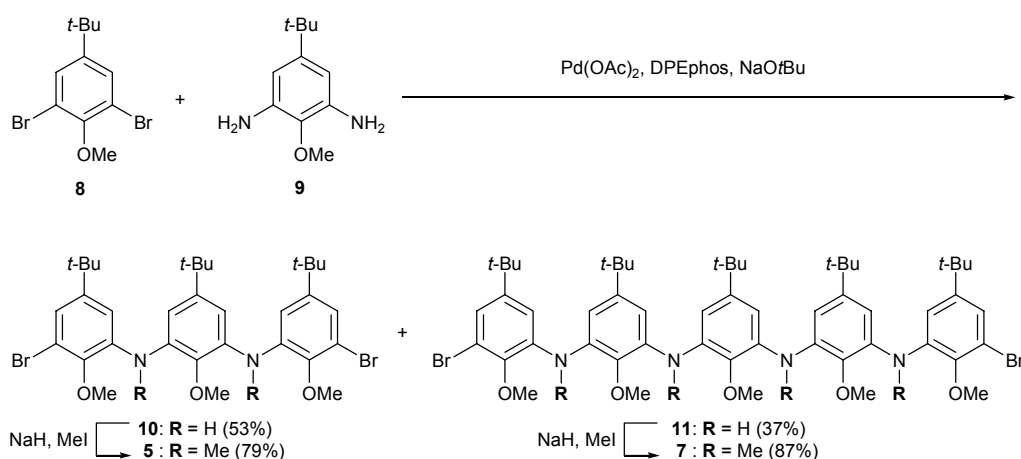


Supplementary Information

Title:	Azacalix[4]arene Cation Radicals: Spin-Delocalised Doublet and Triplet-Ground States Observed in the Macrocyclic <i>m</i> -Phenylene System Connected with Nitrogen Atoms
Authors:	Koichi Ishibashi, Hirohito Tsue,* Naoko Sakai, Satoshi Tokita, Kazuhiro Matsui, Jun Yamauchi and Rui Tamura
Contents:	1. ExperimentalPage S1 2. Molecular structure of azacalix[4]arene 2Page S4 3. DFT calculation.....Page S4 3. Electrochemical measurement.....Page S7 4. EPR measurementPage S8

1. Experimental

General. Melting points were determined on a Yanaco MP-J3 apparatus and are uncorrected. NMR spectra were recorded on a JEOL JNM-A500 instrument using tetramethylsilane (^1H NMR) and solvent resonance (^{13}C NMR) as internal standards. EPR spectra were recorded on a JEOL JES-RE3X spectrometer equipped with a Scientific Instruments 5500-5 variable-temperature unit. Electrochemical measurements were carried out on a BAS ALS600B using a platinum working electrode, a platinum counter electrode and a silver reference electrode, and the potentials were calibrated against Fc/Fc^+ . Infrared spectra were obtained on a Shimadzu IRPrestige-21 spectrometer. Elemental analyses were conducted at the Microanalytical Centre, Kyoto University, Japan. Flash column chromatography were performed with Merck Kiesegel 60 or Kanto Chemical Silica gel 60N. Toluene and DMF were refluxed over and then distilled from CaH_2 under Ar before use. Bis[2-(diphenylphosphino)phenyl] ether (DPEphos),¹ and compounds **5**² and **10**³ were prepared according to the described procedure. Other chemicals were purchased from commercial suppliers and used as received.

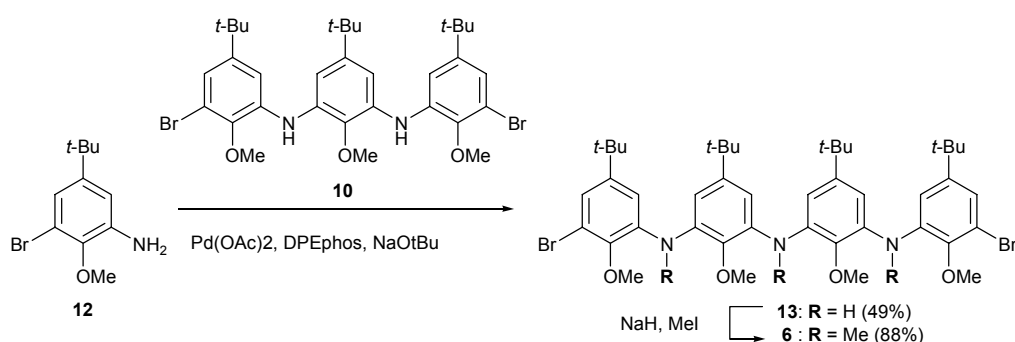


Scheme S1 Synthesis of compound **5** and **7**.

