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Singly *N*-Fused Möbius Aromatic [28]Hexaphyrins(1.1.1.1.1.1)

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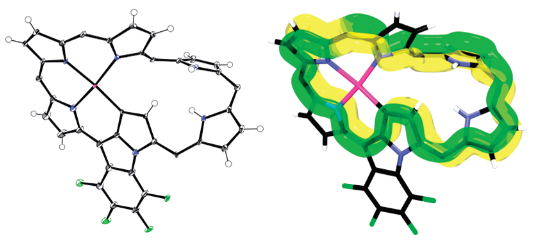

A singly *N*-fused [28]hexaphyrin was isolated and metalated with Pd(OAc)$_2$ to give a conformationally twisted Pd(II) complex that displays distinct Möbius aromatic properties such as a strong ring current and an absorption spectrum characteristic of an aromatic porphyrinoid.

In recent years, expanded porphyrins[1] have been extensively studied because of their attractive properties such as large macrocyclic π-conjugation,[2] multimetal coordination,[3] anion binding,[4] large two-photon absorption (TPA) cross section,[5] and facile aromatic−antiaromatic switching upon two-electron oxidation and reduction.[6] A current highlight is the facile formation of Möbius aromatic molecules from expanded porphyrins by metalation, lowering temperature, protonation, and peripheral fusion reaction.[7]

The concept of Möbius aromaticity, which was first proposed by Heilbronner in 1964, predicts an aromatic nature for a [4n] annulene when lying on a single-sided, twisted Möbius strip.[8] This concept has been challenged from both experimental and theoretical viewpoints. However, the synthesis of a Möbius aromatic molecule has been difficult since the implementation of two conflicting structural features, cyclic full π-conjugation and singly twisted topology within a single molecule, is not easy. Despite this difficulty, Herges and co-workers reported the synthesis of [16]annulene as the first Möbius aromatic molecule, which has a singly twisted conformation and moderate aromatic characters.[9] Recently, Latos-Grażyński and co-workers reported the temperature-dependent topology change between Hückel and Möbius conformations for di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1).[7a] In addition, our research group has demonstrated that *meso*-aryl-substituted expanded porphyrins are an effective platform to achieve Möbius aromatic systems. Moreover, we have revealed that a Möbius antiaromatic molecule is formed upon insertion of phosphorus into [28]hexaphyrin.[7j] In this paper, we report that *N*-fusion reaction of [26]hexaphyrin is an effective means to form Möbius aromatic systems. *N*-Fused hexaphyrin thus formed is conformationally rather flexible and difficult to confirm Möbius aromaticity but its Pd(II) complex is conformationally rigid to lock in a singly twisted conformation.

First, we examined *N*-fusion reaction of *meso*-hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) **1** under controlled conditions. Previously, we prepared doubly *N*-fused [28]hexaphyrins under harsh reaction conditions and found that they are Hückel antiaromatic species.[10] Although these products are considered to be formed via a singly *N*-fused [28]hexaphyrin, which has been elusive so far. After experimental optimization, we found that heating of **1** in a 5:1 mixture of toluene and pyridine at 90 °C for 7 days gave singly *N*-fused

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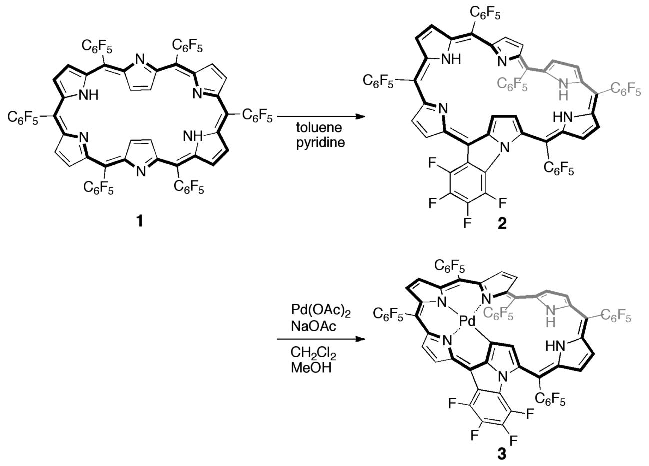
SCHEME 1. **Synthesis of Singly *N*-Fused [28]Hexaphyrins**



