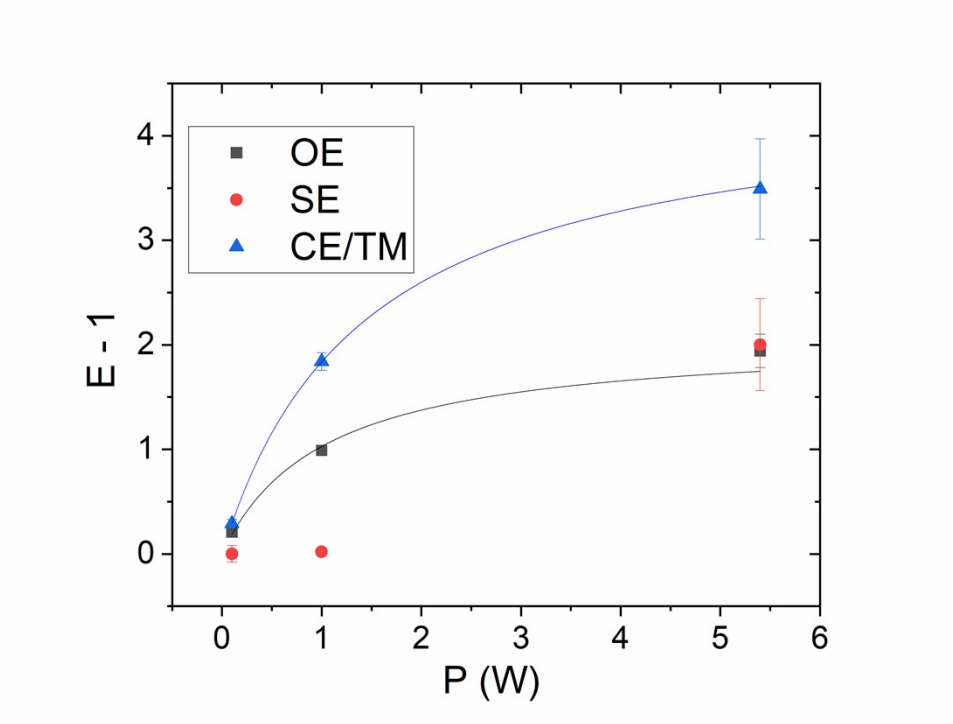

Figure S3. Power dependence of ^{19}F DNP enhancement of Hmim-TFSI via OE, SE, and CE/TM. The lines correspond to fits using the following equation (S2):

$$E(P) = 1 - (1 - E_{max})\frac{P/P_{half}}{1 + P/P_{half}} \qquad \text{(S2)}$$

where P_{half} is a fitting parameter for which the relative saturation factor equals 0.5, and E_{max} is a maximum enhancement value at the infinite power of microwave irradiation.

The temperature behaviour of both ^{1}H and ^{19}F DNP spectra of Hmim-TFSI is presented in Figure S4.

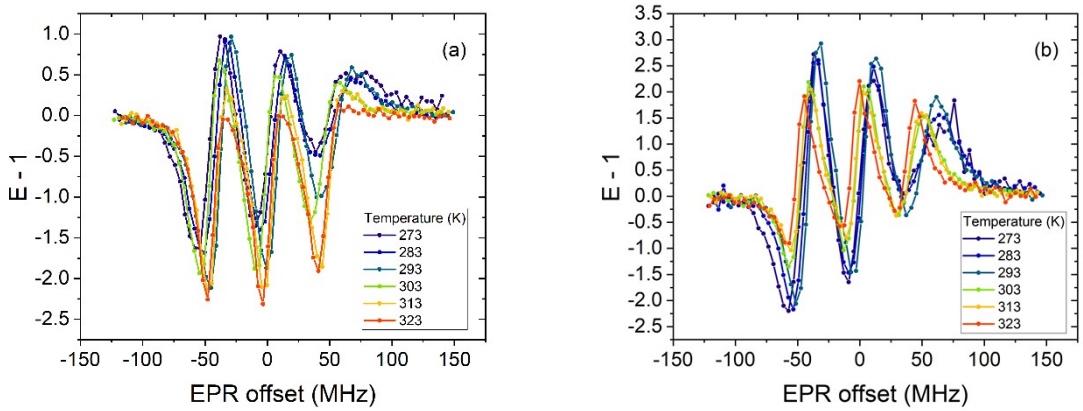

Figure S4. ^{1}H (a) and ^{19}F (b) DNP spectra at different temperatures