

Supplementary Information for:

High-spin polycationic states of an alternate *meta-para*-linked oligoarylamine incorporating two macrocycles

Daisuke Sakamaki,^a Akihiro Ito,^{*a} Ko Furukawa,^b Tatsuhisa Kato,^c and Kazuyoshi Tanaka^a

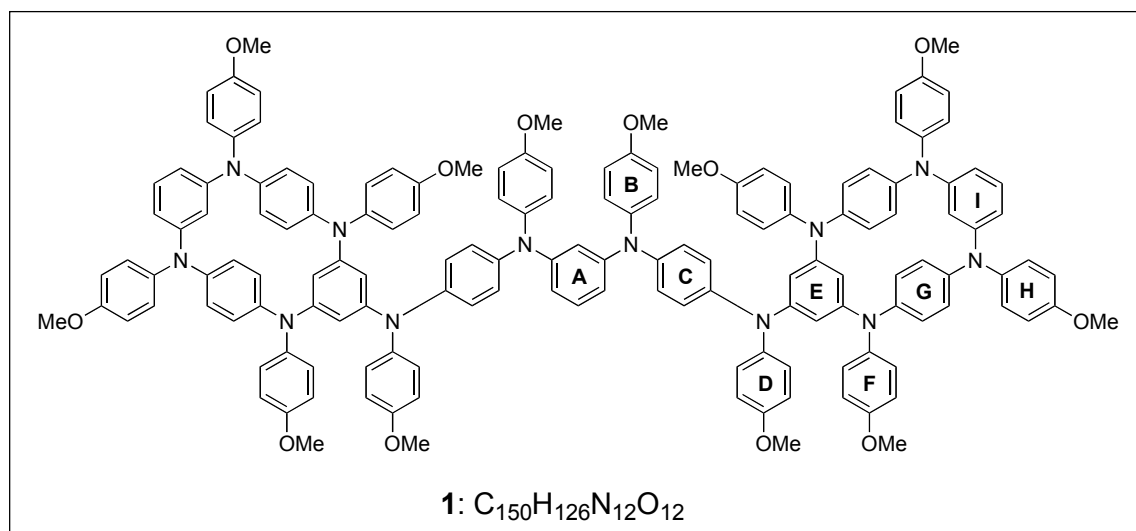
^a *Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: aito@scl.kyoto-u.ac.jp*

^b *Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

^c *Department of Chemistry, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, Japan*

General: Commercial grade reagents were used without further purification. Solvents were purified, dried, and degassed following standard procedures. Elemental analyses were performed by Center for Organic Elemental Microanalysis, Kyoto University. ¹H and ¹³C NMR spectra were measured by a JEOL JNM-EX400 FT-NMR spectrometer. Chemical shifts of NMR spectra are determined relative to tetramethylsilane (TMS) internal standard. Cyclic voltammograms were recorded using an ALS/chi Electrochemical Analyzer Model 612A with a three-electrode cell using a Pt disk (2 mm²) as the working electrode, a Pt wire as the counter electrode, and an Ag/0.01 M AgNO₃ (MeCN) as the reference electrode calibrated against ferrocene/ferrocenium (Fc/Fc⁺) redox couple in a solution of 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte (298 K, scan rate 100 mVs⁻¹). The cw-ESR spectra were measured using a JEOL JES-SRE2X or a JEOL JES-TE200 X-band spectrometer in which temperatures were controlled by a JEOL ES-DVT2 variable-temperature unit or a JEOL ES-DVT3 variable-temperature unit, respectively. The UV-Vis-NIR spectra were measured with a Perkin Elmer Lambda 19 spectrometer. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode quartz cell (light path length = 1 mm). The working and the counter electrodes were a Pt

mesh and a Pt coil, respectively. The reference electrode was an Ag wire. The potential was applied with an ALS/chi Electrochemical Analyzer Model 612A.