[28]hexaphyrin **2** in 17% yield in a reproducible manner (Scheme 1). High-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectrum of **2** indicated the parent negative ion peak at m/z = 1441.0847 (calcd for $C_{66}H_{14}F_{29}N_6$, $[M - H]^-$ 1441.0822), thus indicating the elimination of HF from **1**. The ^{1}H NMR spectrum of **2** in CD_2Cl_2 is very broad at room temperature, probably reflecting complicated conformational changes in the various Hückel and Möbius forms. The spectrum became sharpened upon cooling temperature down to −90 °C but still complicated, exhibiting deshielded signals at δ = 15.45, 15.19, and 15.15 ppm and shielded signals at δ = −0.67, −0.82, −1.24, −1.33, and −2.19 ppm. The deshielded and shielded signals have been assigned due to the inner NH protons on Hückel antiaromatic species and to the inner NH protons and β protons on Möbius aromatic species, respectively. Further investigation of the ^{1}H NMR spectrum of **2** was abandoned because of its complexity.

We then attempted Pd(II) metalation of **2** to lock in its Möbius conformation. Treatment of **2** in a 4:1 mixture of CH_2Cl_2 and methanol with $Pd(OAc)_2$ (5 equiv) in the presence of NaOAc (5 equiv) at room temperature for 12 h provided palladium(II) complex **3** in 30% yield (Scheme 1). Contrary to an expectation that several Pd(II) complexes may be formed from **2** due to its conformational distribution and possible several coordination sites, the single palladium complex was obtained, and notably, none of other regioisomers were observed in the reaction mixture. The HR-ESI-TOF mass spectrum of **3** indicated the parent negative ion peak at m/z = 1544.9712 (calcd for $C_{66}H_{12}F_{29}N_6Pd$, $[M - H]^-$ 1544.9722). Fortunately, its crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of octane into a chlorobenzene solution of **3** at room temperature. The crystal structure clearly reveals its twisted Möbius-type conformation (Figure 1). The palladium(II) ion is bound to a square planar NNNC ligand to fix the twisted conformation. The nitrogen atom of the pyrrole E substitutes the 2-fluorine atom of the adjacent pentafluorophenyl ring to form a fused tricyclic structure. The macrocyclic conjugation is roughly smooth but has two kinks between the pyrroles C and D and the pyrroles D and E with dihedral angles of 60° and 45°, respectively. The ^{1}H NMR spectrum of **3** displays 10 signals that correspond to the outer β-protons in the range of δ = 8.98−5.52 ppm and one singlet due to the inner β-proton of pyrrole E at δ = 1.25 ppm. Accordingly, the difference between the chemical shifts of the most shielded and deshielded β-protons was 7.73 ppm, which is larger than that of normal Möbius aromatic [28]hexaphyrin palladium(II) complex (7.05 ppm).[7b] In addition, the ^{19}F NMR spectrum which shows 29 signals also supports the *N*-fused structure of **3**.

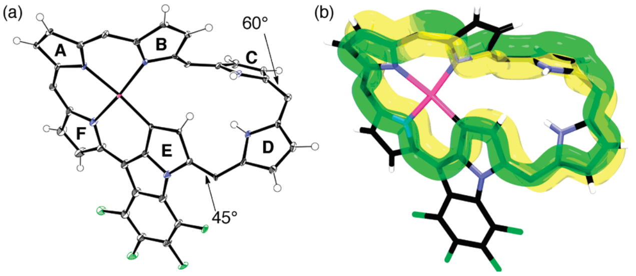


FIGURE 1. (a) X-ray crystal structure and (b) schematic representation of the molecular orbital of **3**. Thermal ellipsoids represent 50% probability. *meso*-Aryl substituents, solvent molecules, and a minor disorder component are omitted for clarity. Dihedral angles at the most distorted points are given.

