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A Stable Non-Kekulé Singlet Biradicaloid from *meso*-Free 5,10,20,25-Tetrakis(Pentafluorophenyl)-Substituted [26]Hexaphyrin(1.1.1.1.1.1)

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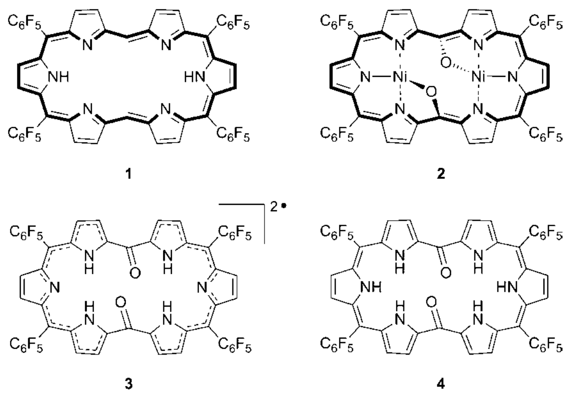
Stable and isolable biradicaloids delocalized over π-conjugated systems are attractive molecules in light of their unique electronic properties[1] and potential applications in molecular electronics,[2a,b] highly colored dyes,[2c] and nonlinear optical materials.[2d] This feature continues to encourage efforts to explore novel molecular motifs that can realize stable biradicaloids. In the past decade, expanded porphyrins have emerged as a new class of macrocycles that exhibit intriguing optical, electrochemical, and coordination properties.[3] Along this line, we have concentrated on exploiting new chemical features of *meso*-aryl-substituted expanded porphyrins.[4] Herein we report a diketohexaphyrin, **3**, that is a non-Kekuké singlet biradicaloid with remarkable chemical stability.

In continuation of our studies of *meso*-free [26]hexaphyrin(1.1.1.1.1.1) **1** (Chart 1),[5] we examined its Ni(II) metalation with Ni(acac)$_2$. In contrast to previous metalations with Zn(II) and Cu(II) salts, which provided mono-*meso*-oxygenated hexaphyrin bismetal complexes,[5b] the *meso*,*meso*-dioxygenated bis-Ni(II) complex **2** was isolated in 24% yield after the usual aqueous workup. The parent ion peak of **2** was observed at *m*/*z* 1272.9467 (calcd for $C_{54}H_{13}N_6F_{20}O_2Ni_2$ $[M + H]^+$: 1272.9482) using high-resolution electrospray ionization time-of-flight mass spectrometry (HR-ESI-TOF-MS). The ^1H NMR spectrum of **2** in $CDCl_3$ showed six outer β-proton signals at 10.66, 9.52, 8.86, 8.74, 8.67, and 8.38 ppm, exhibiting its aromaticity associated with 26 π electrons and a C_{2h}-symmetric structure. The structure of **2** was revealed by single-crystal X-ray diffraction analysis (Figure 1a).[6] The hexaphyrin macrocycle takes a roughly planar conformation, and the two Ni(II) ions are accommodated within an NNNO ligand having square-planar coordination, with the two oxygen atoms displaced from the hexaphyrin mean plane by 0.715 Å.

Demetalation of **2** with methanesulfonic acid in CH_2Cl_2 and subsequent separation over a silica gel column afforded diketohexaphyrin **3** in 83% yield. Compound **3** is very stable toward air and moisture. The parent ion peak was detected at *m*/*z* 1161.1094 (calcd for $C_{54}H_{17}N_6F_{20}O_2$ $[M + H]^+$: 1161.1088) using HR-ESI-TOF-MS. The ^1H and ^{19}F NMR spectra of **3** in $CDCl_3$ showed characteristically broad signals at room temperature, which sharpened as the temperature was decreased. **3** was determined by X-ray crystallographic analysis at 123 K to be a C_2-symmetric, roughly planar *meso*,*meso*-diketohexaphyrin (Figure 1b).[6] Importantly, the C−O bond length is 1.223 Å, which lies well within the normal range of carbonyl C=O double bond lengths, while the adjacent C−C bond lengths are 1.466 and 1.476 Å, typical of normal $C(sp^2)-C(sp^2)$ single bonds. The pyrroles next to the carbonyl groups are assigned as amino-type pyrroles, and the other two are imine-type on the basis of the pyrrole interior C−N−C angles. Consequently, **3** can be delineated as a macrocycle that consists of two non-Kekulé-type radical segments connected by two *meso*-carbonyl groups. This biradical is seemingly stabilized through both the delocalization of the unpaired electrons over the π-conjugated tripyrrolic systems and the steric protection of the C_6F_5 rings. Treatment of **3** with Ni(acac)$_2$ led to the regeneration of **2** in high yield.

Chart 1. Hexaphyrin Molecules **1**−**4** Studied in This Work



The magnetic characteristics of **3** were examined by ESR and SQUID measurements (see the Supporting Information). The ESR spectrum of **3** in the solid state exhibited a signal at $g = 2.003$, indicating the existence of an unpaired electron.[7] Importantly, the ESR signal intensity was temperature-dependent, becoming larger with increasing temperature (Figure 2a). The temperature-dependent

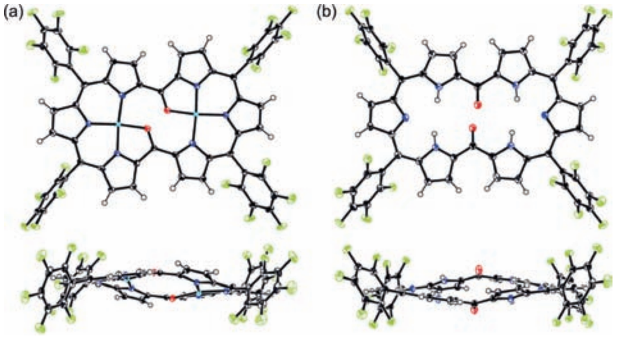


Figure 1. X-ray crystal structures of (a) **2** and (b) **3**: top views (upper) and side views (lower). Solvent molecules have been omitted for clarity. The thermal ellipsoids were scaled to the 50% probability level.

