

## Supplementary Information for:

### ***N*-substituted aza[1<sub>4</sub>]metacyclophane tetracation: a spin quintet tetraradical having four *para*-phenylenediamine-based semi-quinone moieties**

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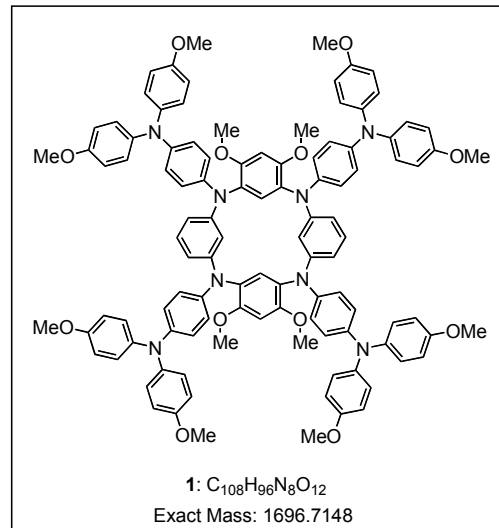
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#### Synthesis of 1.



Anhydrous toluene (5 ml) was added into a mixture of **2** (125 mg, 0.26 mmol), **3** (1.73 g, 4.50 mmol), Pd(dba)<sub>2</sub> (8.0 mg, 0.014 mmol), Ph<sub>5</sub>FcP(*t*-Bu)<sub>2</sub> [1] (19.1 mg, 0.027 mmol), and sodium *tert*-butoxide (122 mg, 1.27 mmol) in a flask under argon, and the solution was heated to reflux for 74 h. After evaporation of the solvent, the residue was chromatographed on a silica gel (toluene/ethyl

acetate = 9:1 as eluent), and recrystallization from acetonitrile/ethyl acetate afforded 1 (262 mg, 60%) as a yellow solid:  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  7.04 (d,  $J$  = 8.7 Hz, 8H), 6.97 (d,  $J$  = 9.2 Hz, 16H), 6.96 (s, 2H), 6.86 (t,  $J$  = 6.0 Hz, 2H), 6.84 (d,  $J$  = 9.2 Hz, 16H), 6.78 (s, 2H), 6.78 (d,  $J$  = 8.7 Hz, 8H), 6.36 (d,  $J$  = 6.0 Hz, 4H), 5.61 (s, 2H), 3.75 (s, 36H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  155.0, 154.4, 148.6, 143.0, 140.5, 139.6, 132.6, 127.8, 127.4, 124.6, 124.4, 121.4, 113.5, 107.3, 106.1, 98.6, 54.4, 53.6; FAB HRMS (*m*-nitrobenzyl alcohol)  $m/z$  (relative intensity %) calcd for  $\text{C}_{108}\text{H}_{96}\text{N}_8\text{O}_{12}$   $[\text{M}]^+$  1696.7148, found 1696.7166 (88.1). Anal. Calcd for  $\text{C}_{108}\text{H}_{96}\text{N}_8\text{O}_{12}$ : C, 76.39; H, 5.70; N, 6.60; O, 11.31. Found: C, 75.05; H, 5.63; N, 6.33; O, 10.74.

## Reference

- [1] (a) Q. Shelby, N. Kataoka, G. Mann and J. 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.

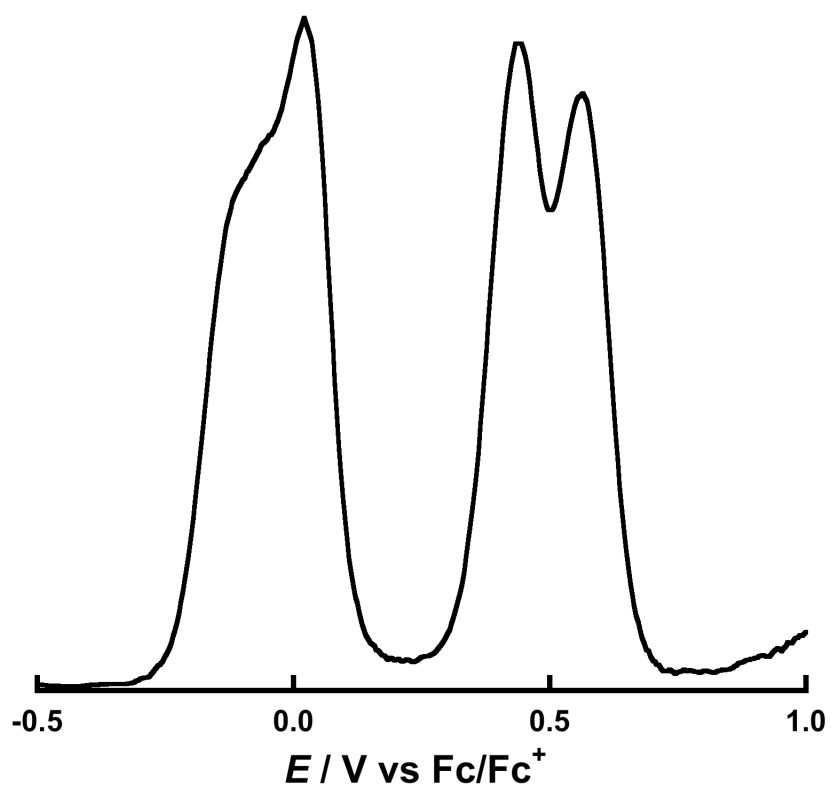


Fig. S1. Differential pulse voltammogram of **1** measured in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> at 298 K (scan rate 0.1 V s<sup>-1</sup>).

