

## Determination of the sign and absolute value of exchange interaction ( $J$ ) in the excited triplet ZnTPP- radical pair systems

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[Abstract] W-band TREPR spectra of excited doublet ( $D_1$ ) and quartet ( $Q_1$ ) states were observed in frozen toluene solution in excited triplet -radical systems such as ZnTPP-3NOPy and ZnTPP-4NOPy. Comparing the thermally polarized (Boltzmann) TREPR signals at two different temperatures, the sign and absolute value of exchange interactions ( $J$ s) between the triplet and radical were determined. It was found that the sign of  $J$  is negative in case of ZnTPP-3NOPy, whereas the exchange interaction for the ZnTPP-4NOPy system is weak and likely to be positive. We also analyzed the spin polarized spectra in terms of obtained  $J$  values.

[Introduction] A triplet-doublet pair generates excited multiplet states such as the quartet ( $Q_1$ ), and doublet ( $D_1$ ) states. The spin selectivity of the decay and the intersystem crossing between these states determine reaction paths and electron spin effects such as CIDEP. To be generated, the spin effect requires both an energy separation and a mixing between the  $Q_1$  and  $D_1$  manifolds by means of exchange ( $J$ ) and dipolar (ZFS and intermoiety) interactions. The W-band (95 GHz) EPR involves the large Zeeman splitting and facilitates to observe a thermally polarized (Boltzmann) signal along with the polarized one in the  $Q_1$  and  $D_1$  states, especially at very low temperatures. Temperature dependent Boltzmann spectra of our system show that the spectral pattern depends on the magnitude and sign of  $J$ . Valuable information regarding the sign and absolute value of  $J$  can be obtained from spectral simulations. The present triplet-radical systems are composed of meso- tetraphenylporphine zinc(II) (ZnTPP)-3-(N-oxy-N-tert-butyl amino) pyridine radical (3-NOPy) and meso- tetraphenylporphine zinc(II) (ZnTPP)-4-(N-oxy-N-tert-butyl amino) pyridine radical (4-NOPy) as shown in Fig-1.

[Experimental] Time-resolved (TR) EPR measurements were performed at 40K and 10K with the W-Band EPR (Bruker) spectrometer. Temperature was controlled by an Oxford CF 935 (W-band) helium gas flow system. The sample

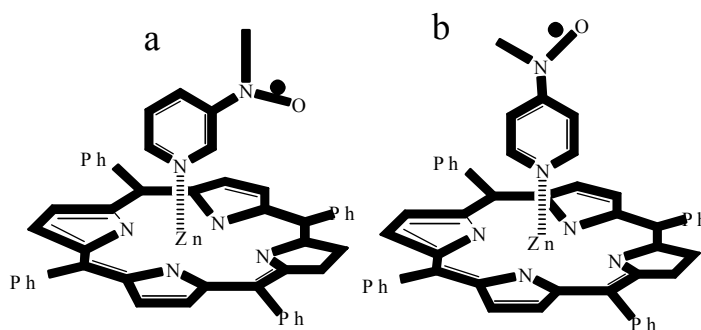


Fig-1. Molecular structures a) ZnTPP-3NOPy and b) ZnTPP-4NOPy

concentrations were set to be approximately 2 mM. The solution was degassed by the freeze-pump-thaw cycles on a vacuum line and selectively photo excited at the lower excited doublet ( $D_2$ ) states by a Spectra Physics MOPO-730 OPO laser (600-620 nm).

[Result and discussion] The Boltzmann and spin polarized signals of  $Q_1$  and  $D_1$  states were observed by W band time resolved EPR. The TREPR spectra of ZnTPP-3NOPy and ZnTPP-4NOPy are shown in Fig-2a and Fig-2b respectively. Each spectrum was acquired at 80.0  $\mu$ s after the laser pulse, when the only the Boltzmann polarization could be detected. In the ZnTPP-3NOPy molecular complex the peak positions at 10K and 40K are at the fields differing by about 1mT, whereas, in ZnTPP-4NOPy, these are located at almost the same fields. We consider the difference in the spectral patterns of these two systems as being due to the difference in sign of exchange interactions between the triplet and radical. In the case of  $J < 0$ , the peak position is shifted at 10K to the higher field. This comes from the different populations of the electron spin states in the  $Q_1$  and  $D_1$  manifolds.

Calculations with a very large  $J$  (more than  $10^3$  GHz) show that the  $D_1$  and  $Q_1$  manifolds are completely separated irrespective of the sign of  $J$ . When  $J$  is negative (the  $D_1$  energy is lower than  $Q_1$ ) and strong, the relative contribution of  $D_1$  increases compared with that of the  $Q_1$  manifold at 10K, which causes a large difference in the peak positions between 40K and 10K. The amount of the shift depends upon the absolute value of  $J$ . In the opposite case of positive  $J$  ( $J > 0$ ), the difference in the peak positions is expected to be much smaller because of the higher contribution of  $Q_1$  and its stronger transition probability. We observed a similar trend in our present systems.

Simulations of the Boltzmann signals show that  $J$  is negative in case of ZnTPP-3NOPy and the absolute value is about 70 GHz, whereas the  $J$  is likely to be positive or very small (less than 1 GHz) for ZnTPP-4NOPy. The absolute values of the exchange interaction, mutual orientations and distances of the ZnTPP and radical moieties are also have been tested by simulations of the spin polarized signals in the systems.

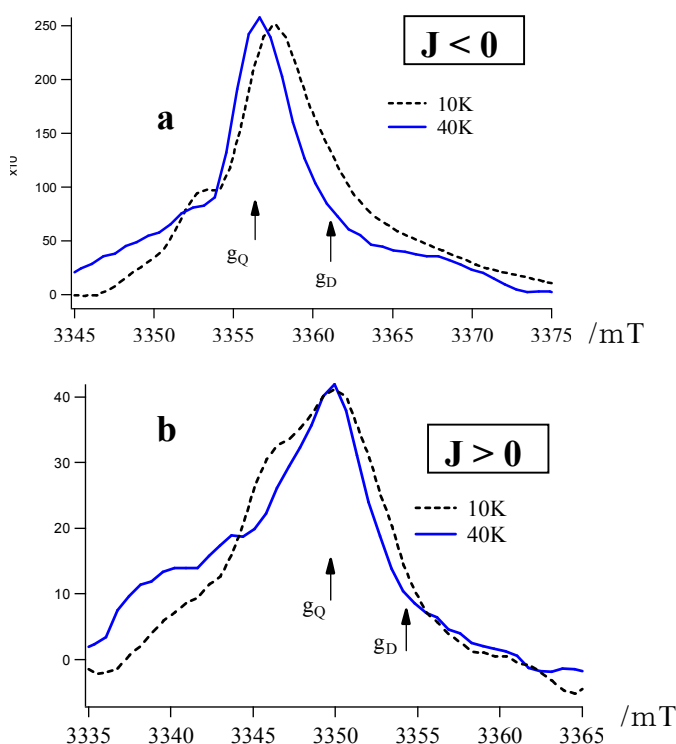


Fig-2. W-band TREPR spectra the ZnTPP-3NOPy (a) and ZnTPP-4NOPy (b) systems at 80  $\mu$ s after the laser pulse