

Supporting Information

Modulation of the electron transfer processes in Au-ZnO nanostructures

M.E. Aguirre,^a A. Armanelli,^a G. Perelstein,^a A. Feldhoff^b, A. J. Tolley^c, and M. A. Grela ^a

^a Departamento de Química, Universidad Nacional de Mar del Plata, Funes 3350, B7602AYL Mar del Plata, Argentina

^b Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Callinstraße 3a, D-30167 Hannover, Germany

^c Centro Atómico Bariloche -R8400AGQ San Carlos de Bariloche - Río Negro, Argentina.

* Corresponding Author. E-mail: magrela@mdp.edu.ar

Contents: Hyperfine coupling constants (MHz) and rotational correlation times used in the simulations.

The experimental EPR spectra were analysed by simulations performed with the Easyspin package developed by Stoll and Schweiger^{1,2} under the fast motion regime. For the computations we used a variable hyperfine coupling constant for the ¹⁴N hyperfine coupling (a_N). The basic three-line spectrum of the nitroxide,^{3,4} is assumed to be widened by the contribution of the equatorial methyl (3x2) and methylene protons (2x2),⁵ whose hydrogen hyperfine coupling constants are adjusted to fit the experimental data, together with the line width l_{wpp} and the correlation time, τ_{corr} .

Free Tempol in ethylene glycol

$$a_N \text{ (MHZ)} = (37.6070, 58.3032, 42.52970)$$

$$a_H \text{ (MHZ)} = (-0.30612, -0.16791, 4.79870); (0.18032, -0.87991, -2.36472); (7.09796, -8.11412, 4.99964); (-10.9136, 10.9660, 4.82184); (2.51803, 2.16138, -5.91349); (-8.08036, 0.37575, 10.0920); (3.6916, -1.02880, 0.85662); (-5.22253, 3.76014, 6.27574); (-4.14949, 9.34677, -2.67067); (-0.57518, -2.18507, 7.94616)$$

$$\tau_{corr} = 1.62 \text{ ns}$$

$$l_{wpp} \text{ (MHZ)} = 1.04$$

Tempol in the ZnO ethylene glycol sol

$$a_N = (42.5011, 52.3213, 43.6962)$$

$$a_H = (-0.30612, -0.16791, 4.79870); (0.18032, -0.87991, -2.36472); (6.72494, -1.69015, -0.333705); (-4.43002, 5.69316, -2.71134); (0.526515, -0.329775, 0.897171); (-3.57238, -1.26125, 7.11211); (1.7236, -1.95071, 4.0384); (-0.349074, 2.80980, -0.506770); (0.734089, -0.332539, 4.442752); (2.141790, 3.35953, -2.9057)$$

$$\tau_{corr} = 3.58 \text{ ns}$$

$$l_{wpp} \text{ (MHZ)} = 1.04$$

Tempol in the ZnO-Au ethylene glycol sol

$$a_N = (36.9738, 57.9921, 43.7801)$$

$$a_H = (-2.09645, 0.64206, 4.98403); (-3.80069, -0.73878, 1.09807); (7.28448, -3.83870, 0.27764); (3.54688, -3.93947, -2.85821); (-3.80660, -0.25182, -5.00918); (-9.49664, -1.88615, 7.73648); (-1.69777, -0.34125, 5.88756); (-2.13772, 1.97292, -3.33179); (2.22498, -3.75625, 4.10981); (1.86136, 3.01204, -0.66517)$$

$$\tau_{corr} = 1.82 \text{ ns}$$

$$l_{wpp} \text{ (MHZ)} = 1.04$$

(¹) S. Stoll, A. Schweiger, *J. Magn. Reson.*, **2006**, 178, 42-55.

(²) S. Stoll, A. Schweiger, *Biol. Magn. Reson.*, **2007**, 27, 299-321

(³) C. C. Whisnant, S. Ferguson and D. B. Chesnut, *J. Phys. Chem.*, 1974, **78**, 1410-1415.

(⁴) J. J. Windle, *J. Mag. Res.* **1981**, 45, 432-439.

(⁵) Y. Nosaka, H. Natsui, M. Sasagawa and A. Y. Nosaka, *J. Phys. Chem. B* **2006**, *110*, 12993-12999.