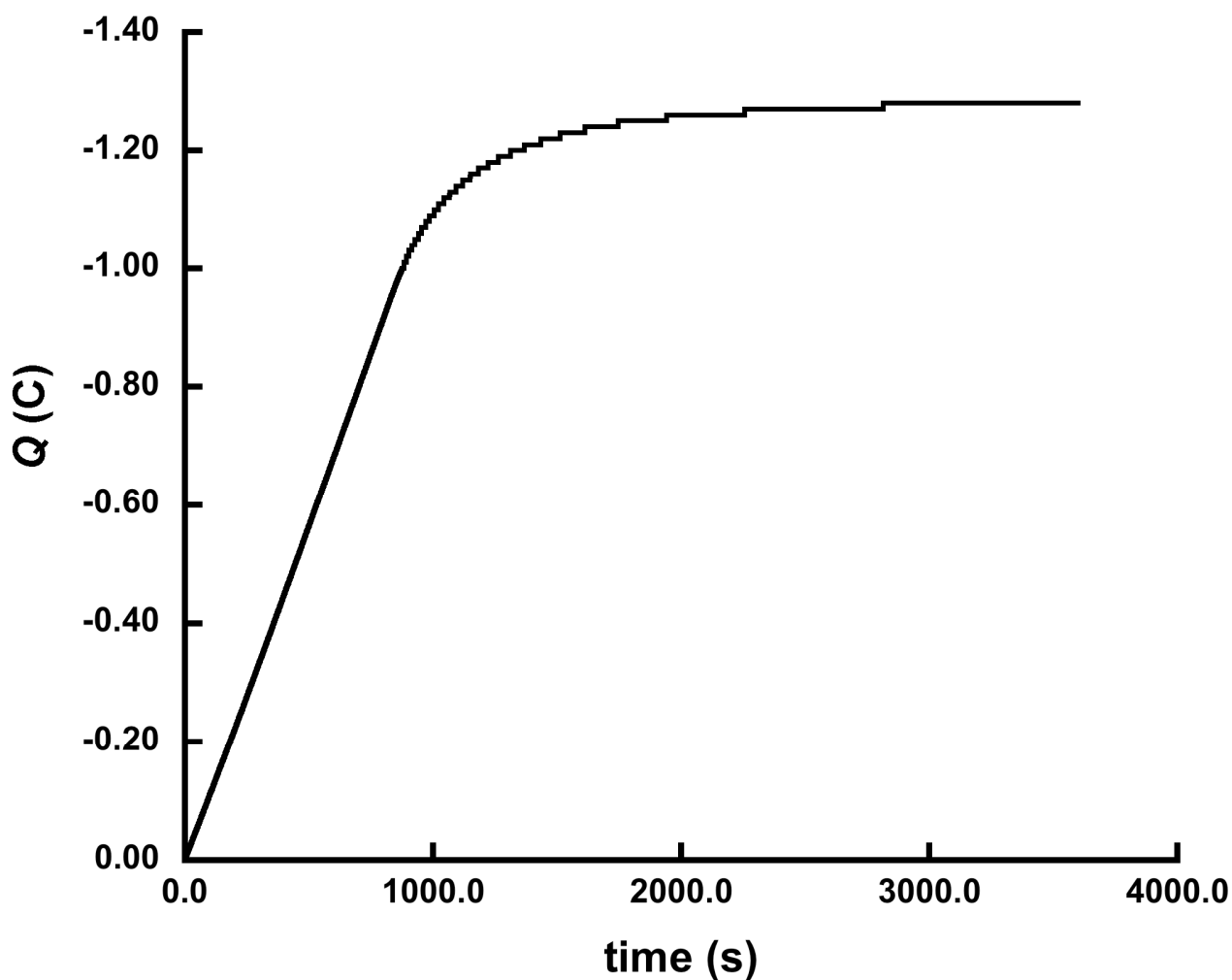


Fig. S2. Controlled potential coulometry at 0.2 V vs  $\text{Fc}/\text{Fc}^+$  for **1** ( $3.5 \mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $n\text{-Bu}_4\text{NBF}_4$  at 298 K. The net charge  $Q$  was determined to be 1.26 C. Hence, 3.73 electrons (vertically four electrons) per molecule were removed at this potential. The same result was obtained by using  $n$ -butyronitrile as solvent [4.18 electrons were removed at the potential corresponding to the second oxidation process].

