# **Supporting Information for**

# Electronic structure of tetraaza[1.1.1.1]*o,p,o,p*-cyclophane and its oxidized states

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### **General Information**

All the purchased reagents were of standard quality, and used without further purification. All the purchased solvents were purified, dried, and degassed by standard procedures. Column chromatography was performed with silica gel (Kanto Chemical Co., Inc., silica gel 60N, spherical neutral). Preparative recycling gel permeation chromatography (GPC) was performed with a Model LC-9201 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL-1H/JAIGEL-2H columns using toluene as an eluent. Elemental analyses were performed by Center for Organic Elemental Microanalysis, Kyoto University. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured by a JEOL JNM-AL400 FT-NMR spectrometer. Variable-temperature <sup>1</sup>H NMR spectra were recorded by a JEOL JNM-AL300 FT-NMR spectrometer. Chemical shifts of NMR spectra are determined relative to internal tetramethylsilane (TMS) standard ( $\delta$ ), and are given in parts per million (ppm). Low resolution (LR) fast-atom-bombardment (FAB) mass spectra (MS) were recorded on a JEOL JMS-HX110A mass spectrometer with 1,8-dihydroxy-9,10-dihydroanthracen- 9-one (dithranol) as a matrix. High resolution electrospray ionization (ESI) mass spectrum was acquired using a mass spectrometer (Thermo Fischer EXACTIVE). UV-Vis-NIR absorption spectra were obtained with a Perkin-Elmer Lambda 950 spectrometer. Fluorescence spectra were recorded on an absolute PL quantum yield measurement system (HAMAMATSU Quantaurus-QY).

#### Synthetic Details

The cyclophane **5** was prepared from N, N, N', N'-tetraanisyl-*ortho*-phenylenediamine **8**<sup>[S1]</sup> and *p*-dibromobenzene by using the Buchwald-Hartwig cross-coupling amination reaction<sup>[S2]</sup> (Scheme S1).



Scheme S1. Synthetic route for 5.

8: A mixture of 1,2-dibromobenzene (2.36 g, 10.0 mmol), 4-anisidine (3.64 g, 29.6 mmol), Pd(OAc)<sub>2</sub> (0.11 g, 0.5 mmol), P(*t*-Bu)<sub>3</sub> (1.0 mmol), and NaO*t*-Bu (2.89 g, 30.0 mmol) in toluene (35 ml) was refluxed under an argon atmosphere for 17 h. The reaction mixture was cooled down to room temperature, and quickly quenched with an aqueous NH<sub>4</sub>Cl. The organic layer was extracted with ethyl acetate, and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the crude product was chromatographed on silica gel (*n*-hexane/ethyl acetate = 4/1 as eluent) to afford **8** (2.60 g, 81.2%) as a brown solid: <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>);  $\delta$  = 3.737 (s, 6H), 6.356 (s, 2H), 6.811-6.841 (m, 6H), 6.950 (d, *J* = 9.03 Hz, 4H), 7.080-7.104 (m, 4H); <sup>13</sup>C NMR (100 MHz, tetrahydrofuran-*d*<sub>8</sub>);  $\delta$  = 55.80, 115.40, 119.19, 120.54, 122.33, 136.82, 138.75, 155.21; FAB LRMS (dithranol): *m/z* calcd for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: 320.39 [M]<sup>+</sup>; found 320.

**5**: A mixture of **8** (0.325 g, 1.02 mmol), 1,4-dibromobenzene (0.249 g, 1.06 mmol),  $Pd(dba)_2$  (0.058 g, 0.10 mmol),  $P(t-Bu)_3$  (0.20 mmol) and NaOt-Bu (0.290 g, 3.02 mmol) in toluene (200 ml) was stirred under an argon atmosphere at room temperature for 21 h and then the reaction mixture was heated to 110 °C, and stirred for 12 h. The reaction solution was cooled down to room temperature, and filtered through Celite. The reaction mixture was washed with brine and the organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the crude product was roughly

purified by chromatography on silica gel (toluene/ethyl acetate = 19/1 as eluent), and further purified by preparative recycling HPLC to afford **5** (0.018 g, 4.5%) as a white solid: <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>);  $\delta$  = 3.746 (s, 12H), 5.972-6.021 (m, 4H), 6.512-6.605 (m, 4H), 6.811-6.840 (m, 8H), 7.024-7.114 (m, 8H), 7.213-7.429 (m, 8H), 6.817 (s, 8H); <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>);  $\delta$  = 55.81, 115.44, 123.52, 123.84, 123.89, 124.21, 125.24, 125.82, 127.83, 128.43, 128.45, 129.84, 133.23, 133.67, 133.69, 141.09, 141.55, 143.62, 143.68, 145.86, 156.08; ESI HRMS: *m/z* calcd for C<sub>52</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>: 788.3357 [M]<sup>+</sup>; found 788.3347.