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- 1 M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics*, 1995, **14**, 3081.
 - 2 H. Tsue, K. Ishibashi, H. Takahashi, R. Tamura, *Org. Lett.*, 2005, **7**, 2165.
 - 3 K. Ishibashi, H. Tsue, S. Tokita, K. Matsui, H. Takahashi, R. Tamura, *Org. Lett.*, 2006, **8**, 5991.

***N,N'*-Bis[3-(3-bromo-5-*tert*-butyl-2-methoxyanilino)-5-*tert*-butyl-2-methoxyphenyl]-5-*tert*-butyl-2-methoxy-1,3-phenylenediamine (11).** Compound **11** was obtained as a by-product when compound **10** was prepared by our described procedure.² A solution of **8** (6.57 g, 20.4 mmol), **9** (1.94 g, 9.97 mmol), Pd(OAc)₂ (119 mg, 0.53 mmol), DPEphos (403 mg, 0.748 mmol), and NaOtBu (2.15 g, 22.3 mmol) in anhydrous toluene (60 ml) was stirred at 80 °C for 17 h under Ar. After cooling to r.t., the reaction mixture was extracted with toluene and washed with saturated NaHCO₃. The organic layer was dried over anhydrous K₂CO₃, filtered, and evaporated. Flash column chromatography on silica gel (hexane/CH₂Cl₂ = 2:1 then 1:2, v/v) gave **10**² (3.58 g, 53%) and **11** (1.92 g, 37%). **11**: mp 234–235 °C; ¹H NMR (CDCl₃, 500 MHz): δ 7.48 (d, *J*=2.2 Hz, 2H, Ar-H), 7.19 (d, *J*=2.2 Hz, 2H, Ar-H), 7.15 (s, 2H, Ar-H), 7.07 (d, *J*=2.2 Hz, 2H, Ar-H), 7.04 (d, *J*=2.2 Hz, 2H, Ar-H), 6.56 (s, 2H, NH), 6.51 (s, 2H, NH), 3.87 (s, 6H, OMe), 3.82 (s, 3H, OMe), 3.80 (s, 6H, OMe), 1.34 (s, 9H, *tert*-Bu), 1.32 (s, 18H, *tert*-Bu), 1.31 (s, 18H, *tert*-Bu); ¹³C NMR (CDCl₃, 125 MHz): δ 148.8, 147.43, 147.36, 143.8, 137.0, 136.4, 136.2, 135.9, 135.6, 135.1, 120.8, 116.6, 112.6, 106.4, 106.0, 105.9, 60.2, 59.9, 59.8, 34.9, 34.8, 31.53, 31.51, 31.3; IR (KBr): 3405 (ν_{N-H}) cm⁻¹; Anal. Calcd for C₅₅H₇₄Br₂N₄O₅: C, 64.07; H, 7.23; N, 5.43. Found: C, 64.29; H, 7.15; N, 5.39.

