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Supporting Information

Solid-state carbon-13 NMR and computational characterization of the N719 ruthenium sensitizer adsorbed on TiO_2 nanoparticles

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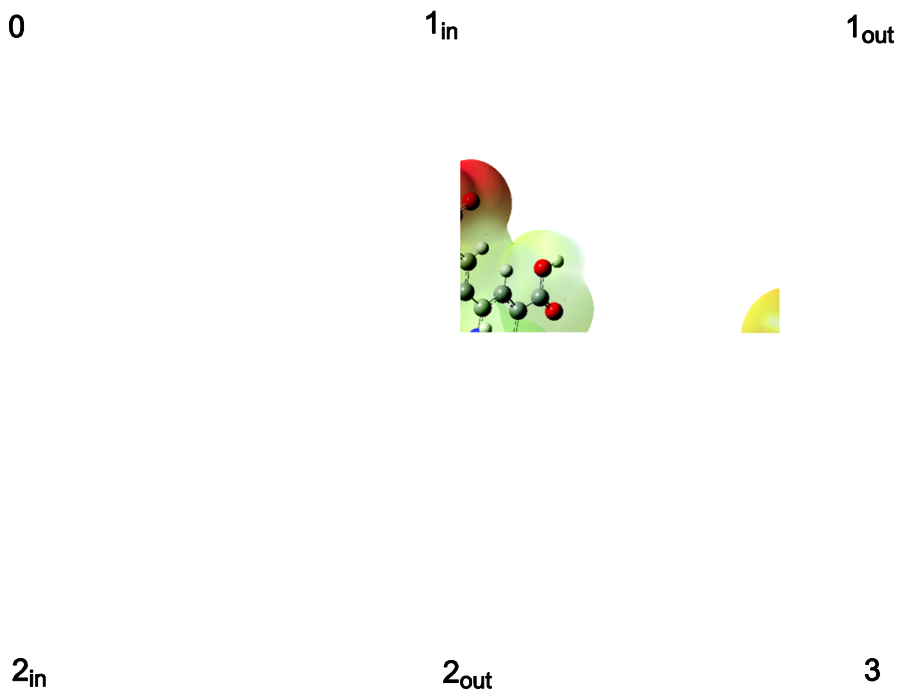

Figure S1 Electrostatic potentials mapped on electron density isosurfaces of the six structures of the N719 dye considered in this study. Structure **0** is used for correlations with experimental solution-phase data whereas the five others are used for correlations with experimental solid-state data. The colors of the surfaces indicate the electrostatic potentials in the range $-0.25 < \delta < +0.25$ eV, from red to blue, respectively. In this scale, green indicates centres with zero potential. The isovalue of the electron density at the isosurface was set to 0.001 $e/(a_0)^3$.