<sup>[</sup>S1] T. Wenderski, K. M. Light, D. Ogrin, S. Bott, C. J. Harlan, *Tetrahedron Lett.* 2004, 45, 6851.

<sup>[</sup>S2] a) J. P. Wolfe, S. Wagaw, J. F. Marcoux, S. L. Buchwald, Acc. Chem. Res. 1998, 31, 805;
b) J. F. Hartwig, Acc. Chem. Res. 1998, 31, 852; c) J. F. Hartwig, Angew. Chem. Int. Ed. 1998, 37, 2046; d) A. R. Muci, S. L. Buchwald, Top. Curr. Chem. 2002, 219, 133.



Fig. S1. Temperature dependent <sup>1</sup>H NMR spectra (300 MHz,  $[D_6]DMSO$ ) of **5**.

## X-ray Crystallography for 5

Data collections were carried out on a Rigaku Mercury CCD (XtaLAB mini) diffractometer using graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at  $-180\pm1^{\circ}$ C. The data were corrected for Lorentz and polarization effects. The structure was solved by using direct methods (SIR92<sup>[S3]</sup>), and expanded by using Fourier techniques, and refined by full-matrix least-squares of  $F^2$  on the basis of 10928 observed reflections and 642 variable parameters (SHELXL-97<sup>[S4]</sup>). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The crystal contains acetone molecules, which were used as one of the mixed solvents. Two acetone molecules per one macrocycle **5** were contained in the crystal, and they were partly disordered and treated properly. All the calculations were performed by using CrystalStructure crystallographic software package,<sup>[S5]</sup> except for refinement, which was performed by using SHELXL-97.<sup>[S4]</sup>

<sup>[</sup>S3] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, J. *Appl. Cryst.* **1994**, *27*, 435.

<sup>[</sup>S4] G. M. Sheldrick, Acta Cryst. A 2008, 64, 112..

<sup>[</sup>S5] CrystalStructure 4.0, Crystal Structure Analysis Package, Rigaku Corporation (2000–2011). Tokyo 196-8666, Japan.

	1 11 1
Crystal color, habit	purple, block
Crystal size [mm]	$0.30\times0.22\times0.10$
Empirical formula	$C_{58}H_{56}N_4O_6$ [5 • (acetone) <sub>2</sub> ]
Formula weight	905.10
T [°C]	$-180\pm1$
λ[Å]	0.71075
Crystal system, space group	triclinic, $P\overline{1}$ (#2)
Ζ	2
<i>a</i> , <i>b</i> , <i>c</i> [Å]	11.879(5), 13.771(5), 15.511(6)
$lpha$ , $eta$ , $\gamma$ [°]	99.018(5), 108.092(5), 90.316(3)
V [Å <sup>3</sup> ]	2378.1(16)
$ ho_{ m calcd} [{ m g \ cm^{-3}}]$	1.264
$\mu$ (MoK $\alpha$ ) [cm <sup>-1</sup> ]	0.819
Detector position [mm]	49.92
$2\theta_{\max}$ [°]	55.1
Collected data	31747
Unique data / R <sub>int</sub>	10928/0.0383
No. of parameters	642
Refinement method	Full-matrix least-squares on $F^2$
Goodness-of-fit on $F^2$	1.085
$R_1 [I > 2\sigma], wR_2$ (all reflections)	0.0772, 0.2240
Residual density [e Å <sup>-3</sup> ]	0.53/-0.62

Table S1: Crystallographic data and structure refinement for **5**.



Fig. S2. ORTEP representation (ellipsoids are set at 50% probability) of two crystallographically independent molecules for **5**. Both molecules adopted a chair conformation with  $C_i$  symmetry. **Molecule 1** appears in Fig. 2 in the text.