Meta-para-linked oligoarylamine incorporating two tetraazacyclophane (1): Anhydrous toluene (100 mL) was added to Pd(dba)₂ (6.4 mg, 0.01 mmol), Ph₅FcP(*t*-Bu)₂ [1] (15.1 mg, 0.02 mmol), and NaO*t*-Bu (0.2054 g, 2.13 mmol) in a flask equipped with a dropping funnel which was charged with a toluene solution (100 mL) of *N,N,N'*-tris(4-anisyl)-1,3,5-benzenetriamine **3** [2] (88.6 mg 0.20 mmol) and *N,N'*-di(4-bromophenyl)-*N,N'*-di(4-anisyl)-1,3-benzenediamine **4** [3] (189.9 mg 0.30 mmol), and the toluene solution was stirred under an argon atmosphere at 110 °C for a while. A half portion of the solution in the dropping funnel was gradually added into the solution containing the toluene solution of the palladium catalyst in the flask for 15 h. The reaction mixture was refluxed for 20 h with stirring, and furthermore the remaining solution in the dropping funnel was added into the reaction mixture for 7 h. The refluxing was continued for 6 h with stirring. The reaction mixture was cooled down to room temperature, washed with brine, and dried over Na₂SO₄. After removal of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (toluene : ethyl acetate = 19:1 as eluent). Finally, the product was washed with *n*-hexane to afford **1** (16.0 mg 7.0 %) as a beige powder: mp 217–220 °C; ¹H NMR

(400 MHz, tetrahydrofuran- d_8) δ = 3.662 (s, 12H, Ar_F-OCH₃ or Ar_H-OCH₃), 3.675 (s, 6H, Ar_B-OCH₃ or Ar_D-OCH₃), 3.704 (s, 6H, Ar_B-OCH₃ or Ar_D-OCH₃), 3.725 (s, 12H, Ar_F-OCH₃ or Ar_H-OCH₃), 5.886 (t, $J=1.95$ Hz, 2H, H_{E-4}), 6.122 (d, $J = 1.95$ Hz, 4H, H_{E-2}), 6.320 (t, $J = 2.20$ Hz, 2H, H_{I-2}), 6.350 (dd, $J = 2.20, 8.05$ Hz, 4H, H_{I-4}), 6.370 (dd, $J = 2.20, 8.29$ Hz, 2H, H_{A-4}), 6.562 (t, $J = 2.20$ Hz, 1H, H_{A-2}), 6.718 (d, $J = 9.03$ Hz, 4H, H_{B-2} or H_{D-2}), 6.723 (d, $J = 9.03$ Hz, 8H, H_{F-2} or H_{H-2}), 6.763-6.861 (m, 39H, H_{A-5}, H_{B-2} or H_{D-2}, H_{C-2}, H_{C-3}, H_{F-2} or H_{H-3}, H_{G-2}, H_{G-3}, H_{I-5}), 6.891 (d, $J = 9.03$ Hz, 4H, H_{B-3} or H_{D-3}), 6.943 (d, $J = 9.03$ Hz, 4H, H_{B-3} or H_{D-3}), 7.000 (d, $J = 9.03$ Hz, 8H, H_{F-3} or H_{H-3}), 7.060 (d, $J = 9.03$ Hz, 8H, H_{F-3} or H_{H-3}); ¹³C NMR (100 MHz, tetrahydrofuran- d_8) δ = 54.60 (Ar_B-OCH₃ or Ar_D-OCH₃), 54.65 (Ar_F-OCH₃ or Ar_H-OCH₃), 54.68 (Ar_B-OCH₃ or Ar_D-OCH₃, Ar_F-OCH₃ or Ar_H-OCH₃), 107.56 (C_{E-4}), 108.16 (C_{E-2}), 112.9 (C_{I-4}), 113.26, 113.29, 113.35 (C_{I-2}, C_{A-2}, C_{A-4}), 114.25 (C_{H-3} or C_{F-3}), 114.26, 114.39 (C_{B-3}, C_{D-3}), 114.41 (C_{H-3} or C_{F-3}), 123.91, 124.58 (C_{C-2}, C_{C-3}), 125.21, 125.53 (C_{G-2}, C_{G-3}), 126.10, 126.17 (C_{B-2}, C_{D-2}), 126.37, 126.88 (C_{F-2}, C_{H-2}), 127.92, 128.93 (C_{A-5}, C_{I-5}), 139.78, 139.99 (C_{F-1}, C_{H-1}), 140.42, 140.59 (C_{B-1}, C_{D-1}), 142.05 (C_{C-1} or C_{C-4}), 142.73, 142.82 (C_{G-1}, C_{G-4}), 142.98 (C_{C-1} or C_{C-4}), 148.97, 149.33 (C_{A-1} or C_{E-1}), 149.42, 149.56 (C_{E-3} or C_{I-1}), 155.87, 155.94 (C_{B-4} or C_{D-4}), 156.02, 156.35 (C_{F-4} or C_{H-4}); FAB HRMS (*m*-nitrobenzyl alcohol) m/z (relative intensity %) calcd for C₁₅₀H₁₂₆N₁₂O₁₂ [M]⁺ 2286.9618, found 2286.9661 (65.3).