***N,N'*-Bis[3-(3-bromo-5-*tert*-butyl-2-methoxy-*N,N'*-methylanilino)-5-*tert*-butyl-2-methoxyphenyl]-5-*tert*-butyl-2-methoxy-*N,N'*-dimethyl-1,3-phenylenediamine (7).** To a solution of **11** (516 mg, 0.500 mmol) in anhydrous DMF (5 ml) was added 60% NaH (206 mg, 5.15 mmol) at 0 °C under Ar. After stirring for 10 min, MeI (140 μl, 2.25 mmol) was added. Stirring was continued at r.t. overnight, and then Et₂O was added to the reaction mixture. The organic layer was washed with brine, dried over Na₂SO₄, filtered, and evaporated. Flash column chromatography on silica gel (hexane/EtOAc = 19:1, v/v) gave **7** (472 mg, 87%) as colourless solid, mp 94–96 °C; ¹H NMR (CDCl₃, 500 MHz): δ 7.13 (d, *J*=2.3 Hz, 2H, Ar-H), 6.85 (d, *J*=2.3 Hz, 2H, Ar-H), 6.70 (d, *J*=2.4 Hz, 2H, Ar-H), 6.67 (s, 2H, Ar-H), 6.65 (d, *J*=2.4 Hz, 2H, Ar-H), 3.67 (s, 6H, OMe), 3.52 (s, 3H, OMe), 3.49 (s, 6H, OMe), 1.22 (s, 18H, *tert*-Bu), 1.20 (s, 9H, *tert*-Bu), 1.19 (s, 18H, *tert*-Bu); ¹³C NMR: δ 147.8, 147.4, 145.9, 145.7, 144.8, 144.7, 144.4, 144.0, 143.7, 143.0, 122.9, 118.8, 117.8, 115.3, 115.1, 114.6, 59.8, 58.7, 58.6, 40.0, 39.6, 34.5, 31.4, 31.3, 31.2; Anal. Calcd for C₅₉H₈₂Br₂N₄O₅: C, 65.18; H, 7.60; N, 5.15. Found: C, 65.15; H, 7.70; N, 5.03.



Scheme S2 Synthesis of compound **4**.

3-Bromo-5-*tert*-butyl-2-anisidine (12). A mixture of 2-bromo-4-*tert*-butyl-6-nitroanisole⁴ (5.79 g, 20.1 mmol), FeCl₃·6H₂O (286 mg, 1.06 mmol), and activated carbon (500 mg) in MeOH (50 ml) was refluxed for 30 min. To the mixture was added H₂NNH₂·H₂O (5.0 ml, 103 mmol) over 15 min, and then refluxing was continued

4 M.-H. Hao, Z. Xiong, R. A. Aungst, A. L. Davis, D. Cogan, D. R. Goldberg, *US Pat.*, 245 536, 2005.

for further 40 min. After cooling to r.t., the reaction mixture was filtered through Celite and concentrated. The residue was dissolved in CH₂Cl₂. The organic layer was washed with saturated NaHCO₃, dried over anhydrous K₂CO₃, filtered, and evaporated. Flash column chromatography on silica gel (hexane/CH₂Cl₂ = 4:5, v/v) gave **12** (4.57 g, 88%), mp 48–49 °C; ¹H NMR (CDCl₃, 500 MHz): δ 6.91 (d, *J*=2.3 Hz, 1H, Ar-H), 6.69 (d, *J*=2.3 Hz, 1H, Ar-H), 3.86 (bs, 2H, NH₂), 3.81 (s, 3H, OMe), 1.25 (s, 9H, *tert*-Bu); ¹³C NMR (CDCl₃, 125 MHz): δ 149.1, 141.9, 140.5, 119.6, 116.5, 112.5, 59.5, 34.4, 31.2; IR (KBr): 3480 (ν_{N-H}), 3368 (ν_{N-H}) cm⁻¹; Anal. Calcd for C₁₁H₁₆BrNO: C, 51.18; H, 6.25; N, 5.43. Found: C, 51.14; H, 6.05; N, 5.47.