	Bond	Bond length (Å)		
	Molecule 1	Molecule 2		
N1-C1	1.445(3)	1.436(3)		
N2-C4 C1-C2	1.388(4)	1.393(3)		
C2–C3 C3–C4	1.387(3) 1.405(4)	1.382(3) 1.409(4)		
C4–C5	1.407(4) 1.303(4)	1.404(3)		
C1-C0 C5-C6	1.395(4) 1.390(3)	1.390(3)		
N2–C7 N3–C12	1.433(3) 1.423(3)	1.434(3) 1.430(3)		
C7–C8 C8–C9	1.398(4) 1.388(4)	1.399(4) 1.392(4)		
C9–C10 C10_C11	1.388(4) 1.387(4)	1.392(4)		
C10-C11 C11-C12	1.387(4) 1.403(4)	1.397(4)		
C12–C7	1.406(4)	1.411(4)		

Table S2: Crystallographically determined bond lengths for **5**.

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## DFT Calculations for a Model Compound 5'

Quantum chemical calculations were performed on the basis of density functional method by using several functionals: B3LYP,<sup>[S6]</sup> M06-2X,<sup>[S7]</sup> theory (DFT) set,<sup>[S10]</sup> SVWN5<sup>[S9]</sup>  $\omega$ B97X-D,<sup>[S8]</sup> employing 6-31G\* and basis and B3PW91/6-31+G\*\*.<sup>[S11]</sup> Full geometrical optimization of a model compound 5', 5'' and  $5^{2+}$  in which all the methoxy groups are replaced by hydrogen atoms were carried out and furthermore, their local minimum structures were checked by performing subsequent frequency analyses. All these computational approaches are implemented in Gaussian 09 package of ab initio MO calculation.<sup>[S12]</sup>

- [S6] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [S7] Y. Zhao, D. G. Truhler, J. Phys. Chem. 2006, 110, 5121.
- [S8] J.-D. Chai, M. Head-Gordon, Phys. Chem. Chem. Phys. 2008, 10, 6615.
- [S9] S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200.
- [S10] W. J. Hehre, L. Radom, P.v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.
- [S11] J. P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 1996, 54, 16533.
- [S12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09 (Revision C.01), Gaussian, Inc., Wallingford CT, 2010.

As mentioned in the text, macrocycle **5** has two conformational isomers, the boat form and the chair form, in solution. We carried out geometry optimizations on these two conformers for a model compound **5**', in which all the methoxy groups are replaced by hydrogen atoms, at the B3LYP/6-31G\* level. As the result, the local minimum structures for both the boat form with  $C_i$  symmetry and the chair form with  $C_1$ symmetry were found (Fig. S3). The boat form was calculated to be slightly stable by 0.26 kcal mol<sup>-1</sup> as compared with the chair form, and this result is in good accordance with the observed <sup>1</sup>H NMR spectrum for **5**. However, all the functionals tested, including B3LYP, could not perfectly reproduce the characteristics of the X-ray structure of **5**, as shown in Table S3.



Fig. S3. B3LYP-optimized structures of 5': (a) the chair form and (b) the boat form.

	rl	r2	r3
X-ray structure	1.445(3) [1.436(3)]	1.399(3) [1.397(3)]	3.185(4) [3.196(4)]
B3LYP/6-31G*	1.4319	1.4163	3.2878
M06-2X/6-31G*	1.4308	1.4016	3.2177
ωB97X-D/6-31G*	1.4277	1.4017	3.2368
SVWN5/6-31G*	1.4162	1.3920	3.1610
B3PW91/6-31+G**	1.4277	1.4100	3.2598

Table S3: Comparison of selected geometrical parameters (in Å) between the X-ray structure of **5** and the DFT-optimized structures for the chair conformation of **5**'.



The frontier Kohn–Sham orbital energy diagrams of chair and boat conformers at B3LYP/6-31G\* level are shown in Figures S4 and S5. In both conformers, the HOMO and (HO-1)MO were quasi-degenerate, and furthermore, the (HO-2)MO and (HO-3)MO were also quasi-degenerate. In both conformers, the MO coefficients were fully delocalized over the two *para*-phenylenediamine moieties and also the two *ortho*-phenylene moieties.



Fig. S4. Frontier Kohn-Sham orbitals of the chair conformer of 5' at the B3LYP/6-31G\* level.



Fig. S5. Frontier Kohn-Sham orbitals of the boat conformation of 5' at the B3LYP/6-31G\* level.

