Supplementary Information for:

Trimacrocyclic Arylamine and its Polycationic States

Akihiro Ito,*^a Yuko Yamagishi,^a Koji Fukui,^a Syuuzi Inoue,^a Yasukazu Hirao,^b Ko Furukawa,^c Tatsuhisa Kato^d and Kazuyoshi Tanaka^{a,b}

^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 CREST, Japan Science and Technology Agency (JST), Japan

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

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



N, *N*^{*}, *N*^{**}-tris(4-chlorophenyl)-1,3,5-benzenetriamine (3). To a mixture of phloroglucinol (1.26 g, 10.0 mmol), 4-chloroaniline (5.75 g, 45.1 mmol), and iodine (0.156 g, 0.6 mmol) was added toluene (5 ml) under argon atmosphere, and then the reaction mixture was refluxed with stirring for 29 h. After evaporation of the solvent, the residue was thoroughly washed with MeOH to afford **3** (3.87 g, 85%) as a purple solid: mp 232–234 °C; ¹H NMR (400 MHz, tetrahydrofuran- d_8) δ 7.29 (s, 3H), 7.14 (d, *J* = 8.8 Hz, 6H), 7.02 (d, *J* = 8.8 Hz, 6H), 6.32 (s, 3H); ¹³C NMR (100 MHz, tetrahydrofuran- d_8) δ 145.83, 143.60, 129.46, 124.76, 119.40, 100.05; EI HRMS (*m*-nitrobenzyl alcohol) *m/z* (relative intensity %) calcd for C₂₄H₁₈N₃O₃ [M]⁺ 453.0566, found 453.0569 (100).



N,*N*,*N*^{*},*N*^{*},*N*^{**}



Trimacrocyclic arylamine (1). Anhydrous toluene (8 ml) was added into a mixture of 4 (314 mg, 0.40 mmol), *N*,*N*²-bis(4-methoxyphenyl)-1,3-benzenediamine [1] (772 mg, 2.41 mmol), Pd(dba)₂ (13.7 mg, 0.024 mmol), Ph₃FcP(*t*-Bu)₂ [2] (29.4 mg, 0.041 mmol), and sodium *tert*-butoxide (1.07 g, 11.3 mmol) in a flask under argon, and the solution was heated to reflux for 16 h. After filtration through Celite, the filtrate was chromatographed on a silica gel (toluene/ethyl acetate = 2:1 as eluent), and recrystallization from toluene/*n*-hexane afforded 1 (58 mg, 9.5 %) as white powder: mp > 300 °C; ¹H NMR (400 MHz, tetrahydrofuran-*d*₈) *δ* 7.06 (d, *J* = 8.8 Hz, 12H), 7.03 (d, *J* = 8.8 Hz, 12H), 6.88 (m(=t+d), 3H+12H), 6.81 (d, *J* = 8.8 Hz, 12H), 6.38 (dd, *J* = 8.4, 2.0 Hz, 6H), 6.33 (d, *J* = 2.0 Hz, 3H), 5.62 (s, 3H), 3.73 (s, 18H); ¹³C NMR (100 MHz, tetrahydrofuran-*d*₈) *δ* 157.19, 150.46, 150.29, 144.74, 142.66, 140.83, 133.98, 129.76, 128.14, 127.64, 126.40, 115.24, 113.97, 102.14, 55.50; FAB HRMS (*m*-nitrobenzyl alcohol) *m/z* (relative intensity %) calcd for C₁₀₂H₈₁N₉O₆ [M]⁺ 1527.6310, found 1527.6316 (46.7).

[1] F. E. Goodson and J. F. Hartwig, Macromolecules, 1998, 31, 1700.

[2](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.

Pulsed ESR Measurements: The magnetic moments with distinct spin quantum numbers (*S*) precess with their specific nutation frequency (ω_n) in the presence of a microwave irradiation field and a static magnetic field. The nutation frequency for a transition from $|S, M_S > \text{to} | S, M_S + 1 > \text{can}$ be expressed as $\omega_n = [S(S+1) - M_S(M_S+1)]^{1/2}\omega_0$ under certain conditions. This indicates that ω_n can be scaled with the total spin quantum number *S* and the spin magnetic quantum number M_S in the unit of ω_n (= ω_0) for the doublet species; $\sqrt{2}$ for S = 1, $\sqrt{3}$ and 2 for S = 3/2. 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.



Fig. S1. Differential pulse voltammogram of 1 measured in CH_2Cl_2 containing 0.1 M *n*-Bu₄NBF₄ at 298 K (scan rate 0.1 V s⁻¹).



Fig. S2. Vis-NIR spectra during the stepwise electrochemical oxidation of **5** in CH₂Cl₂/0.1M n-Bu₄NBF₄ at room temperature: **5**⁺ (dotted line) and **5**²⁺ (solid line).

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2008



Fig. S3. CW-ESR spectra of **1** at 123 K after addition of (a) 1 equiv, (b) 2 equiv, and (c) 3 equiv of oxidant.



Fig. S4. 2D ESTN spectra of 1 in toluene/*n*-hexane (8:2 (v/v)) at 5 K after the addition of (a) 1 equiv and (b) 4 equiv of oxidant.