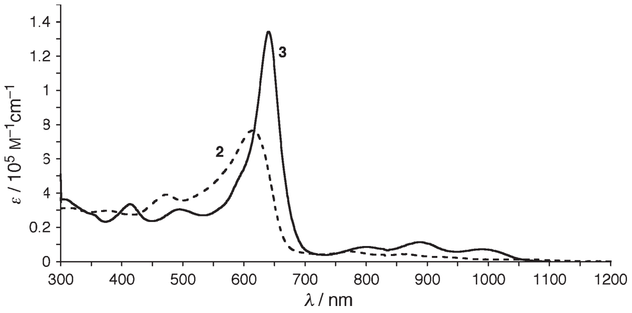


FIGURE 2. UV/vis absorption spectra of **2** (---) and **3** (—) in CH_2Cl_2.

The UV/vis absorption spectra of **2** and **3** in CH_2Cl_2 are shown in Figure 2. The spectrum of **2** shows a Soret-like band at 615 nm and Q-like bands at 775 and 857 nm. However, its absorption coefficient is not so large, and Q-like bands are relatively weak. These features suggest that the aromaticity of **2** is not so strong because of the interconversion among several twisted Möbius conformations and a planar Hückel conformation, which should be aromatic and antiaromatic, respectively. Furthermore, the absorption spectra of **2** in polar solvents display the appearance of a new peak at 535 nm (see Figure S2, Supporting Information). The peaks at 535 and 615 nm are derived from Hückel antiaromatic species and Möbius aromatic species, respectively. In addition, in the ^{1}H NMR spectra of **2** in THF-d_8, remarkably deshielded signals due to Hückel antiaromatic species are observed at δ = 21.08 and 20.76 ppm (see Figure S8, Supporting Information). These results suggest that the relative contribution of the Hückel conformation increases in polar solvent.

On the other hand, the absorption spectrum of **3** shows an intense Soret-like band at 640 nm and Q-like bands at 801, 888, and 987 nm. The observed red shift and enhancement of Soret-like band upon Pd(II) metalation are in line with metalation-induced rigidification of the twisted Möbius conformation. The absorption spectrum of **3** is rather solvent independent, again reflecting its conformational robustness. It is interesting to note that the Soret-like band of **3** is the most red-shifted among the reported Möbius aromatic hexaphyrins, probably due to the presence of the fused tricyclic moiety that is well conjugated with the π-electronic network of the [28]hexaphyrin.

To obtain the further insight for Möbius aromaticity, we performed DFT calculations (B3LYP/6-31G(d)/LANL2DZ) (see the Supporting Information).[11] These calculations revealed nearly degenerate HOMO/HOMO−1 and LUMO/LUMO+1 for **3**, which are characteristic of aromatic expanded porphyrins. The nucleus-independent chemical shift (NICS) value[12] at the center of macrocycle was calculated to be −13.2 ppm, and the harmonic oscillator model of aromaticity (HOMA)[13] was estimated to be 0.70. For the metal complexes of [28]hexaphyrins, NICS and HOMA value were reported to be in the ranges of −11.9 to +15.7 ppm and 0.39−0.64, respectively.[7b,14] On the basis of these comparisons, the [28]hexaphyrin Pd(II) complex **3** has a 28π-electronic system, whose aromaticity is stronger than those of the previously reported hexaphyrin complexes.

The electrochemical properties were studied by cyclic voltammetry in CH_2Cl_2 versus ferrocene/ferrocenium ion (Fc/Fc^+) with tetrabutylammonium hexafluorophosphate as electrolyte. Free-base **2** underwent two reversible oxidations at 0.06 and 0.34 V, and one reversible reduction at −0.92 V. The complex **3** underwent two reversible oxidations at 0.27 and 0.56 V, and one irreversible and one reversible reduction at −1.02 and −1.48 V, respectively.

In summary, the singly *N*-fused [28]hexaphyrin **2** was isolated from the controlled *N*-fusion reaction and was metalated to give Möbius aromatic Pd(II) complex **3** as a single isomer, which exhibits a distinct ring current and Soret-like band at 640 nm, being the longest wavelength of Soret-like band among the Möbius aromatic [28]hexaphyrins studied so far.