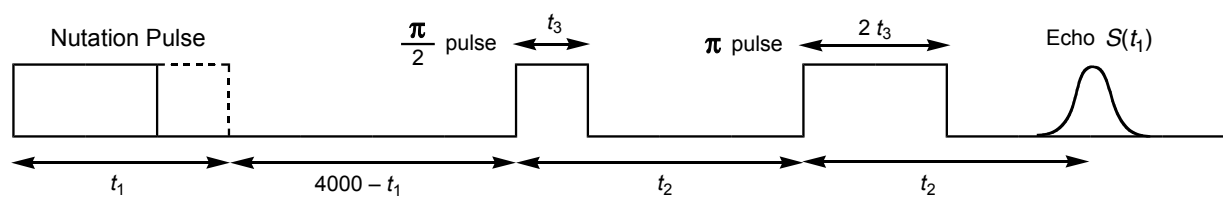
References

- [1](a) Q. Shelby, N. Kataoka, G. Mann and J. F. Hartwig, *J. Am. Chem. Soc.*, 2000, **122**, 10718; (b) N. Kataoka, Q. Shelby, J. P. Stambuli and J. F. Hartwig, *J. Org. Chem.*, 2002, **67**, 5553.
- [2] Ng. Ph. Buu-Hoï, *J. Chem. Soc.*, 1952, 4346.

[3] S. I. Hauck, K. V. Lakshmi and J. F. Hartwig, *Org. Lett.*, 2000, **1**, 2057.

Pulsed ESR Measurements: The magnetic moments with distinct spin quantum numbers (S) precess with their specific nutation frequency (ω_{nut}) in the presence of a microwave irradiation field and a static magnetic field. The nutation frequency for a transition from $|S, M_S\rangle$ to $|S, M_S+1\rangle$ can be expressed as $\omega_{nut} = [S(S+1) - M_S(M_S+1)]^{1/2}\omega_0$ under certain conditions. This indicates that ω_{nut} can be scaled with the total spin quantum number S and the spin magnetic quantum number M_S in the unit of ω_0 ($= \omega_{doublet}$). For determination of spin-multiplicity for high-spin molecules by using the pulsed ESR technique, see: (a) J. Isoya, H. Kanda, J. R. Norris, J. Tang and M. K. Brown, *Phys. Rev. B*, 1990, **41**, 3905; (b) A. V. Astashkin and A. Schweiger, *Chem. Phys. Lett.*, 1990, **174**, 595; (c) K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma, Y. Shirota, *J. Am. Chem. Soc.*, 1997, **119**, 6607. (d) H. Bock, K. Gharagozloo-Hubmann, M. Sievert, T. Prisner and Z. Havlas, *Nature*, 2000, **404**, 267. (e) A. Ito, H. Ino, K. Tanaka, K. Kanemoto and T. Kato, *J. Org. Chem.*, 2002, **67**, 491.

Pulsed ESR measurements were carried out on a Bruker ELEXSYS E580 X-band FT ESR spectrometer. The microwave pulse power of 10 mW provided by the microwave bridge was boosted to level of 1 kW using a traveling wave tube (TWT) amplifier. The ESTN measurements were performed by the three-pulse sequence shown below. The two-pulse ($\pi/2 - \pi$ pulses) electron spin-echo signal $S(t_1)$ was detected by increasing the width (t_1) of the nutation pulse. We employed appropriate phase cycles in order to suppress undesirable signals and artifacts which arise from an inaccurate pulse length [1,2]. The observed signal $S(t_1, B)$ as a function of external magnetic field B is converted into a nutation frequency $S(\omega_{nut}, B)$ spectrum. The parameters used for the measurements were $t_2 = 400$ ns, $t_3 = 8$ ns.