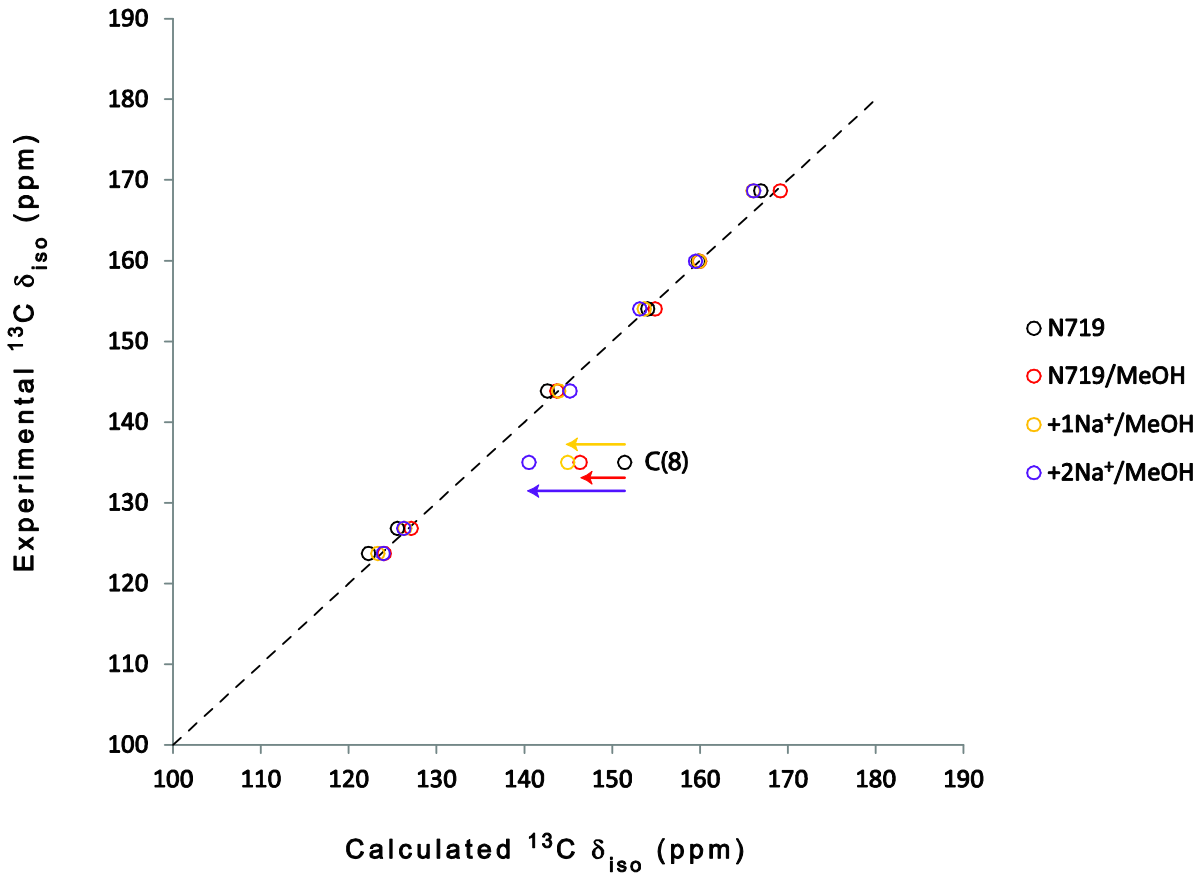

Figure S2 Correlation between experimental and calculated solution-phase ^{13}C shifts of N719. Black circles indicate correlations with structure **0** without solvation effects. Red circles show correlations when the PCM solvation method is included in the calculations. Yellow and purple data points indicate correlations using the PCM method including one or two Na^+ ions, respectively, positioned along the –NCS vector at a distance r = 4.07 Å from the S atom, equal to the sum of the van der Waals radii of S and Na. Colour-coded arrows show the changes in shielding of C(8) for the four calculations.

