Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information

Intermolecular Distances of Carboxylated TEMPO Derivatives on TiO_2 Evaluated by Spin-probe ESR

Yuta Kano, Kohei Kushimoto, Kenji Komaguchi*, Yousuke Ooyama, Ichiro Imae, Joji Ohshita,

and Yutaka Harima*

Department of Applied Chemistry, Graduate School of Engineering,

Hiroshima University, Higashi-Hiroshima 739-8527, Japan

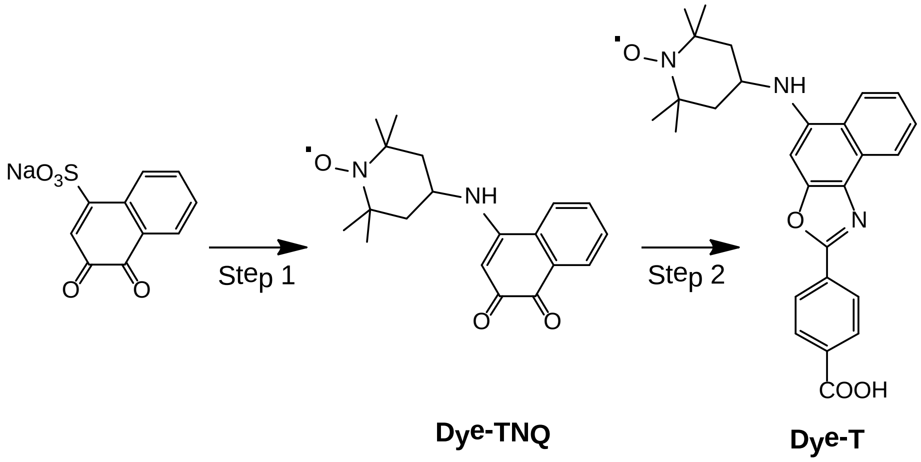
*Corresponding authors: Kenji Komaguchi and Yutaka Harima
Department of Applied Chemistry, Graduate School of Engineering,
Hiroshima University, Higashi-Hiroshima 739-8527, Japan
E-mail: okoma@hiroshima-u.ac.jp (K. Komaguchi),
harima@mls.ias.hiroshima-u.ac.jp (Y. Harima)

Synthesis of Dye-T

The synthetic pathway of Dye-T is shown in Scheme S1.

4-(1-oxyl free radical-2,2,6,6-tetramethyl-piperidin-4-ylamino)-[1,2]naphthoquinone (Dye-TNQ). A suspended solution of 1,2-naphtoquinone-4-sulfonic acid sodium salt (4.04 g, 14.6 mmol, Alfa Aesar) in 20 ml acetic acid was mixed with 4-amino-TEMPO (2.50 g, 14.6 mmol, Tokyo Chemical Industry), nickel(II) chloride (1.89 g, 14.6 mmol, Nacalai Tesque), and sodium acetate (1.20 g, 14.6 mmol, Nacalai Tesque), and ground in mortar and further stirred at 60 °C for 12 h. The mixture was dissolved in 200 ml CH_2Cl_2, and then filtered and concentrated. After removing solvents under reduced pressure, the residue was chromatographed on silica gel (60N, spherical, neutral, CH_2Cl_2/CH_3OH (7:1) as eluent, Kanto Chemical) to give Dye-TNQ (1.93 g, 5.92 mmol, yield 40%). R_f = 0.50. ^{1}H-NMR δ_H (DMSO-d_6): 8.23 (d, 1H, J = 7.8 Hz), 7.98 (d, 1H, J = 6.8 Hz), 7.82 (t, 1H, J = 6.3 Hz), 7.69 (t, 1H, J = 7.3 Hz), 7.26 (s, 1H), 5.74 (s, 1H), 1.91 (s, 12H), 1.68 (t, 1H, J = 12.2 Hz), 1.16 (s, 2H), 1.12 (s, 2H) ppm. ^{13}C-NMR δ_C (DMSO-d_6): 181.68, 181.62, 153.82, 131.17, 131.10, 130.66, 129.38, 125.81, 125.21, 123.57, 57.85, 52.93, 26.06, 20.97 ppm. FT-IR-ATR: ν(C=O) 1688 cm^{-1}, ν(N-H) 3390 cm^{-1}. MS(EI): m/z 328.0 [M$^+$].