References

- [1] J.-M. Fauth, A. Schweiger, L. Braunschweiler, J. Forrer and R. R. Ernst, *J. Magn. Res.*, 1986, **66**, 74.
- [2] C. Gemperle, G. Aebli, A. Schweiger and R. R. Ernst, *J. Magn. Res.*, 1990, **88**, 241.

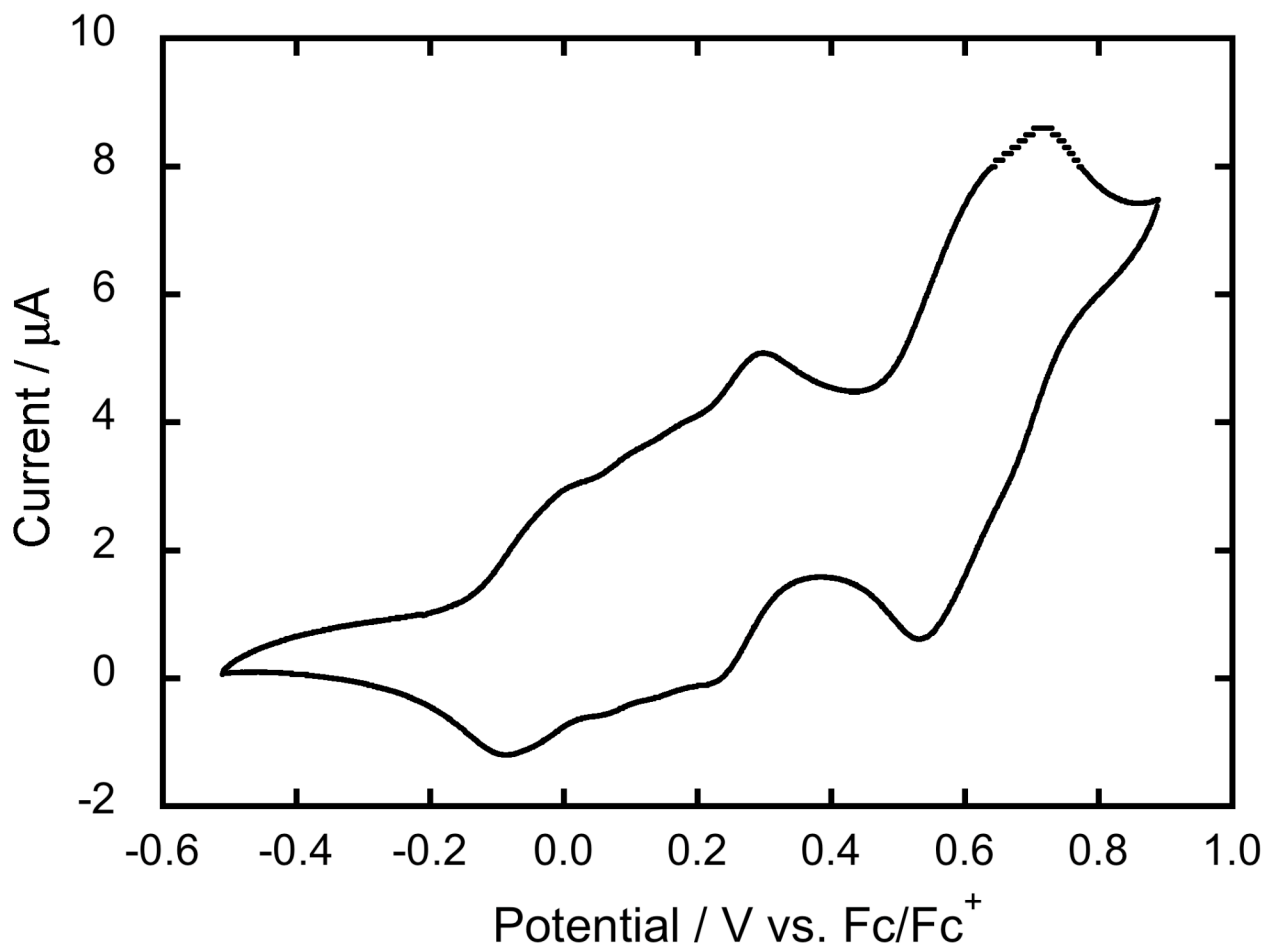


Fig. S1. Cyclic voltammogram of **1** measured in CH_2Cl_2 containing 0.1 M $n\text{-Bu}_4\text{NBF}_4$ at 298 K (scan rate 0.1 V s^{-1}).

