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Editorial

Spin switching in corrole radical complex

Spintronics is a cutting-edge field of developing new electronic devices by manipulating the electron spin and magnetic moment [1]. Traditional spintronic research mainly focuses on transition metals and inorganic semiconductors, while organic molecules have the advantage of being extremely easy to realize efficient spin control by modifying the specific external conditions for desired electronic structures and magnetic characteristics. Corrole, as a ring-contracted porphyrin, is the aromatic analog of the central macrocycle of vitamin B_{12}. Corrole has a squeezed inner cavity and three inner NHs in its free-base form, making it easier to stabilize high-valent metal ions and thus a promising candidate in spintronics.

When coordinated to metal ions such as Cu, Co, and Fe, the electron-rich corrole ligand could be partially oxidized to exhibit radical character, making it difficult to determine the exact oxidation states of central metals and ligands. The most controversial debate was the Cu(II)/Cu(III) dilemma on copper corrole [2]. The compound was initially thought to be a closed-shell Cu(III) complex in 2000, but significant experimental and theoretical evidence over the next twenty years progressively revealed its open-shell singlet state ground state comprised of a Cu(II) core and partially oxidized radical ligand (Fig. 1a).

Shen Z. and Wu F. from Nanjing University have developed a series of metallocorroles with extended π-conjugation systems, which not only facilitated the formation and stabilization of radical ligands, but also allowed spin configurations of complexes to be easily controlled [3–5]. Recently, Shen, Wu, and co-workers reported that the unambiguous Cu(II) corrole with fully oxidized $[4n+1]\pi$ radical ligand was obtained through the benzo-fusion at the β-position of corrole ligand [6]. The ground-state conversion of copper corrole radical from singlet to triplet was achieved *via* a retro-Diels-Alder reaction (Fig. 1b).

The authors first synthesized a bicyclo[2.2.2]octadiene (BCOD) fused corrole **1-Cu** by employing the classic H_2O-MeOH approach with starting materials 4,7-dihydro-4,7-ethano-2*H*-isoindole and 3,5-di–*tert*–butyl–benzaldehyde. Heating solid **1-Cu** at 250 °C in vacuo cut the C–C bond in the BCOD bridge, eliminated the ethylene, and quantitatively afforded the benzo-fused **2-Cu**. The singlet ground state of **1-Cu** was clearly confirmed by the peripheral BCOD protons signals that appeared in the region of 6.60∼2.09 ppm, while the signals of benzo protons in **2-Cu** were located in a range of −6.2∼−25.6 ppm, demonstrating its enhanced paramagnetism.

The conformations of copper corroles were assumed to be “inherently saddle distorted” owing to the strong d-π interactions of antiferromagnetically coupled Cu(II) corrole radicals. When compared to other copper corroles, **2-Cu** stood out due to its highly planar macrocycle with a mean plane deviation value of only 0.024 Å (Fig. 1c). The planar structure could perfectly sustain the ferromagnetic coupling ($S = 1$) between Cu(II) and corrole radical.

The theoretical analysis of **2-Cu** was conducted by the authors for three different states, including a close-shell singlet Cu(III) (CS), an open-shell singlet antiferromagnetically coupled Cu(II) corrole radical (OS) and a triplet ferromagnetically coupled Cu(II) corrole radical (T). A lower T state was discovered for **2-Cu** than the CS and OS states with a calculated singlet-triplet energy gap of 2.28 kcal/mol, providing theoretical support for the triplet ground state (Fig. 1d). The strongest support for the triplet ground state came from temperature- and field-dependent superconducting quantum interference device (SQUID) magnetometry. The χT value of **2-Cu** in 2 K was 0.77 cm^3 K/mol, and it reached approximately 1 cm^3 K/mol at 300 K. The singlet-triplet energy gap was estimated to be 1.66 kcal/mol by fitting the χT–T plot (Fig. 1e). The field-dependent magnetization plot of **2-Cu** at 2 K was fitted to a Brillouin function with $S = 0.89$, which was close to the value ($S = 1$) corresponding to the triplet ground state (Fig. 1f). The magnetic hysteresis of **2-Cu** was observed at 2 K. Moreover, **2-Cu** exhibits remarkable stability in air despite its radical character. The calculated density plots of spin and SOMO both demonstrate that the density is concentrated mostly in the inner corrole ring, which is nicely protected by fused benzenes with low reactivity.

The research conducted by Shen’s group introduces a new approach to the fine-tuning of interactions between metal center and corrole ligand and provides a promising strategy for the creation of stable corrole radical complexes with distinctive high-spin systems. The strategy will further trigger the development of novel functional materials based on corroles and their work will encourage an increasing amount of spintronics research for the use of innovative magnetic and electrical devices.

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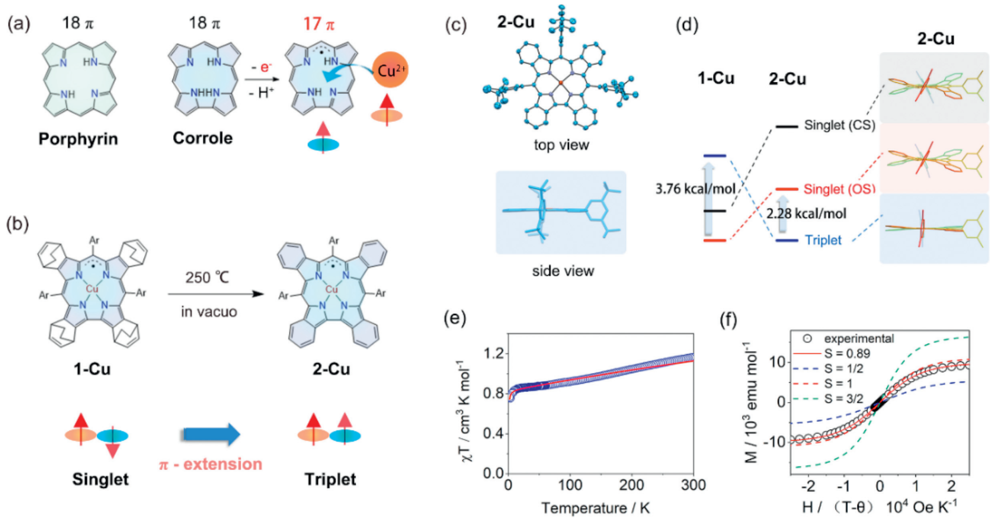

Fig. 1. (a) Structure of 18π porphyrin and corrole, and schematic of the 17π corrole radical formation during coordination. (b) Schematic representation of the singlet-to-triplet conversion from **1-Cu** to **2-Cu**. (c) Single-crystal X-ray diffraction structure of **2-Cu**. (d) DFT calculated structures and relative energies of **1-Cu** and **2-Cu** in triplet, open-shell singlet and closed-shell singlet states. (e) Observed (circle) and simulated (line) χT–T curve of **2-Cu** at $H = 5000$ Oe. (f) Observed (circle) and simulated (line) M-H curves of **2-Cu** with different S values.

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