4-[5-(1-oxyl free radical-2,2,6,6-tetramethyl-piperidin-4-ylamino)-naphtho[1,2-*d*]oxazol-2-yl]benzoic acid (Dye-T). To a solution of Dye-TNQ (0.70 g, 2.14 mmol) in 30 ml acetic acid was added terephthalaldehydic acid (0.32 g, 2.14 mmol, Nacalai Tesque) and ammonium acetate (4.94 g, 64.1 mmol, Nacalai Tesque), and the solution was stirred and refluxed at 90 °C for 3 h. The solution was then concentrated and dried under reduced pressure. The residue was chromatographed on silica gel (the same as before; acetic acid/toluene (3:2) as eluent) and dried at room temperature under reduced pressure (0.80 g, 1.74 mmol, yield 82%). The product was further purified by reprecipitation from a THF/hexane mixed solvent (THF as good solvent, hexane as poor solvent) to give greenish yellow crystals of Dye-T. The spin activity (percentage of nitroxide radicals alive) in the product was 14–15% at this stage, suggesting that most of the TEMPO substituent in Dye-T loses the magnetic susceptibility in the synthesis process. In order to regenerate susceptibility of the TEMPO (Samuni, A.; Krishna, C. M.; Riesz, P.; Finkelstein, E.; Russo, A. *Free Radic. Biol. Med.* **1989**, *6*, 141.; Shiba, T.; Yamamoto, M.; Kudou, W.; Ichikawa, K. Yamada, K-I.; Watanabe, T.; Utsumi, H. *J. Pharm. Sci.* **2008**, *97*, 4101.), potassium ferricyanide ($K_3[Fe(CN)_6]$) (165 mg, 0.5 mmol, Aldrich) was added to a 50 ml THF solution of Dye-T (4.58 mg, 0.01 mmol), and the mixture was vigorously stirred at room temperature for 3 h. The solution was filtered through a layer of celite powder (Nacalai Tesque) as filter aid, and the filtrate was concentrated and dried to give greenish yellow crystals of reoxidized Dye-T (4.20 mg, 0.009 mmol). The spin activity was 72.5% for the reoxidized Dye-T as a final product: R_f = 0.20. decomposition: 240 °C. ^{1}H-NMR δ_H (DMSO-d_6): 8.42 (d, 1H, J = 8.8 Hz), 8.24 (d, 1H, J = 8.8 Hz), 8.13 (d, 2H, J = 7.8 Hz), 8.02 (d, 2H, J = 7.8 Hz), 7.57 (t, 1H, J = 7.3 Hz), 7.40 (t, 1H, J = 7.8 Hz), 7.24 (s, 1H), 6.72 (s, 1H), 5.57 (s, 1H), 1.87 (s, 12H), 1.56 (t, 1H, *J* = 15.6 Hz), 1.24 (s, 2H), 1.14 (s, 2H) ppm. ^{13}C-NMR δ_C (DMSO-d_6): 172.24, 168.92, 150.08, 149.12, 136.49, 136.21, 131.43, 130.35, 130.14, 129.87, 128.71, 126.88, 126.66, 125.34, 121.98, 116.58, 58.53, 49.38, 26.01, 21.97 ppm. FT-IR-ATR: ν(C=O) 1714 cm^{-1}, ν(N-H) 3371 cm^{-1}. MS(FAB): *m*/*z* 459.0 [MH$^+$].



Scheme S1. Synthesis of Dye-T: (Step 1) 4–amino–TEMPO, NiCl$_2$, CH$_3$COONa, CH$_3$COOH, 60 ºC, 12 h, yield 40%; (Step 2) terephthalaldehydic acid, CH$_3$COONH$_4$, CH$_3$COOH, 90 ºC, 3 h, yield 82%.

