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Syntheses of corrole derivatives and their supramolecular interactions with fullerenes in solution and the solid state

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ABSTRACT

Supramolecular interactions of cobalt corrole and fullerene were investigated both in solution and the solid state. Results reveal that cobalt corrole has the attractive ability to be used as host for fullerene. The cocrystals of cobalt corrole and C_{60}/C_{70} suitable for X-ray crystallographic analysis were obtained and structure details are discussed.

Corroles are one carbon short analogs of porphyrins bearing a direct pyrrole–pyrrole linkage, and have recently emerged as an independent research area.[1] Benefiting from the prominent contributions of Gross, Paolesse, and Gryko to the preparation methods,[2] corroles have nowadays been widely applied in the fields of coordination chemistry, catalysis, sensors, and photoactive molecule arrays.[3]

In comparison with porphyrins, the well-known 18-π-aromatic tetrapyrrolic macrocycles, corroles exhibit some interesting properties, including trianionic character, smaller cavity, lower oxidation potential, higher fluorescence quantum yield, larger stokes shift, and relatively more intense absorption of red light.[4] Corroles, as trianionic ligands with contracted core, have distinctly different coordination chemistry compared with porphyrins.[1,3] The lower oxidation potential of corroles allows the covalently linked corrole-fullerene dyads have a long-lived charge-separated state in nonpolar solvents.[5] This novel feature was not evident in porphyrin–fullerene donor–acceptor systems.[6]

Host molecules for trapping fullerenes are of great importance owing to their potential application in the extraction, solubilization, and function modifications of fullerenes.[7] Supramolecular assembly is considered as a convenient and effective way to construct fullerene based architectures.[8] Unlike the porphyrin–fullerene supramolecular systems which have been a protagonist of interest in the porphyrin scenario,[9] the supramolecular chemistry of corrole and fullerene is still in its infancy, although a few covalently linked fullerene–corrole dyads have been synthesized and studied.[10] Utilizing supramolecular method to construct corrole–fullerene systems may not only avoid the difficulty of corrole derivatization and destroying the π-conjugation system of fullerene, but also provide us materials with novel properties. In view of the electronic deficiency of fullerene, corrole macrocycle which is much more electron-rich than porphyrin would be attractive in the capture of fullerene.[3a,4] But to the best of our knowledge, supramolecular complexation of fullerenes with corrole derivatives has not been demonstrated so far. A pioneering attempt was reported by Wim Dehaen but the system they chose might be not very suitable to give a conclusion.[11] All facts mentioned above inspire us to investigate the supramolecular interactions between corrole and fullerene. In this Letter, we present our primary study on the potential ability of corrole as host for fullerene.

Initially, the freebase, copper, and cobalt corroles (Scheme 1) were studied on their abilities of interaction with fullerene in solution. ^{13}C NMR spectra of fullerene are commonly used as a useful tool to reveal the dynamics of complexation in host–guest chemistry of fullerene.[9d] An upfield shift due to ring current effect of host was usually observed in the ^{13}C NMR of the fullerene guest, and the extent of variation of chemical shift indicates the binding strength between the host and guest. In a general way, the larger the upfield shift is, the greater the binding. A 1:1 mixture of C_{60} and the corresponding corrole in $CDCl_3/CS_2$ ($v/v = 1:1$) gave C_{60} shifts at 143.111 ppm for freebase corrole **2**, 143.164 ppm for copper corrole **3**, and 142.830 ppm for PPh_3–cobalt corrole **4** at 25 °C (Table S1). In comparison with the chemical shift of pure C_{60} (143.229 ppm), cobalt corrole shows more obvious attraction of

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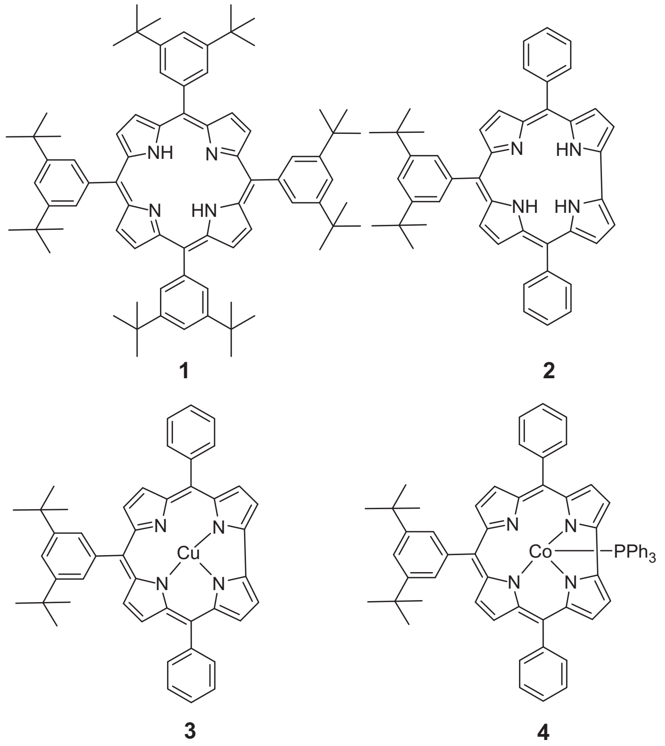


Scheme 1. Structures of compounds **1**–**4** studied herein.