Experimental Section

The synthetic details of *meso*-hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) (**1**) were previously described.[15]

***meso*-Hexakis(pentafluorophenyl)-Substituted Singly *N*-Fused [28]-Hexaphyrin(1.1.1.1.1.1) (2).** A solution of **1** (146 mg, 0.1 mmol) in toluene (40 mL) and pyridine (8 mL) was stirred for 7 days under N_2 atmosphere at 90 °C. After the removal of the solvent, silica gel column chromatography using a 1:2 mixture of CH_2Cl_2 and *n*-hexane provided a dark blue fraction. After evaporation, the product **2** was obtained as a violet solid (24.6 mg, 17.1 μmol, 17%): ^{1}H NMR (600.17 MHz, CD_2Cl_2, 25 °C) δ 15.29 (brs, NH), 15.20 (brs, NH), 14.74 (s, NH), 11.12 (br, NH), 9.98 (s), 9.47 (d, J = 4.8 Hz), 8.87 (s), 8.66 (s), 8.36 (d, J = 4.8 Hz), 8.12 (s), 8.00 (s), 7.95 (d, J = 4.8 Hz), 7.78 (brs), 7.73 (d, J = 2.1 Hz), 7.71 (d, J = 2.1 Hz), 7.62 (d, J = 4.8 Hz), 7.46 (s), 7.10 (br), 6.94 (brs), 6.90 (brs), 6.82 (brs), 6.77 (brs), 6.71 (brs), 6.65 (brs), 6.44 (brs), 6.23 (d, J = 4.2 Hz), 6.14 (d, J = 4.8 Hz), 5.92 (brs), 5.85 (d, J = 4.2 Hz), 5.79 (d, J = 4.2 Hz), 5.66 (d, J = 4.2 Hz), 5.46 (s), 5.24 (d, J = 4.2 Hz), 4.90 (s), 4.69 (s), 4.04 (brs), −0.08 (d, J = 4.8 Hz), −0.89 (d, J = 4.8 Hz), −1.79 (d, J = 4.8 Hz), −1.86 (s, NH); (600.17 MHz, CD_2Cl_2, −90 °C) δ 15.45 (brs, NH), 15.19 (s, NH), 15.15 (s, NH), 9.47 (s), 9.05 (s), 8.01 (br), 8.72 (s), 8.39 (d, J = 4.8 Hz), 8.34 (brs), 8.14 (s), 8.08 (d, J = 4.2 Hz), 8.03 (m), 7.91 (s), 7.87 (d, J = 4.2 Hz), 7.84 (m), 7.78 (m), 7.71 (m), 7.56 (d, J = 4.2 Hz), 7.53 (d, J = 4.2 Hz), 7.34 (d, J = 4.2 Hz), 7.17 (s), 6.71 (d, J = 4.2 Hz), 6.67 (d, J = 4.2 Hz), 6.19 (d, J = 4.2 Hz), 6.11 (m), 6.00 (brs), 5.92 (m), 5.89 (m), 5.80 (d, J = 4.2 Hz), 5.77 (m), 5.73 (br), 5.56 (s), 5.53 (s), 5.13 (d, J = 4.8 Hz), 5.08 (d, J = 4.2 Hz), 4.98 (d, J = 4.2 Hz), 4.76 (d, J = 4.2 Hz), 4.22 (br), 3.87 (s), 3.77 (s), −0.67 (brs, NH), −0.82 (s), −1.24 (s), −1.33 (s), −2.19(s); (600.17 MHz, THF-d_8, −100 °C) δ = 21.08 (brs), 20.76 (brs), 14.66 (brs), 14.53 (brs), 14.26 (brs), 13.53 (brs), 9.34 (s), 9.02 (m), 8.86 (s), 8.79 (m), 8.47 (m), 8.34 (m), 8.18 (s), 8.03 (m), 7.96 (m), 7.86 (s), 7.81 (s), 7.71 (s), 7.58 (m), 5.47 (s), 5.43 (s), 5.28 (s), 5.01 (s), 4.86 (s), 4.78 (s), 4.70 (s), 4.64 (s), −0.42 (brs), −1.15 (s), −1.67 (s); ^{19}F NMR (564.73 MHz, CD_2Cl_2, 25 °C) δ −133.70 (d, J = 20.7 Hz), −136.01 (s), −136.14 (m), −136.72 (d, J = 24.2 Hz), −136.84 (d, J = 24.2 Hz), −137.50 ∼ −139.83 (m), −140.90 (m), −141.56 (d, J = 20.7 Hz), −141.15 (d, J = 20.7 Hz), −149.72 (m), −150.87 (t, J = 20.7 Hz), −151.26 (brs), −151. 64 (t, J = 20.7 Hz), −152.05 (t, J = 20.7 Hz), −152.19 (t, J = 20.7 Hz), −152.51 (t, J = 20.7 Hz), −152.76 (t, J = 20.7 Hz), −152.86 (t, J = 20.7 Hz), −153.01 ∼ −153.18 (m), −153.34 (t, J = 20.7 Hz), −153.50 (t, J = 20.7 Hz), −154.02 (t, J = 20.7 Hz), −154.68 (t, J = 20.7 Hz), −155.89 (t, J = 20.7 Hz), −158.51 (t, J = 20.7 Hz), −158.66 (brs), −160.23 (m), −160.74 (t, J = 20.7 Hz), −160.90 ∼ −162.08 (m), −162.98 (t, J = 20.7 Hz), −163.65 (t, J = 20.7 Hz), −164.04 (brs); UV−vis (CH_2Cl_2) λ (ε, $M^{-1}\,cm^{-1}$) = 311 (32000), 375 (30000), 473 (39000), 615 (76000), 775 (5800), 857 (4500) nm; HRMS (ESI-TOF, negative) calcd for $C_{66}H_{14}F_{29}N_6$ $[M - H]^-$ 1441.0822, found 1441.0847.

