Supplementary Information for:

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

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General: Commercial grade regents 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), Ph$_5$FcP(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 Na$_2$SO$_4$. 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; $^1$H NMR
(400 MHz, tetrahydrofuran-$d_6$) $\delta = 3.662$ (s, 12H, Ar$_F$–OCH$_3$ or Ar$_H$–OCH$_3$), 3.675 (s, 6H, Ar$_B$–OCH$_3$ or Ar$_D$–OCH$_3$), 3.704 (s, 6H, Ar$_B$–OCH$_3$ or Ar$_D$–OCH$_3$), 3.725 (s, 12H, Ar$_F$–OCH$_3$ or Ar$_H$–OCH$_3$), 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); $^{13}$C NMR (100 MHz, tetrahydrofuran-$d_6$) $\delta$ = 54.60 (Ar$_B$–OCH$_3$ or Ar$_D$–OCH$_3$), 54.65 (Ar$_F$–OCH$_3$ or Ar$_H$–OCH$_3$), 54.68 (Ar$_B$–OCH$_3$ or Ar$_D$–OCH$_3$, Ar$_F$–OCH$_3$ or Ar$_H$–OCH$_3$), 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 C$_{150}$H$_{120}$N$_{12}$O$_{12}$ [M]$^+$ 2286.9618, found 2286.9661 (65.3).

References


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 $S(\omega_{\text{nut}}, B)$ spectrum. The parameters used for the measurements were $t_2 = 400$ ns, $t_3 = 8$ ns.
References


Fig. S1. Cyclic voltammogram of 1 measured in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$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 CH₂Cl₂ at 123 K after addition of 1 equiv., 2 equiv., 3 equiv., 4 equiv. and 6 equiv. of oxidant.