Supporting Information
for
Controlling the Orientation of Spin-Correlated Radical Pairs by Covalent Linkage to Nanoporous Anodic Aluminum Oxide Membranes

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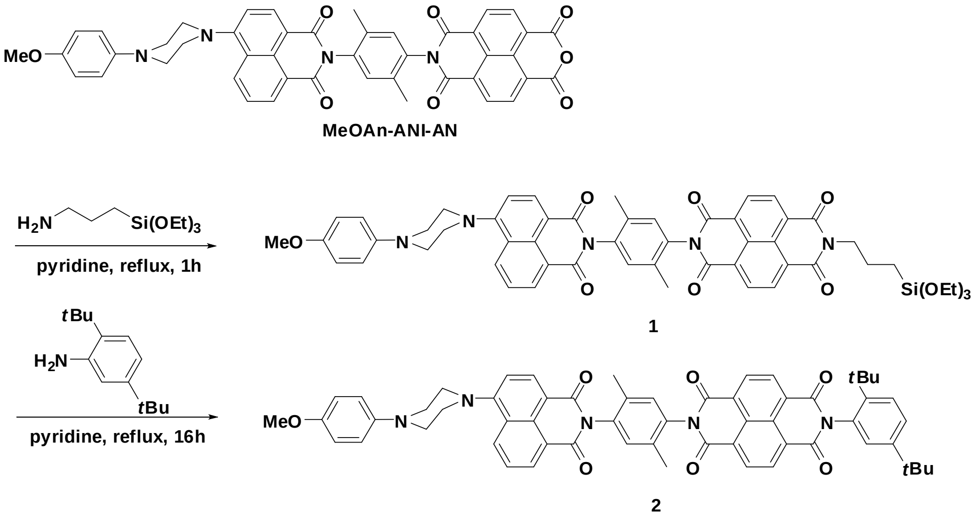
Synthesis. Proton and carbon nuclear magnetic resonance spectra were recorded on a Varian 500 spectrometer. Laser desorption mass spectra were obtained with the Bruker Autoflex III mass spectrometer using dithranol as a matrix. High-resolution mass spectroscopy was further performed on an Applied Biosystems API3000 (ESI-APCI). Commercially available reagents were purchased from Sigma-Aldrich Co. and used without further purification. All solvents were spectrophotometric grade unless otherwise noted. Preparatory thin layer chromatography was performed using Sorbent Technologies (Atlanta, GA) C_{18}-coated silica gel.



Compound 1. A mixture of **MeOAn-ANI-AN** (25 mg, 0.033 mmol)[1] and (3-aminopropyl)triethoxysilane (22 mg, 0.099 mmol) was dissolved in pyridine (2 mL) and refluxed for 1 h. The solvent was removed by rotary evaporator and the resulting solid was dissolved in dichloromethane and purified by preparatory thin layer chromatography on C_{18} gel (CH_2Cl_2/hexane/acetone = 30/20/1) to afford pure **1** as a yellow solid (21 mg, 65% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.0 Hz, 2H), 8.80 (d, *J* = 8.0 Hz, 2H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.33

(d, *J* = 8.0 Hz, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 4.21 (t, *J* = 8.0 Hz, 2H), 3.83 (q, *J* = 7.0 Hz, 6H), 3.80 (s, 3H), 3.48 (br, 4H), 3.42 (br, 4H), 2.21 (br, 6H), 1.88 (quin, *J* = 8.0, 2H), 1.21 (t, *J* = 7.0, 9H), 0.76 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.01, 163.59, 162.70, 162.40, 156.19, 154.17, 145.23, 135.59, 135.19, 134.58, 134.04, 133.06, 131.66, 131.38, 131.29, 130.99, 130.78, 130.64, 130.42, 127.18, 126.91, 126.78, 126.59, 126.29, 125.85, 123.23, 118.56, 116.68, 115.13, 114.49, 58.41, 55.53, 53.19, 50.95, 43.31, 29.65, 21.50, 18.25, 17.30, 7.95; MS (MALDI) m/z 959; HRMS (ESI$^+$) calculated for $C_{54}H_{54}N_5O_{10}Si$ (MH$^+$) 960.3640, found: 960.3632.