The DFT optimizations for two conformers of the cation  $(5^{,+})$  were also carried out (Figs. S6 and S7). The calculated spin densities are shown in Figs. S8 and S9. For both conformers, two local minimum structures with the different charge distributions were found at the B3LYP/6-31G\* level: the structure with the localized spin (or the positive charge) on one para-PD unit, and the structure with the delocalized spin over the two para-PD units. For the chair conformer, the spin-localized structure was calculated to be stable than the spin-delocalized one by 1.05 kcal mol<sup>-1</sup> (Fig. S6). In the spin-localized structure, the C-N bond lengths (1.3752 Å) in the positively charged para-PD unit were significantly shortened compared to those of another para-PD unit (1.4315), and as a result, the positively charged *para*-phenylene ring adopted a bent structure. On the other hand, the structure with the delocalized spin had an almost  $C_i$  symmetric shape, and the C-N bond length alternation occurred in both *para*-PD moieties, in a similar way to the crystal structure of 5. On the contrary, for the boat conformers, the delocalized structure was calculated to be slightly stable (Fig. S7). However, the energy difference between the two conformers indicates quasi-degeneracy  $(0.02 \text{ kcal mol}^{-1})$ . These two conformers also showed similar C-N bond length alternation to the corresponding structures of the chair conformer. In the spin-localized structure of the boat conformer, the C-N bonds in the positively charged *para*-PD unit (1.3718 and 1.3851 Å) were also shorter than those in another para-PD unit (1.4277 and 1.4306 Å), and in the spin-delocalized one, each para-PD units had both longer and shorter C-N bonds. For both conformers, the energy difference between the spin-localized and delocalized structures was considerably small, and moreover, the interconversion between the two structures can be occurred without the flipping of the *ortho*-phenylene units requiring high activation energy. These results suggest that the generated radial spin can easily move all over the macrocycle in both conformers.



Fig. S6. B3LYP-optimized structures for a) the spin-localized chair conformer and b) the spin-delocalized chair conformer of  $5^{*+}$ . Bond lengths are shown in Å.



Fig. S7. B3LYP-optimized structures for a) the spin-localized boat conformer and b) the spin-delocalized boat conformer of  $5''^+$ . Bond lengths are shown in Å.



Fig. S8. Spin density distributions for the chair conformer of  $5^{,+}$ : a) the spin-localized structure; b) the spin-delocalized structure (UB3LYP/6-31G\*; black: positive spin, white: negative spin; spin isosurface value = 0.003 electron au<sup>-3</sup>).



Fig. S9. Spin density distributions for the boat conformer of  $5^{*+}$ : a) the spin-localized structure; b) the spin-delocalized structure (UB3LYP/6-31G\*; black: positive spin, white: negative spin; spin isosurface value = 0.003 electron au<sup>-3</sup>).



Fig. S10. B3LYP-optimized structures for (a) the boat conformer and (b) the chair conformer of  $5^{2^+}$ . Bond lengths are shown in Å.

#### **Electrochemical Measurements**

The redox properties were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K with 0.1 M tetra-n-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) as supporting electrolyte (scan rate 100 mV s<sup>-1</sup>) using an ALS/chi Electrochemical Analyzer model 612A. A three-electrode assembly was used, which was equipped with platinum disk (2 mm<sup>2</sup>), a platinum wire, and Ag/0.01 M AgNO<sub>3</sub> (acetonitrile) as the working electrode, the counter electrode, and the reference respectively. The redox potential electrode, was referenced against а ferrocene/ferrocenium redox potential ( $Fc^{0/+}$ ) measured in the same electrolytic solution.

#### **Spectroelectrochemical Measurements**

Spectroelectrochemical measurements were carried out with a custom-made optically transparent thin-layer electrochemical (OTTLE) cell (light pass length = 1 mm) equipped with a platinum mesh, a platinum coil, and a silver wire as the working electrode, the counter electrode, and the pseudo-reference electrode, respectively. The potential was applied with an ALS/chi Electrochemical Analyzer model 612A.

# **ESR Measurements**

ESR spectra were recorded on a JEOL JES-TE200 X-band ESR spectrometer, in which the temperature was controlled by a JEOL ES-DVT3 variable-temperature unit.



Fig. S11. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of 5, measured in  $CH_2Cl_2$  containing 0.1 M  $nBu_4NBF_4$  at 298 K (scan rate 100 mV s<sup>-1</sup>).



Fig. S12. Temperature dependence of the ESR spectrum for 5<sup>++</sup> in CH<sub>2</sub>Cl<sub>2</sub>.