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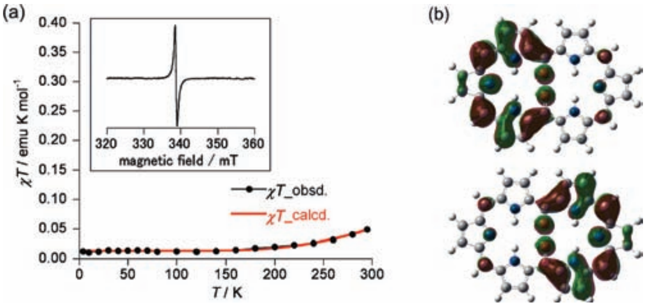
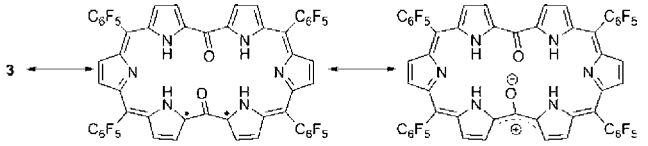


Figure 2. (a) Temperature-dependent magnetic susceptibility estimated from ESR measurements on **3**. The inset shows the ESR spectrum of **3** in the solid state at room temperature. (b) Calculated singly occupied molecular orbitals (SOMOs) of **3** at the B3LYP/6-31G(d,p) level.

Scheme 1. Resonance Contributors of **3**



magnetic susceptibility of **3** also showed an increase in the χT value with increasing temperature, following the trend of the temperature-dependent ESR intensity. By fitting the temperature-dependent ESR intensity data to the Bleaney−Bowers equation,[8] the J value was estimated to be $J/k_B = -645$ K, which corresponds to an energy gap of -2.56 kcal mol^{-1} between the singlet and triplet states (Figure 2a). These results indicate that **3** has a distinct biradical character with a singlet ground state. As indicated in Scheme 1, resonance contributors of **3** can be written as an oxyallyl subunit that is known to resonate between biradical and zwitterionic electronic structures.[9] The observed biradical nature of **3** was supported by density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level. Symmetry breaking of the unrestricted DFT (UDFT) solution afforded an energy lowering of 2.89 kcal mol^{-1} relative to the closed-shell solution. The UDFT calculations confirmed that the $S = 0$ state lies below the $S = 1$ state. The J_{S-T} value was calculated to be -2.45 kcal mol^{-1}, which is in good agreement with the experimental value. The singlet biradical character of **3** was estimated to be 62% on the basis of a CASSCF(2,2) calculation. In addition, the zwitterionic character of the closed-shell resonance contributor was also suggested.[10]

In contrast to the absorption spectrum of **1**, which contains features of typical aromatic expanded porphyrins, the absorption spectra of **2** and **3** are extended up to the near-IR (NIR) range with intense Q-band-like bands (Figure 3). The absorption spectrum of **3** was confirmed to be rather solvent-independent. Cyclic voltammetry of **3** revealed two reversible oxidation and reduction potentials at 0.26 and 0.64 V and at −0.58 and −0.89 V (vs the ferrocene/ferrocenium ion couple), respectively, in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as a supporting electrolyte. Hence, the gap between the first oxidation and reduction potentials ($\Delta E = E^1_{ox} - E^1_{red}$) was small (0.84 V), in line with the biradicaloid character. Open-aperture *Z*-scan measurements revealed the two-photon absorption (TPA) cross section of **3** to be $\sigma^{(2)} = 3800$ GM, which is as large as the value of 3700 GM for the singlet biradical corrole dimer.[1e,11] This result also supports the biradicaloid character of **3**, since it has been well-established that molecules having an intermediate biradical character exhibit an enhanced third-order nonlinear optical response.[2d]

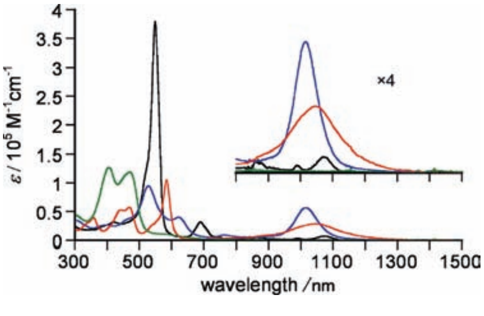


Figure 3. UV−vis−NIR absorption spectra of **1** (black), **2** (blue), **3** (red), and **4** (green) in CH_2Cl_2.

In addition, diketohexaphyrin **3** was reduced with hydrazine to give **4** in 44% yield, thus demonstrating open-shell to closed-shell conversion. The ^{1}H NMR spectrum of **4** in acetone-d_6 exhibited β-proton signals at 7.06, 6.51, and 5.92 ppm and N−H proton signals at 12.37 and 9.96 ppm, indicating its D_{2h}-symmetric structure and diamagnetic character. The macrocyclic conjugation of **4** is disrupted by the presence of two *meso*-carbonyl groups, as seen from disappearance of the low-energy band in its absorption spectrum.

In summary, the diketohexaphyrin **3** was characterized as a rare example of a chemically stable non-Kekulé biradicaloid on the basis of the temperature-dependent magnetic susceptibility, theoretical calculations, and TPA measurements. Current investigations are focused on applying this unique biradicaloid system to functional systems, and the results of those studies will be reported in due course.

Supporting Information Available: Sample preparation, characterization, and X-ray crystallographic details for **2** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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