Compound 2. A mixture of **MeOAn-ANI-AN** (50 mg, 0.066 mmol)[1] and 2,5-di-*tert*-butylaniline (22 mg, 0.099 mmol) was dissolved in pyridine (2 mL) and refluxed for 12 h. The solvent was removed by rotary evaporator and the resulting solid was dissolved in dichloromethane and purified by column chromatography on silica gel (CH_2Cl_2/hexane/acetone = 15/5/2) to afford pure **2** as a yellow solid (21 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (d, *J* = 8.0 Hz, 2H), 8.88 (d, *J* = 8.0 Hz, 2H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 7.23 (s, 1H), 7.04-7.01 (m, 3H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.21 (t, *J* = 8.0 Hz, 2H), 3.82 (s, 3H), 3.49 (br, 4H), 3.43 (br, 4H), 2.21 (br, 6H), 1.33 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.05, 163.85, 163.56, 162.38, 156.22, 154.25, 150.37, 145.31, 143.68, 135.68, 135.24, 134.63, 134.58, 134.02, 133.07, 132.00, 131.66, 131.49, 131.34, 130.82, 130.75, 130.68, 130.44, 129.01, 127.49, 127.42, 127.30, 127.12, 127.01, 126.37, 125.90, 123.33, 118.60, 116.84, 115.17, 114.55, 55.58, 53.24, 50.99, 35.57, 34.28, 31.92, 31.19, 29.70, 17.40; MS (MALDI) m/z 943; HRMS (ESI$^+$) calculated for $C_{59}H_{54}N_5O_7$ (MH$^+$) 944.4023, found: 944.4021.

Surface modification of nanoporous anodic aluminum oxide (AAO). Nanoporous anodized alumina oxide membranes (Synkera symmetric ceramic membrane, 25 mm diameter, 50 μm thick with 150 nm pores and 2×10^9 cm^{-2} density) were purchased from Synkera. The AAO membranes were successively sonicated in de-ionized water (10 min) and isopropyl alcohol (10 min) and baked at 65^{o}C under vacuum for 3 h. Then they were immersed in 2.5 mL of a solution of **1** (0.1 mM) with constant shaking at room temperature for 24 h. The surface-modified AAO membrane was washed with dichloromethane (5 × 2 mL) to remove unbound molecules and dried in a vacuum oven at 65^{o}C for 3 h. For measurements, the functionalized AAO membrane was cut into small rectangles (~ 5 × 2 mm) and put into an X-band tube as a stack of 5 membranes. For samples with C_{60} as an internal standard, one ~5 x 2 mm film of 1 wt% C_{60} in polystyrene (MW = 280 kD) was added to the stack of AAO membranes.

Time-Resolved EPR (TREPR) Spectroscopy. Samples for TREPR measurements were prepared by loading the stack of functionalized AAO membranes into 3.8 mm o.d. (2.4 mm i.d.) quartz tubes, evacuating the tubes to 10^{-4} Torr, (samples with solvent were subjected to five freeze-pump-thaw degassing cycles on a vacuum line with pumping to 10^{-4} Torr), and the sealing the tubes using a hydrogen torch. TREPR measurements at 295 K were carried out using Bruker Elexsys E580 spectrometer operating at 9.5 GHz. The samples were excited using a frequency-tripled Quanta-Ray Lab-150 Nd-YAG laser operating at a 10 Hz repetition rate that was used to pump a Basiscan OPO to generate 7 ns, 416 nm, 1.0 mJ pulses. The laser polarization was set to 54.7° relative to the direction of the static magnetic field to avoid magnetophotoselection effects on the spectra. The field modulation was disabled to achieve a time response of $Q/\pi\nu \approx 30$ ns, where Q is the quality factor of the resonator and ν is the resonant frequency, while microwave signals in emission (e) and/or enhanced absorption (a) were detected in both the real and the imaginary channels (quadrature detection). Sweeping the magnetic field gave 2D spectra versus both time and magnetic field. For each kinetic trace, the signal acquired prior to the laser pulse was subtracted from the data. Kinetic traces recorded at magnetic field values off-resonance were considered background signals, whose average was subtracted from all kinetic traces. The spectra were subsequently phased into a Lorentzian part and a dispersive part, and the former, also known as the imaginary magnetic susceptibility χ'', is presented. Simulation of the spectra of the spin-polarized RPs was performed using a home-written MATLAB™ program[2] following published procedures.[3]

Singular Value Decomposition (SVD). A time-dependent spectral matrix was created that contained the TREPR spectra collected at different times. SVD followed by global fitting to two exponential decays was performed to obtain the decay associated spectra using Surface Xplorer (Figure S3).[4]

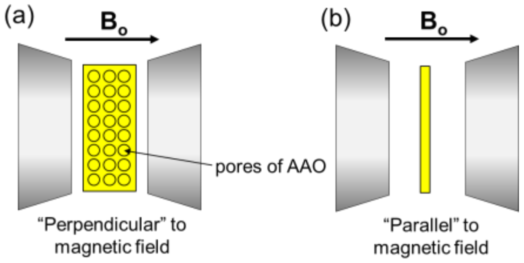


Figure S1. Definition of the direction of AAO pores with respect to the magnetic field: (a) perpendicular; (b) parallel.