***N*-[3-(3-Bromo-5-*tert*-butyl-2-methoxyanilino)-5-*tert*-butyl-2-methoxyphenyl]-*N'*-(3-bromo-5-*tert*-butyl-2-methoxyphenyl)-5-*tert*-butyl-2-methoxy-1,3-phenylenediamine (**13**)**. A solution of **10** (4.05 g, 5.99 mmol), **12** (774 mg, 3.01 mmol), Pd(OAc)₂ (34 mg, 0.15 mmol), DPEphos (123 mg, 0.228 mmol), and NaOtBu (358 mg, 3.73 mmol) in anhydrous toluene (30 ml) was stirred at 80 °C for 15 h under Ar. After cooling to r.t., the reaction mixture was filtered through Celite and evaporated. After flash column chromatography on silica gel (hexane/CH₂Cl₂ = 1:2, v/v), precipitation from CH₂Cl₂/MeOH gave **13** (1.25 g, 49%) as colourless solid, mp 222–224 °C; ¹H NMR (CDCl₃, 500 MHz): δ 7.47 (d, *J*=2.1 Hz, 2H, Ar-H), 7.17 (d, *J*=2.1 Hz, 2H, Ar-H), 7.07 (d, *J*=2.1 Hz, 2H, Ar-H), 7.04 (d, *J*=2.1 Hz, 2H, Ar-H), 6.56 (s, 2H, NH), 6.51 (s, 1H, NH), 3.87 (s, 6H, OMe), 3.79 (s, 6H, OMe), 1.32 (s, 18H, *tert*-Bu), 1.31 (s, 18H, *tert*-Bu); ¹³C NMR (CDCl₃, 125 MHz): δ 148.8, 147.4, 143.8, 137.0, 136.6, 135.8, 135.1, 120.9, 116.6, 112.7, 106.5, 106.1, 60.3, 59.9, 34.9, 34.8, 31.5, 31.3; IR (KBr): 3421 (ν_{N-H}) cm⁻¹; Anal. Calcd for C₄₄H₅₀Br₂N₃O₄: C, 61.90; H, 6.97; N, 4.92. Found: C, 61.95; H, 6.94; N, 4.98.

***N*-[3-(3-bromo-5-*tert*-butyl-2-methoxy-*N'*-methylanilino)-5-*tert*-butyl-2-methoxyphenyl]-*N'*-(3-bromo-5-*tert*-butyl-2-methoxyphenyl)-5-*tert*-butyl-2-methoxy-*N,N'*-dimethyl-1,3-phenylenediamine (**6**)**. To a solution of **13** (874 mg, 1.02 mmol) in anhydrous DMF (10 ml) was added 60% NaH (437 mg, 10.9 mmol) at 0 °C under Ar. After stirring for 10 min, MeI (320 μl, 5.05 mmol) was added. Stirring was continued at r.t. overnight, and then Et₂O was added to the reaction mixture. The organic layer was washed with brine three times, dried over Na₂SO₄, filtered, and evaporated. After purification by flash column chromatography on silica gel (hexane/EtOAc = 19:1, v/v), precipitation from CH₂Cl₂/MeOH gave **6** (807 mg, 88%) as colourless solid, mp 154–156 °C; ¹H NMR (CDCl₃, 500 MHz): δ 7.13 (d, *J*=2.3 Hz, 2H, Ar-H), 6.85 (d, *J*=2.3 Hz, 2H, Ar-H), 6.70 (d, *J*=2.3 Hz, 2H, Ar-H), 6.66 (d, *J*=2.3 Hz, 2H, Ar-H), 3.66 (s, 6H, OMe), 3.48 (s, 6H, OMe), 3.26 (s, 6H, NMe), 3.20 (s, 3H, NMe), 1.22 (s, 18H, *tert*-Bu), 1.20 (s, 18H, *tert*-Bu); ¹³C NMR (CDCl₃, 125 MHz): δ 147.8, 147.4, 146.0, 144.9, 144.7, 143.8, 143.1, 123.0, 118.8, 117.8, 115.4, 115.3, 59.8, 58.8, 40.1, 39.7, 34.49, 34.47, 31.4, 31.2; Anal. Calcd for C₄₇H₆₅Br₂N₃O₄: C, 63.01; H, 7.31; N, 4.69. Found: C, 63.29; H, 7.27; N, 4.69.

2. Molecular Structure of azacalix[4]arene **2**

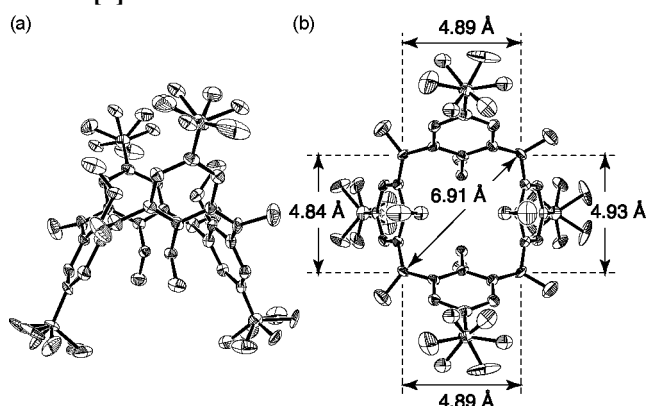


Fig. S1 ORTEP drawings of azacalix[4]arene **2**²: (a) side and (b) top views. All the *tert*-butyl groups are disordered over two positions. The displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Inclination of the phenyl rings are in the range of 56–64° with respect to the best plane defined by four bridging nitrogen atoms.

