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 Tanakaa,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

3: \( \text{C}_{24}\text{H}_{18}\text{N}_3\text{Cl}_3 \)

\( \text{N, N',N''-tris(4-chlorophenyl)-1,3,5-benzenetriamine (3).} \) 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; \(^1\text{H NMR (400 MHz, tetrahydrofuran-d}_8\) \( \delta \) 7.29 (s, 3H), 7.14 (d, \( J = 8.8 \text{ Hz, 6H})\), 7.02 (d, \( J = 8.8 \text{ Hz, 6H})\), 6.32 (s, 3H); \(^{13}\text{C NMR (100 MHz, tetrahydrofuran-d}_8\) \( \delta \) 145.83, 143.60, 129.46, 124.76, 119.40, 100.05; EI HRMS (m-nitrobenzyl alcohol) \( m/z \) (relative intensity %) calcd for \( \text{C}_{24}\text{H}_{18}\text{N}_3\text{O}_3 \text{[M]}^+ \) 453.0566, found 453.0569 (100).
**N,N′,N″,N‴,N‴′-hexaxis(4-chlorophenyl)-1,3,5-benzenetriamine (4).**  
*p*-Bromochlorobenzene (8.63 g, 45.0 mmol), 3 (1.37 g, 3.00 mmol), NaOttBu (1.29 g, 13.5 mmol), Pd(OAc)$_2$ (34 mg, 0.15 mmol), and 1,1′-bis(diphenylphosphanyl)ferrocene (DPPF) (0.174 g, 0.30 mmol) were dissolved in toluene (30 ml) under argon atmosphere. The resulting solution was refluxed for 32 h with stirring. After evacuation of the solvent, CH$_2$Cl$_2$ and saturated aqueous solution of NaCl were added to the residue. The resulting organic layer was dried over MgSO$_4$, filtered, and concentrated. The residue was purified on column chromatography on silica gel using ethyl acetate / n-hexane (1:1 (v/v)), and was further recrystallized from ethyl acetate / n-hexane to yield 4 (1.89 g, 80%) as a white solid: mp 206–208 °C; $^1$H NMR (400 MHz, C$_6$D$_6$) δ 6.90 (d, $J = 8.8$ Hz, 12H), 6.65 (d, $J = 8.8$ Hz, 12H), 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), 6.43 (s, 3H); $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 149.3, 145.3, 130.0, 129.1, 125.6, 113.0; EI HRMS (m-nitrobenzyl alcohol) m/z (relative intensity %) calcd for C$_{42}$H$_{27}$N$_3$O$_6$ [M]$^+$ 783.0336, found 783.0336 (49.9).
Trimacrocyclic arylamine (1). Anhydrous toluene (8 ml) was added into a mixture of 4 (314 mg, 0.40 mmol), \( N,N'-\text{bis}(4\text{-methoxyphenyl})\)-1,3-benzenediamine [1] (772 mg, 2.41 mmol), Pd(dba)\(_2\) (13.7 mg, 0.024 mmol), Ph\(_3\)FcP(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; \(^1\)H NMR (400 MHz, tetrahydrofuran-\( d_8\)) \( \delta 7.06\) (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); \(^{13}\)C NMR (100 MHz, tetrahydrofuran-\( d_8\)) \( \delta 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 \text{C}_{102}\text{H}_{81}\text{N}_{9}\text{O}_6 [M]^+ 1527.6310, found 1527.6316 (46.7).


**Pulsed ESR Measurements:** The magnetic moments with distinct spin quantum numbers (S) precess with their specific nutation frequency (ωn) in the presence of a microwave irradiation field and a static magnetic field. The nutation frequency for a transition from |S, MS> to |S, MS +1> can be expressed as $\omega_n = [S(S+1) - MS(MS+1)]^{1/2} \omega_0$ under certain conditions. This indicates that ωn can be scaled with the total spin quantum number S and the spin magnetic quantum number MS in the unit of $\omega_0$ (= ω0) 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
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$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NBF$_4$ 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 5²⁺ (solid line).
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.