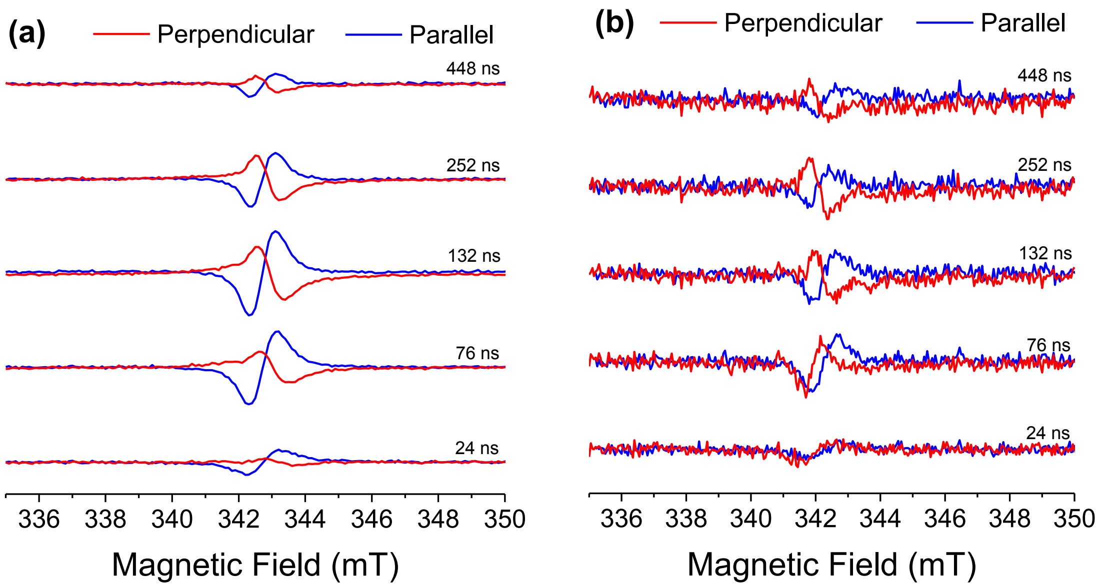


Figure S2. TREPR spectra of **1**-AAO in (a) toluene and (b) DCE with perpendicular and parallel orientation at 295 K at indicated times following a single 416 nm, 7 ns laser pulse.

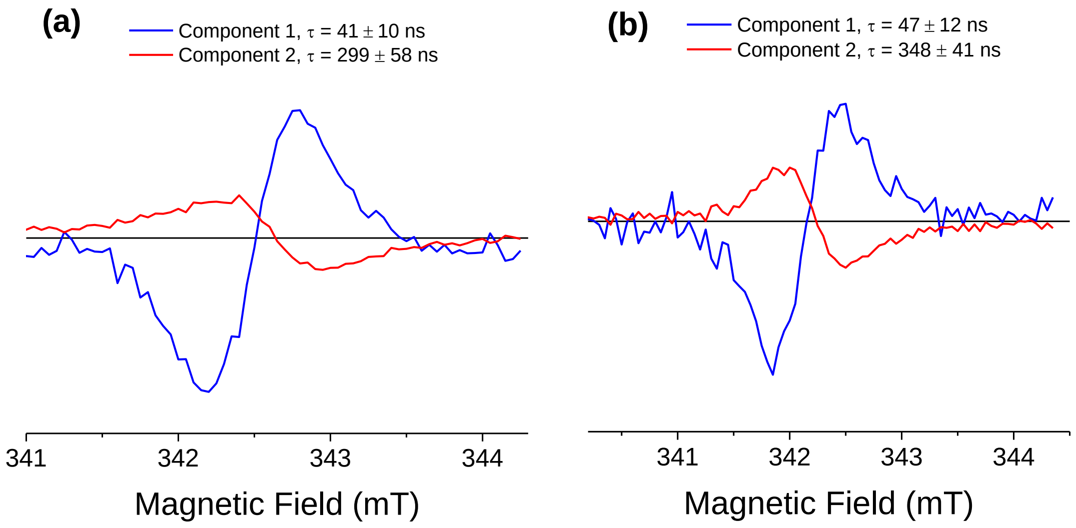


Figure S3. Singular value decomposition (SVD) analysis of **1**-AAO in (a) THF and (b) DCE.

References:

1. E. A. Weiss, L. E. Sinks, A. S. Lukas, E. T. Chernick, M. A. Ratner and M. R. Wasielewski, *J. Phys. Chem. B*, 2004, **108**, 10309-10316.
2. *MATLAB*, The Mathworks, Inc., MA, 2006.
3. U. Till and P. J. Hore, *Mol. Phys.*, 1997, **90**, 289-296.
4. Surface Xplorer, Ultrafast systems LLC, Sarasota, FL 34234, USA.