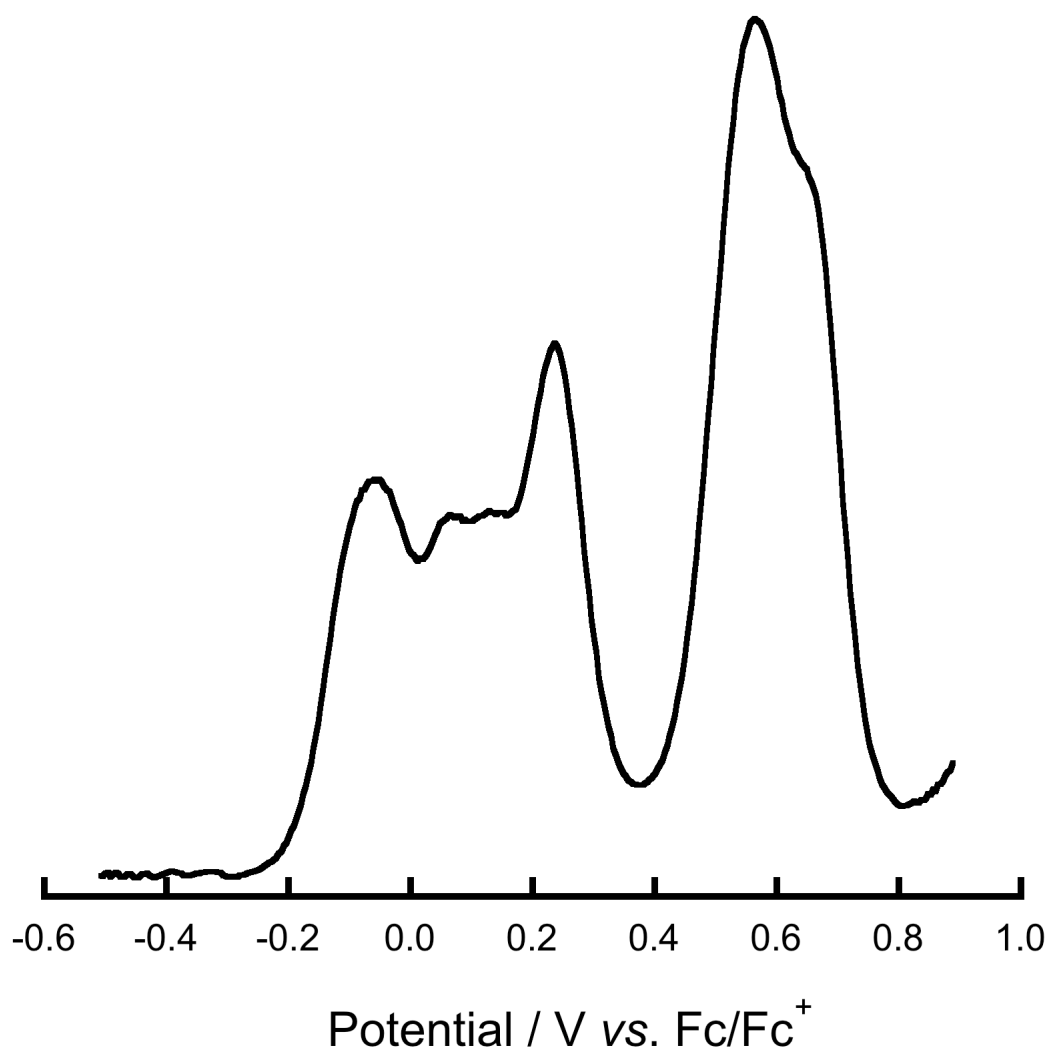


Fig. S2. Differential pulse voltammogram of **1** measured in CH₂Cl₂ containing 0.1 M *n*-Bu₄NBF₄ at 298 K (scan rate 0.1 V s⁻¹).