3. DFT calculation

All the calculations were performed with the Gaussian 03W program package.⁵ For the calculations, model compound **3** was used in which *tert*-butyl groups of **2** were replaced by methyl groups. The geometries of **3**, monocation radical **3**⁺ and dication radical **3**²⁽⁺⁺⁾ in singlet and triplet states were optimised at a B3LYP/6-31G** level.

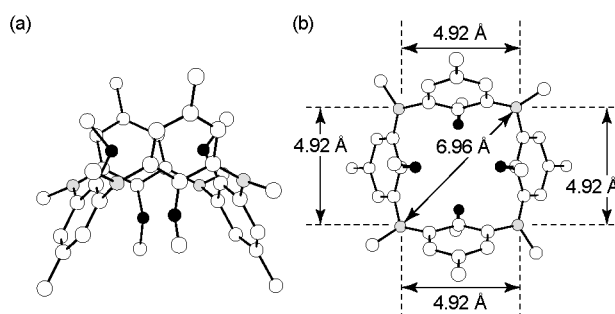


Fig. S2 The optimised structure of model compound **3** calculated at a B3LYP/6-31G** level: (a) side and (b) top views. Hydrogen atoms are omitted for clarity. Inclination angles of the phenyl rings are 61.5° with respect to the plane defined by four nitrogen atoms.

5 Gaussian 03W, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

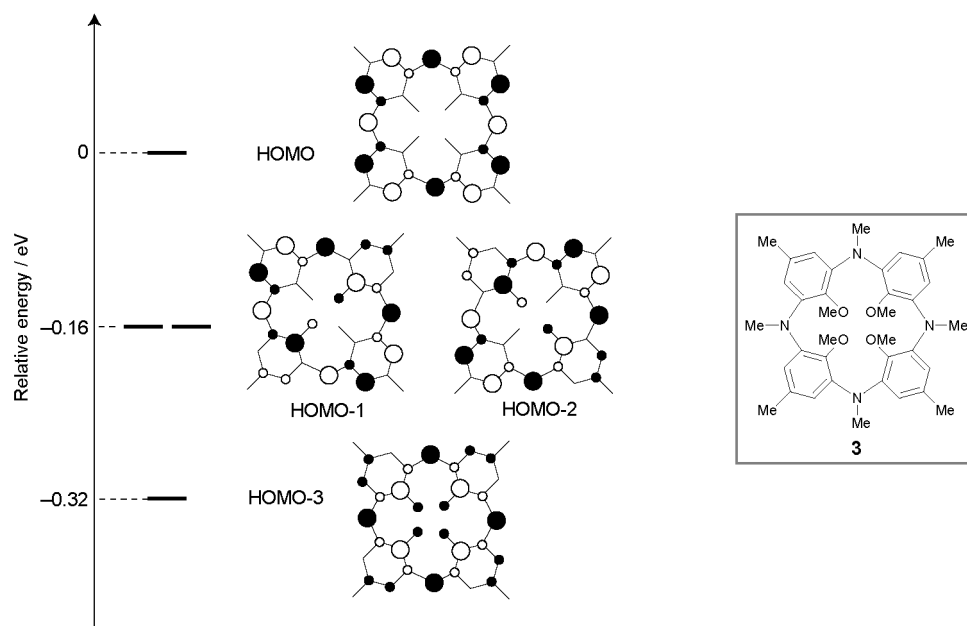


Fig. S3 Schematic representation of NBMO shapes and energy diagram in the model compound **3** calculated at a B3LYP/6-31G**//B3LYP/6-31G** level.