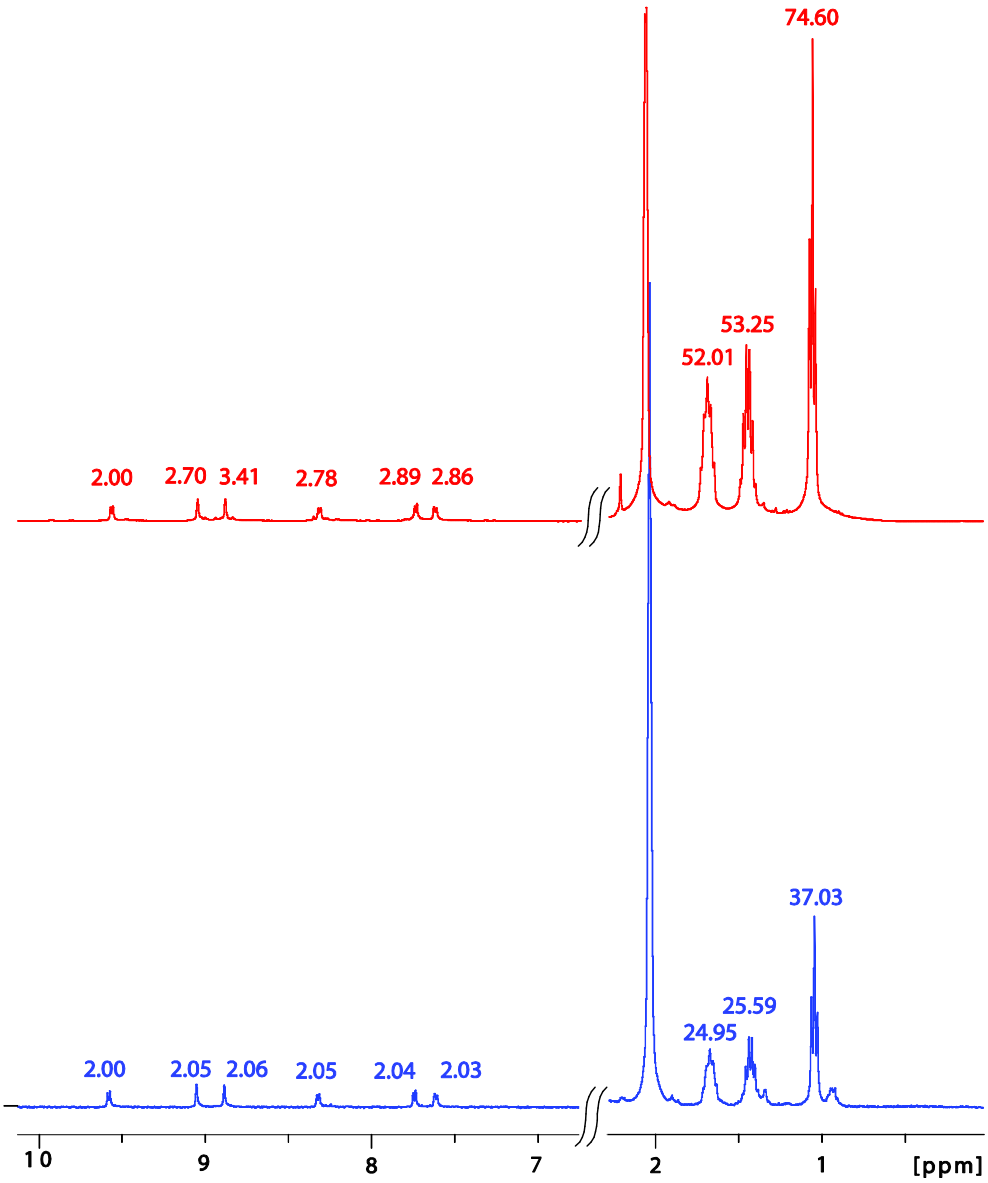

Figure S3 (Bottom) Proton spectrum with integrals of N719 in methanol-d4 solution in the absence of TiO_2 powder at 9.4 T (400 MHz). The three $C\underline{H}_3$-$C\underline{H}_2$-$C\underline{H}_2$ signals of the counterion TBA appear below 2 ppm. (Top) Proton spectrum of a solution remaining after adding TiO_2 powder. The integral of the highest-frequency signal has been normalized to 2 in both spectra. The relatively high integrals of the TBA signals in the top spectrum prove that a fraction of TBA remains in solution when N719 is attached to the TiO_2 surface.

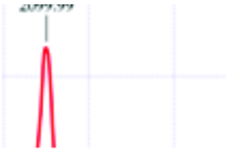

Figure S4 FTIR spectrum of N719 adsorbed on TiO_2 powder. The strong signal at 2099.99 cm^{-1} corresponds to the –NCS group. The weak signal at 2965.95 cm^{-1} corresponds to the remaining TBA cation.