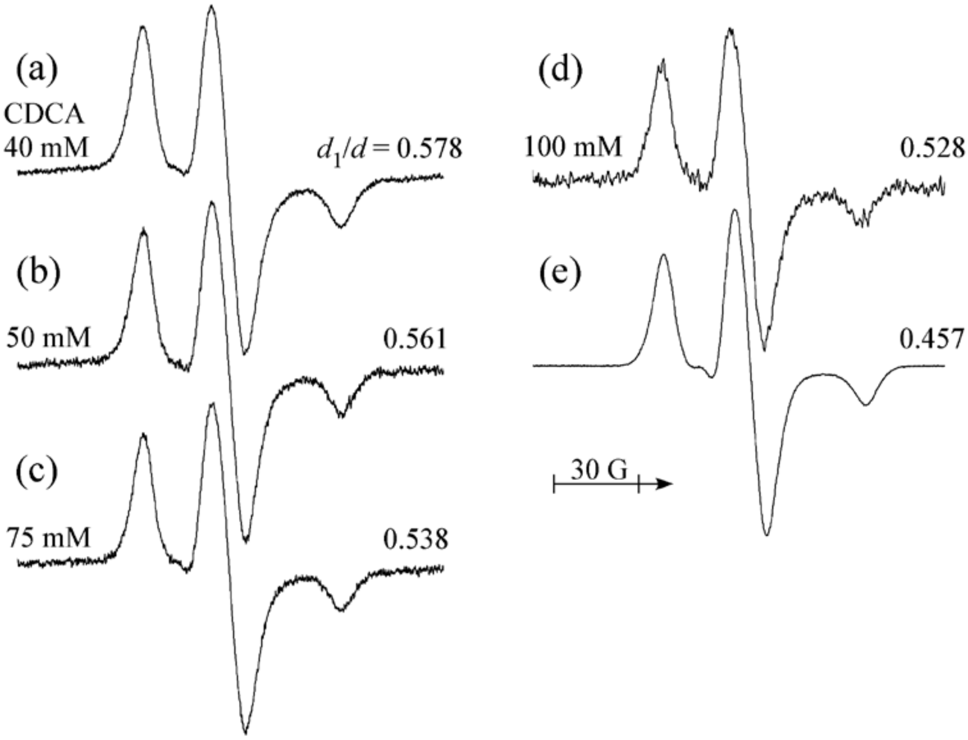


Fig. S1. ESR spectra observed at 77 K for Dye-T adsorbed on the TiO$_2$ surface in the presence of CDCA; x_{esr} = 2.03 nm (a), 2.16 nm (b), 2.38 nm (c), 2.51 nm (d) together with d_1/d values, and for a glass matrix (dichloromethane : toluene = 1 : 4) containing TEMPO molecules (0.001 M, x_{cal} = 6.56 nm) (e).

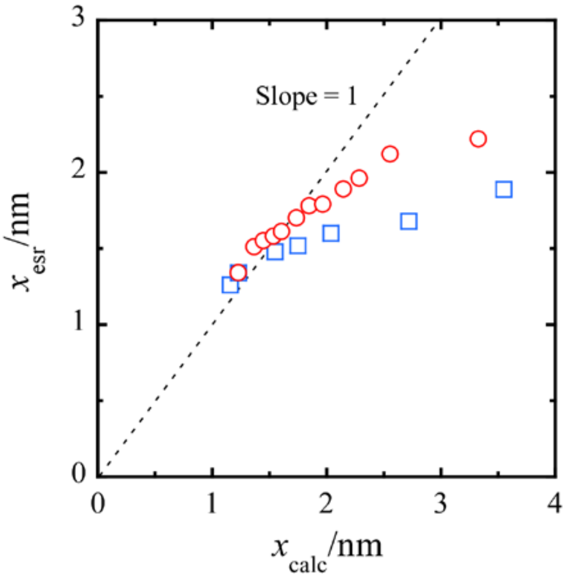


Fig. S2. Plots of x_{esr} *vs.* x_{calc} for Dye-T adsorbed on the TiO_2 surface in the presence (○) and absence (□) of CDCA. Ethanol is used as solvent for loading of Dye-T on TiO_2.

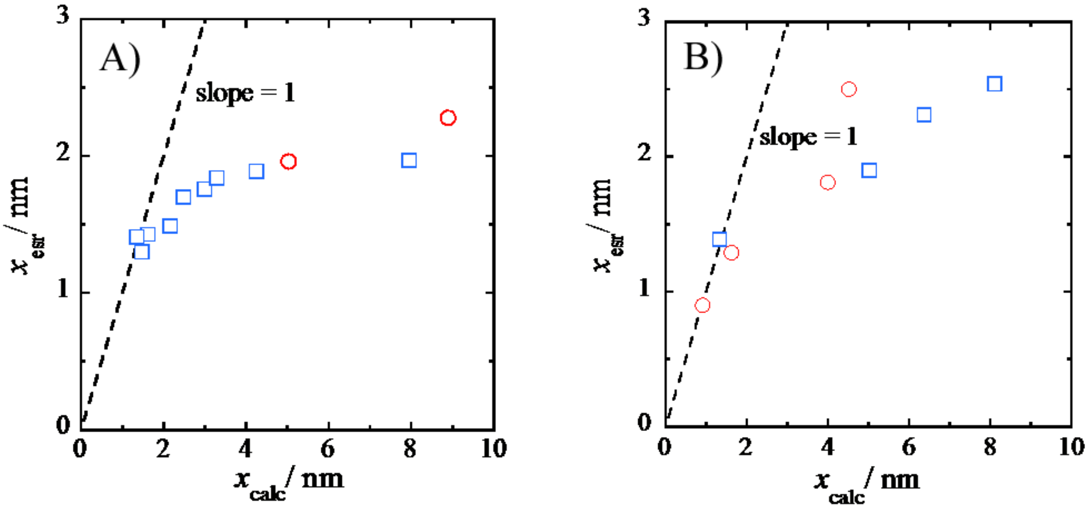


Fig. S3. Plots of x_{esr} *vs.* x_{calc} for 4CT adsorbed on the TiO_2 surface in the presence (○) and absence (□) of 4TBC. Solvents used for loading of 4CT on TiO_2 are A) THF and B) acetone.