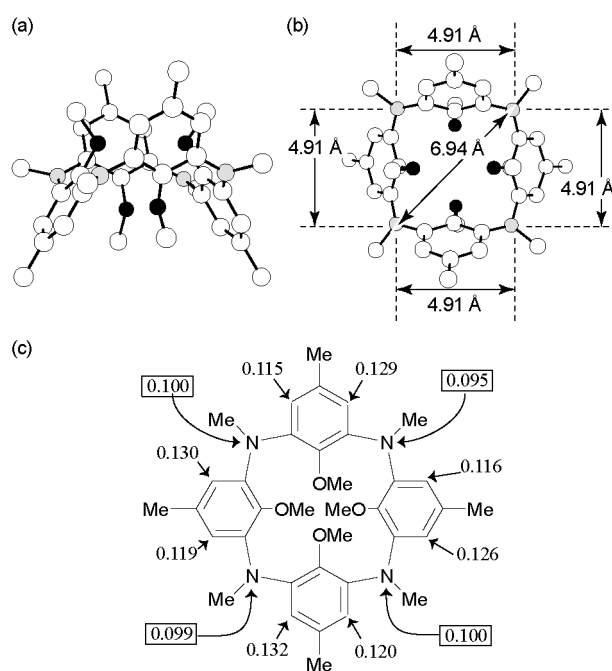


Fig. S4 The optimized structure of monocation radical **3⁺** calculated at a B3LYP/6-31G** level: (a) side and (b) top views. Hydrogen atoms are omitted for clarity. Inclination angles of the phenyl rings are around 60° with respect to the plane defined by four nitrogen atoms. (c) The selected spin densities of monocation radical **3⁺** calculated at a B3LYP/6-31G** level.

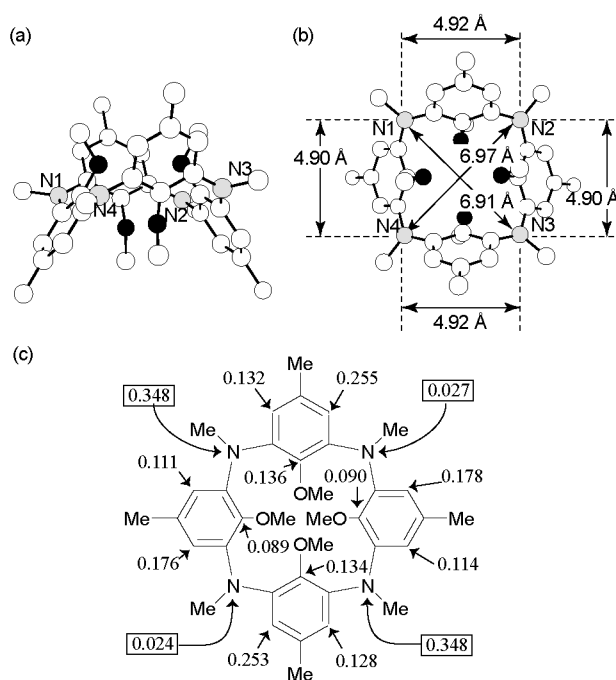


Fig. S5 The optimised structure of dication radical $3^{2(+)}$ in a triplet state calculated at a B3LYP/6-31G** level: (a) side and (b) top views. Hydrogen atoms are omitted for clarity. Inclination angles of the phenyl rings are in the range of 56-57° with respect to the plane defined by four nitrogen atoms. (c) The selected spin densities of dication radical $3^{2(+)}$ in triplet state calculated at a B3LYP/6-31G** level.

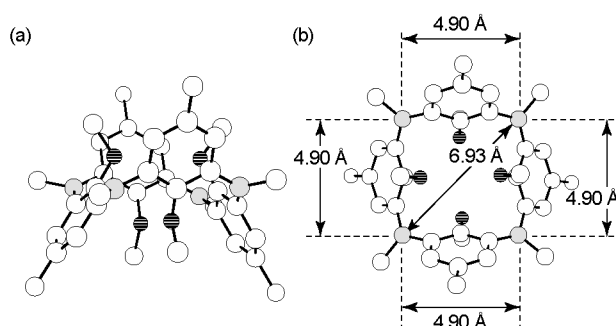


Fig. S6 The optimised structure of dication radical $3^{2(+)}$ in a singlet state calculated at a B3LYP/6-31G** level: (a) side and (b) top views. Hydrogen atoms are omitted for clarity. Inclination angles of the phenyl rings are in the range of 59° with respect to the plane defined by four nitrogen atoms.