Palladium(II) Complex of *meso*-Pentafluorophenyl Substituted Singly *N*-Fused [28]Hexaphyrin(1.1.1.1.1.1) (3). To a solution of **2** (35.6 mg, 25 μmol) in CH_2Cl_2 (20 mL) and methanol (5 mL) was added sodium acetate (12.0 mg, 147 μmol). After the solution was stirred for 5 min, $Pd(OAc)_2$ (27.6 mg, 123 μmol) was added, and the reaction mixture was stirred for 12 h under N_2 atmosphere. The mixture was filtered through a Celite pad, and the solvent was removed. The crude product was purified by silica gel column chromatography using a 1:2 mixture of CH_2Cl_2 and *n*-hexane to give **3** as a blue-green fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave the violet crystals of **3** (11.3 mg, 7.3 μmol, 30%). Single crystals suitable for X-ray crystallographic analysis were obtained by vapor diffusion of octane into chlorobenzene solution of **3**: ^{1}H NMR (600.17 MHz, $CDCl_3$, 25 °C) δ 8.98 (d, J = 4.8 Hz, 1H, outer β-H), 7.95 (d, J = 4.8 Hz, 1H, outer β-H), 7.91 (d, J = 4.8 Hz, 1H, outer β-H), 7.82 (d, J = 4.8 Hz, 1H, outer β-H), 7.70 (d, J = 4.8 Hz, 1H, outer β-H), 7.63 (d, J = 4.8 Hz, 1H, outer β-H), 7.58 (m, 1H, outer β-H), 7.38 (d, J = 4.8 Hz, 1H, outer β-H), 6.79 (dd, J = 4.2 Hz, J = 2.4 Hz, 1H, outer β-H), 5.52 (dd, J = 4.2 Hz, J = 2.4 Hz, 1H, outer β-H), 5.14 (brs, 1H, NH), 1.82 (brs, 1H, NH), 1.25 (s, 1H, inner β-H); ^{13}C NMR (150.91 MHz, $CDCl_3$, 25 °C) δ 158.0, 151.4, 149.2, 147.2, 147.1, 146.6, 145.4, 144.1, 140.2, 139.7, 138.4, 137.8−137.2 (multiplet), 135.1, 134.8, 134.3, 129.3, 129.1, 128.9, 128.6, 123.4, 112.0, 117.7, 114.4, 113.8, 112.9, 111.4, 110.4, 108.0, 104.8, 103.9, 99.3, 99.1, 95.8, 94.5, 89.0, 87.2; ^{19}F NMR (564.73 MHz, $CDCl_3$, −40 °C) δ −133.44 (dd, J = 24.2 Hz, J = 13.8 Hz, 1F), −135.98 (dd, J = 24.2 Hz, J = 6.9 Hz, 1F, *o*-F), −136.32 (d, J = 20.7 Hz, 1F, *o*-F), −136.56 (dd, J = 24.2 Hz, J = 6.9 Hz, 1F, *o*-F), −137.03 (d, J = 20.7 Hz, 1F, *o*-F), −137.51 (dd, J = 24.2 Hz, J = 6.9 Hz, 1F, *o*-F), −137.72 (m, 2F, *o*-F), −138.27 (d, J = 20.7 Hz, 1F, *o*-F), −140.55 (d, J = 20.7 Hz, 1F, *o*-F), −142.86 (d, J = 24.2 Hz, 1F, *o*-F), −150.67 (td, J = 24.2, 13.8 Hz, 1F), −151.22 (t, J = 20.7 Hz, 1F, *p*-F), −151.50 (t, J = 20.7 Hz, 1F, *p*-F), −151.84 (t, J = 20.7 Hz, 1F, *p*-F), −151.90 (t, J = 20.7 Hz, 1F, *p*-F), −152.58 (t, J = 20.7 Hz, 1F), −153.91 (t, J = 20.7 Hz, 1F, *p*-F), −159.55 (dd, J = 20.7,