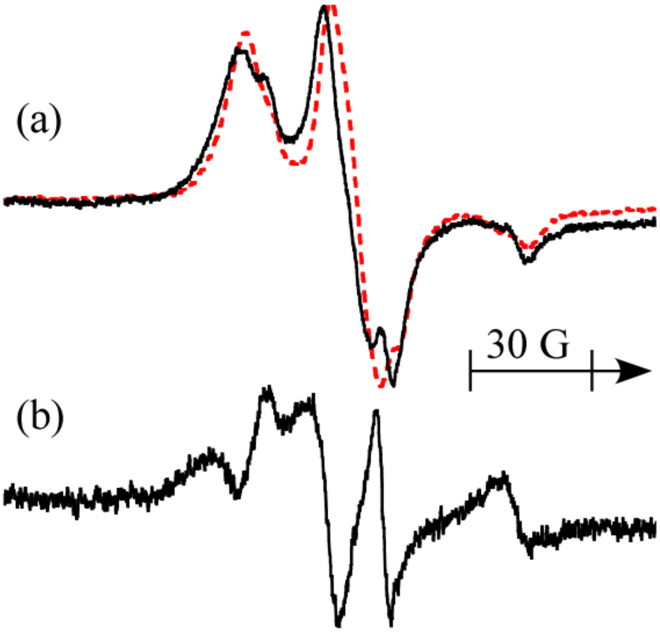


Fig. S4. (a) ESR spectra of 4CT-loaded TiO_2 particles prepared from THF solutions of 0.36 mM 4CT containing (——) 80 mM and (----) 50 mM of 4TBC. (b) Difference ESR spectrum obtained by subtraction of the two spectra in (a).

ESR spectral distortion of 4CT-loaded TiO_2 at lower concentrations

In the ESR experiments with 4CT, it was found that as the adsorbed amount of 4CT was decreased by increasing the concentration of coadsorbates, 4TBC or CDCA, the ESR spectrum underwent deformation to have new peaks, or rather the new peaks became increasingly visible by a decrease in intensity of the original signal (black solid spectrum in Figure S4(a)). The additional signal shown in Fig. S4(b) may be due to crystalline defects of TiO_2 or the nitroxide unit of TEMPO adsorbing on, most likely, the Lewis acid site of TiO_2. The spectral distortion caused by the additional signal started to occur in the x_{calc} range beyond 10 nm and thus was unlikely to affect the the ESR analysis to obtain the plot of Fig. 4B. No such spectral distortion was observed for Dye-T loaded TiO_2 with and without CDCA.

Derivation of eq 3.

Let $w(r)\mathrm{d}r$ denote the probability that the nearest neighbor to a radical occurs between r and r + dr. This probability must be clearly equal to the probability that no radicals exist interior to r times the probability that a radical does exist in the thin walled circle between r and dr. Accordingly, the function $w(r)$ must satisfy the relation

$$w(r)\mathrm{d}r = \left[1 - \int_0^r w(r)dr\right] \times 2\pi rs\,\mathrm{d}r \qquad \text{- - -} \quad \text{(S1)}$$

where s denotes the average number of radicals per unit area. From eq S1 we derive:

$$\frac{d}{dr}\left[\frac{w(r)}{2\pi rs}\right] = -2\pi rs\,\frac{w(r)}{2\pi rs} \qquad \text{- - - -} \quad \text{(S2)}$$

Hence $w(r) = 2\pi rs\exp(-\pi r^2 s)$ ---- (S3)

since, according to eq S1

$$w(r) \rightarrow 2\pi rs \quad \text{as} \quad r \rightarrow 0 \qquad \text{----} \quad \text{(S4)}$$

Equation S3 gives then the required law of distribution of the nearest neighbor.

Using the distribution eq S3 we can derive an exact formula for the "average distance" x_{calc} between the radicals. For, by definition

$$x_{\text{calc}} = \int_0^\infty rw(r)\mathrm{d}r \qquad \text{----} \quad \text{(S5)}$$

or, if we use eq S3

$$x_{\text{calc}} = \int_0^\infty \exp(-\pi r^2 s)\, 2\pi r^2 s\, \mathrm{d}r \qquad \text{----} \quad \text{(S6)}$$

After some elementary reduction, eq S6 becomes eq 3.

$$x_{\text{calc}} = \left(\frac{1}{\pi s}\right)^{1/2} \int_0^\infty x^{1/2} \exp(-x)\, \mathrm{d}x$$

$$= \Gamma(3/2)/(\pi\, s)^{1/2} \qquad \text{----} \quad \text{(3)}$$

Substituting for Γ(3/2), we find

$$x_{\text{calc}} = (1/2)\, s^{-1/2}. \qquad \text{----} \quad \text{(S7)}$$