4. Electrochemical measurement

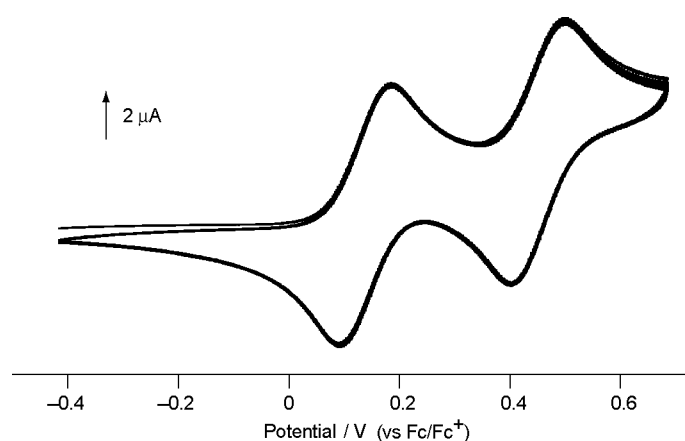


Fig. S7 Cyclic voltammogram of azacalix[4]arene **2** (1 mM) in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NClO}_4$ (0.1 M) at 298 K, scan rate 100 mV sec^{-1} , scans were repeated 10 times and potential calibrated against Fc/Fc^+ .