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[14] Previously reported NICS value of metal complexes were calculated at the B3LYP/6-31G(d)/SDD level.[7b] The NICS value of palladium complex was calculated to be −11.52 ppm at the same condition in this paper (B3LYP/6-31G(d)/LANL2DZ). See also Figure S17, Supporting Information.

[15] Taniguchi, R.; Shimizu, S.; Suzuki, M.; Shin, J.-Y.; Furuta, H.; Osuka, A. *Tetrahedron Lett.* **2003**, *44*, 2505–2507.

17.3 Hz, 1F, *m*-F), −159.90 (dd, J = 20.7, 17.3 Hz, 1F, *m*-F), −160.07 (dd, J = 20.7, 17.3 Hz, 1F, *m*-F), −160.36 (t, J = 20.7 Hz, 2F, *m*-F), −160.52 (dd, J = 20.7, 17.3 Hz, 1F, *m*-F), −160.86 (dd, J = 20.7, 17.3 Hz, 1F, *m*-F), −161.00 (dd, J = 20.7, 17.3 Hz, 1F, *m*-F), −161.91 (dd, J = 24.2, 20.7 Hz, 1F), −163.87 (dd, J = 41.4, 20.7 Hz, 1F, *m*-F), and −168.83 (dd, J = 20.7, 17.3 Hz, 1F, *m*-F); UV−vis (CH_2Cl_2) λ (ε, $M^{-1}\,cm^{-1}$) = 414 (34000), 495 (30000), 640 (130000), 801 (7800), 888 (12000), 987 (7200) nm; HRMS (ESI-TOF, negative) calcd for $C_{66}H_{12}F_{29}N_6Pd$ $[M - H]^-$ 1544.9722, found 1544.9712. Crystallographic data: $C_{66}H_{13}F_{29}N_6Pd \cdot 2(C_6H_5Cl)$, M_r = 1772.32, monoclinic, space group $P2_1/c$ (no. 14), a = 7.4640(9) Å, b = 22.733(3) Å, c = 38.698(5) Å, β = 92.730(3)°, V = 6559(5) Å^3, T = 90(2) K, Z = 4, ρ_{calc} = 1.795 g cm^{-3}, R_1 = 0.0810 [$I > 2\sigma(I)$], R_w (all data) = 0.1464, GOF = 1.004. CCDC-792529 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: General experimental methods, HR-ESI-TOF mass spectra, UV/vis absorption spectra, NMR spectra, cyclic voltammograms, X-ray crystal structure, results of DFT calculations, CIF file for **3**, and complete ref 11 (as ref S5). This material is available free of charge via the Internet at http://pubs.acs.org/.