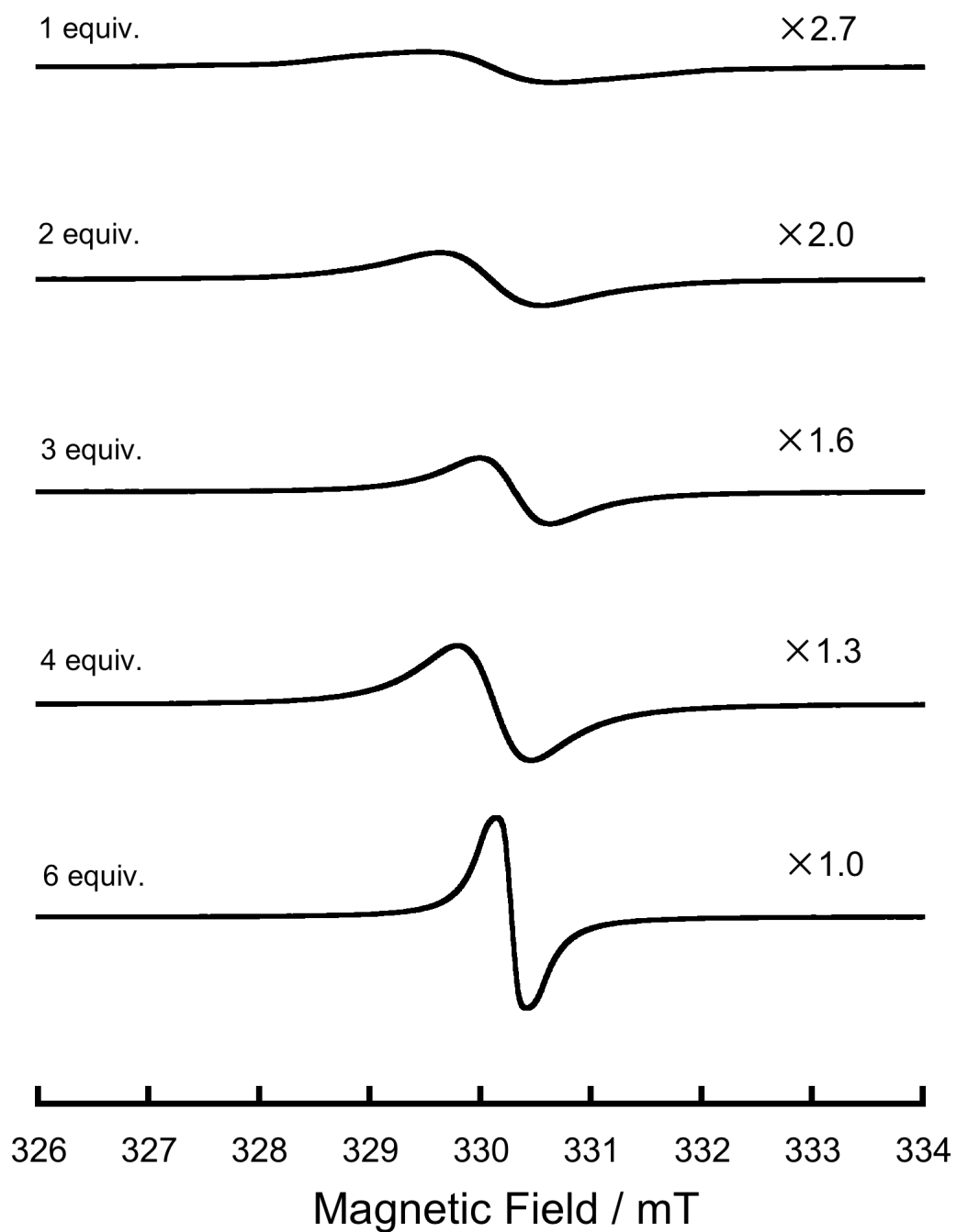


Fig. S3. CW-ESR spectra of **1** in CH_2Cl_2 at 123 K after addition of 1 equiv., 2 equiv., 3 equiv., 4 equiv. and 6 equiv. of oxidant.