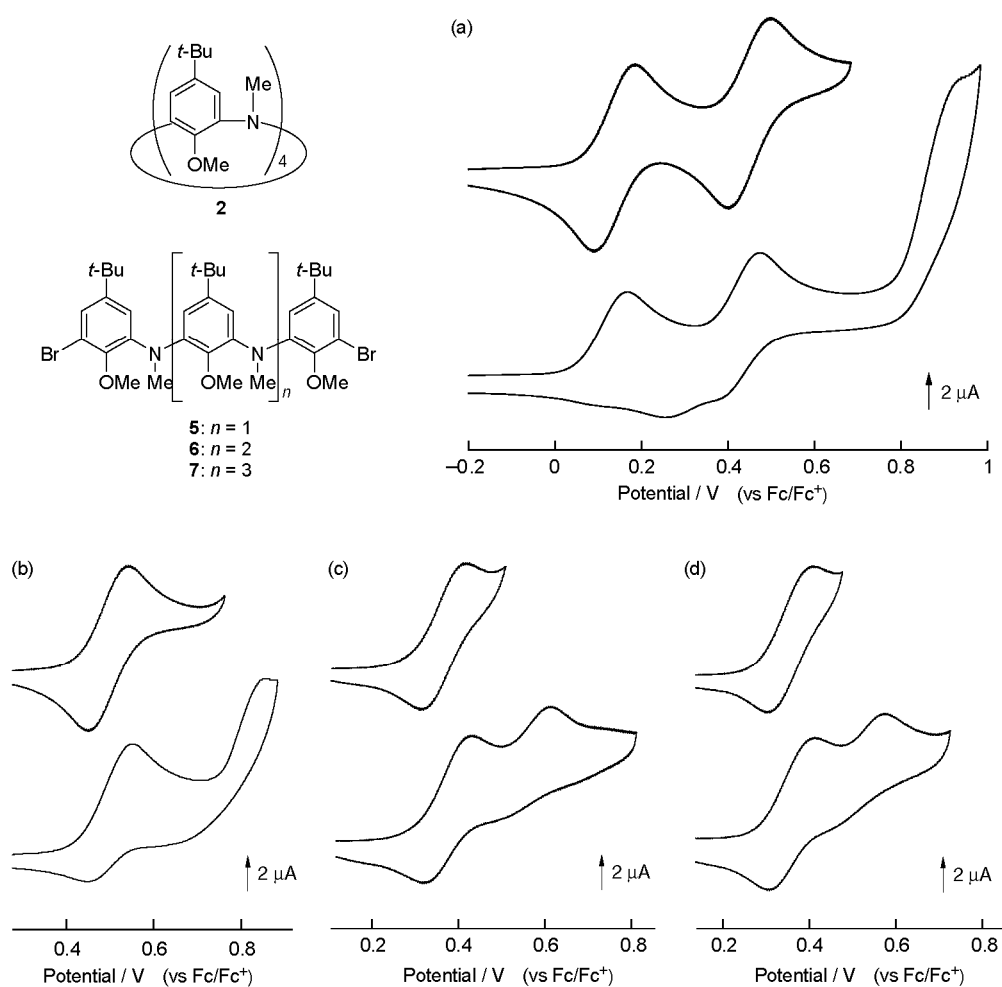


Fig. S8 Cyclic voltammograms of (a) azacalix[4]arene **2** (1 mM), (b) **5** (1 mM), (c) **6** (1 mM) and (d) **7** (1 mM) in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NClO}_4$ (0.1 M) at 298 K, scan rate 100 mV sec^{-1} and potential calibrated against Fc/Fc^+ .

5. EPR measurement

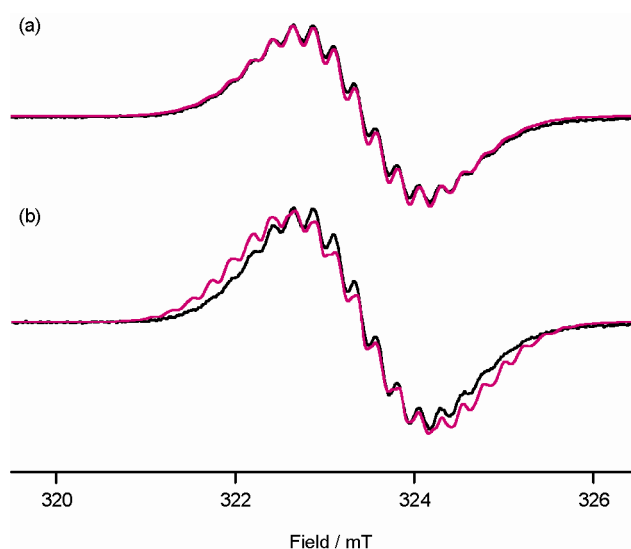


Fig. S9 Observed and simulated EPR spectra of monocation radical 2^{+} ; black line: observed EPR spectrum at 223 K in CH_2Cl_2 containing 0.1 M Bu_4NClO_4 ; red line: simulated EPR spectra. In panel (a), EPR simulation was performed with the following parameters where spin-delocalisation to four nitrogen atoms was assumed: $A_{\text{N}} = 0.200$ mT (for the four equivalent nitrogen atoms), $A_{\text{NCH}_3} = 0.255$ mT (for the twelve equivalent *N*-methyl hydrogen atoms), $A_{\text{ArH}} = 0.247$ mT (for the eight equivalent aromatic hydrogen atoms), and line width = 0.18 mT. In panel (b), EPR simulation was performed with the following parameters where spin-delocalisation to two nitrogen atoms was assumed: $A_{\text{N}} = 0.358$ mT (for the two equivalent nitrogen atoms), $A_{\text{NCH}_3} = 0.456$ mT (for the six equivalent *N*-methyl hydrogen atoms), $A_{\text{ArH}} = 0.200$ mT (for the four equivalent aromatic hydrogen atoms), and line width = 0.15 mT.

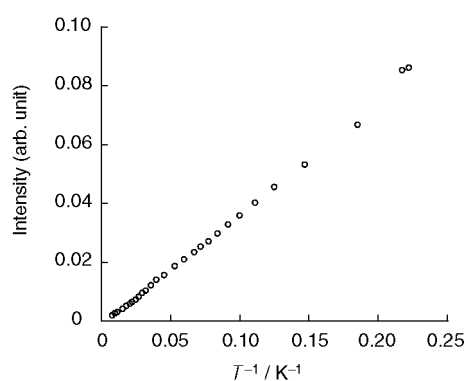


Fig. S10 Temperature dependence of the signal intensities for the forbidden transition ($\Delta M_s = \pm 2$) of dication radical $2^{2(+)}$.