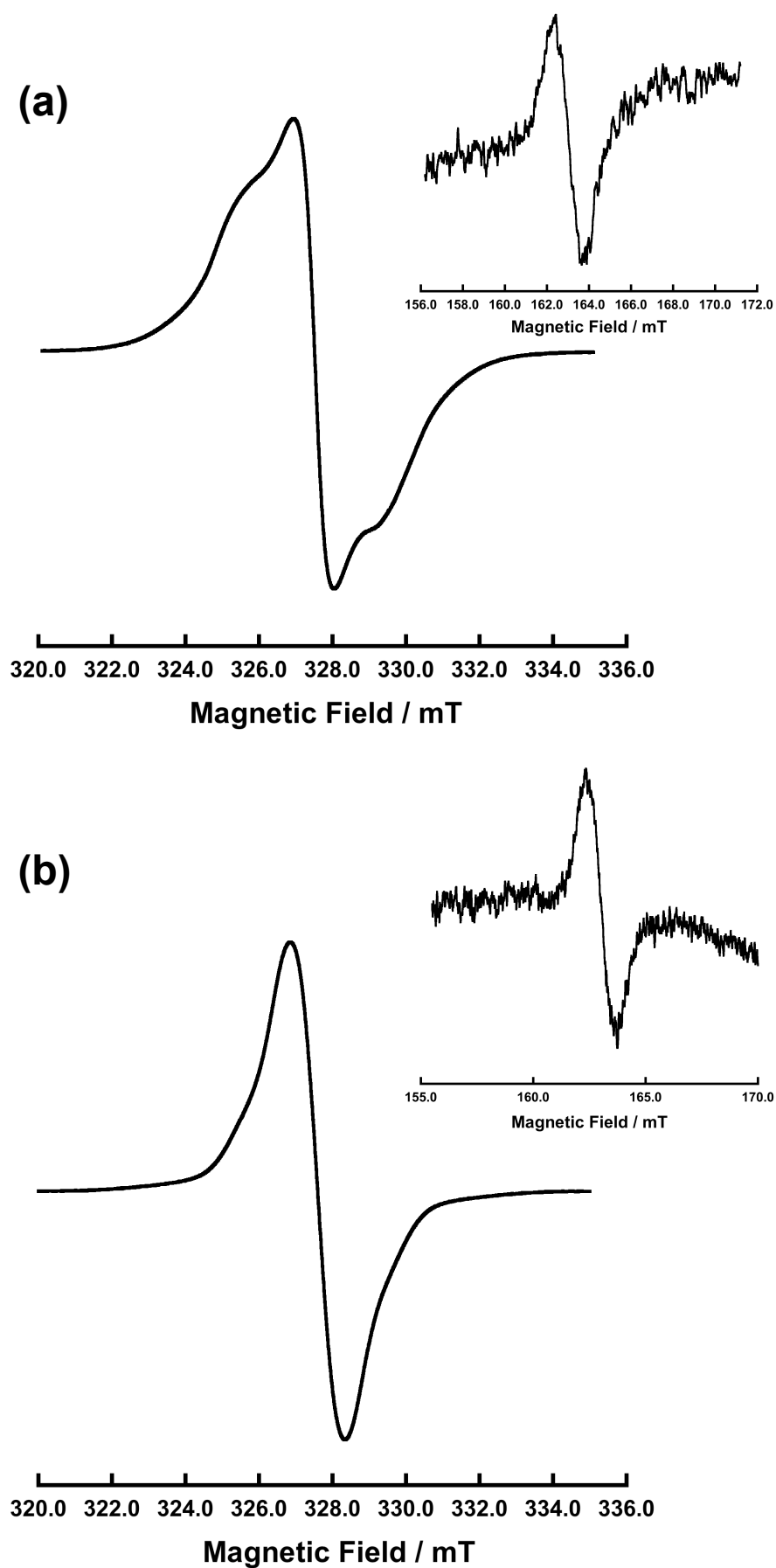


Fig. S3. CW-ESR spectra of **1** at 123 K after addition of (a) 2 equiv and (b) 4 equiv of oxidant.

**Pulsed ESR Measurements:** The magnetic moments with distinct spin quantum numbers ( $S$ ) precess with their specific nutation frequency ( $\omega_n$ ) 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  $\omega_n = [S(S+1) - M_S(M_S+1)]^{1/2} \omega_0$  under certain conditions. This indicates that  $\omega_n$  can be scaled with the total spin quantum number  $S$  and the spin magnetic quantum number  $M_S$  in the unit of  $\omega_n (= \omega_0)$  for the doublet species;  $\sqrt{2}$  for  $S=1, 2$  and  $\sqrt{6}$  for  $S=2$ . 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 ELEXES E580 X-band FT ESR spectrometer. 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. The observed signal  $S(t_1, B_0)$  as a function of external magnetic field  $B_0$  is converted into a nutation frequency  $S(\omega_n, B_0)$  spectrum. The parameters used for the measurements were  $t_2 = 400$  ns,  $t_3 = 8$  ns.