Table 1
Binding constants (M^{-1}) for fullerene in $CDCl_3/CS_2$ = 1:1 solution

Host/guest	K_a	Host/guest	K_a
4·C_{60}	79	**4**·C_{70}	605
5·C_{60}	1139	**5**·C_{70}	3878
6·C_{60}	1046	**6**·C_{70}	4305

C_{60} than freebase and copper corroles. This can be comprehended by the reported X-ray crystal structures of freebase and copper corroles. The steric hindrance between the three NH protons within the rather limited N4 coordination core in freebase corrole, and copper-specific metal ligand orbital interaction in copper corrole make an alternately tilted up and down of the pyrrole rings in them.[1] Such distortions from planarity of the macrocycles will weaken their interactions with C_{60}. In the case of cobalt corrole **4**, the macrocycle core is nearly planar and benefits its interaction with C_{60},[1c] which results in a larger upfield shift. In consideration of the larger upfield shift of C_{60} found in **4**·C_{60} than 3,5-di-*tert*-butyl porphyrin complex **1**·C_{60} (142.997 ppm), the PPh_3-cobalt-corrole might be used as a qualified candidate host to form an inclusion of fullerene.

The association of **4** and C_{60} in solution was investigated by ^1H NMR titrations. An upfield shift tendency of the proton resonance was observed (Fig. S25), and the Job plot shows a clear stoichiometry of 1:1 for complex **4**·C_{60} (Fig. S26). The K_a value was evaluated to be 79 M^{-1} using nonlinear curve fitting plot for the 1:1 binding isotherm as described by Connors (Table 1, Fig. S27).[7c,12]

Further exploring was conducted to the ellipsoidal C_{70} species at the same condition. Similar upfield shift trend as the complex of cobalt corrole **4** with C_{60} was detected in the ^1H NMR experiment. Job plot indicates the host **4** and guest C_{70} takes a typical 1:1 stoichiometric format to form the inclusion. The cobalt corrole **4** shows approximately seven times stronger binding ability toward C_{70} (605 M^{-1}, Figs. S28–S30) than C_{60}. This should be attributed to the ovality of C_{70}, which permits a maximization of π–π interactions. Because of its elliptical shape, C_{70} shows five in-equivalent ^{13}C NMR signals. This is often utilized to assure its conformation in the cavity of the complex.[9b] In our case, the upfield shift degree of equatorial carbon atoms of C_{70} was found to be more pronounced than those of the pole carbon atoms (Table S2). So we conclude that the C_{70} tends to adopt a side-on conformation interacting with the cobalt corrole.

To obtain more detailed structure information about the interaction between cobalt corrole and C_{60}, cocrystals of **4** and C_{60} were obtained by slow diffusion of diethyl ether to a toluene solution of **4** and C_{60} at −20 °C. The packing diagram is shown in Figure 1. X-ray crystallographic analysis shows each C_{60} ball is surrounded by two corrole hosts (Fig. 2a) and the unit cell consists of two 2:1 complexes of **4** and C_{60} (Fig. 1). Such 2:1 complex packs in a zigzag manner in the crystal. In the 2:1 complex **4**·C_{60}, two corrole planes, with a Co–Co distance of 10.27 Å, subtend an angle of 75°. To relieve the steric hindrance, the 3,5-di-*tert*-butyl phenyls in corroles take a nearly opposite direction. C_{60} is symmetrically centered over two corroles, and one of its 5:6 ring-juncture C–C bonds is located right above the central metal ion of the corrole (Fig. 2b). The distances between these atoms within the 5:6 ring-juncture C–C bond and Co atom are 3.10 and 3.27 Å, respectively. With respect to the central N atoms, the closest distance is measured to be 3.00 Å. Furthermore, the nearest distance of the carbon atoms of corrole macrocycle toward C_{60} is 3.25 Å, which is slightly but definitely shorter than the typical interlayer distance of graphite (3.35 Å).[9b] Due to the coordination effect of the PPh_3, the Co atom is slightly out of the plane on the opposite side of the corrole from the fullerene. The distance of Co and P is 2.20 Å, no change is observed before and after co-crystallization with C_{60}.[1c] So the interaction between fullerene and metal Co might be negligible, and the π–π interaction between the planar cobalt corrole macrocycle and C_{60} convex surface may be considered as the dominant influence on forming the complex.

The crystals of **4**·C_{70} suitable for X-ray diffraction analysis were also obtained, with a slight change of the above method by using methanol instead of diethyl ether. While the cobalt corrole moiety is fully ordered, the C_{70} moiety is disordered between two orientations with the 0.523(5):0.477(5) occupancies (Figs. S44–S46). Comparing the result of C_{60}, C_{70} adopts a 1:1 binding mode to form the co-crystal, and it is bound 'side-on' rather than 'end-on' to the center of cobalt corrole, consistent with the structural deductions based on ^{13}C NMR experiment. The unit cell in this case includes two 1:1 complexes of **4** and C_{70}, and such 1:1 complex packs in a columnar manner in the crystal (Fig. 3).

Since the cobalt corrole has been proved that it can form stable supramolecular complexes with C_{60} and C_{70} both in solution and the solid state, it is meaningful to wonder if a cooperative effect of corrole can enhance the binding ability toward fullerene. Accordingly, two jaw-like bis-corroles **5** and **6** (Scheme 2) with different cavity size were designed and synthesized.[9d,13] The synthetic routes are shown in Scheme S1.

NMR titration experiments were conducted using the same method mentioned for **4** and C_{60}. The progressive shielding of the aromatic protons of corroles in **5** and **6** upon addition of the C_{60} guests fits well to a 1:1 binding isotherm (Fig. 4), and affords binding constants of 1139 M^{-1} for **5** and 1046 M^{-1} for **6** (Table 1). Job plots also agree with the 1:1 assembly mode for the supramolecular complexes (Figs. S32, S38). In addition, the ^{13}C NMR signal of C_{60} in **5**·C_{60} (142.182 ppm) shows slightly higher upfield shift than that in **6**·C_{60} (142.350 ppm), which reconfirms the greater binding ability of **5** toward C_{60} (Table S1).

Similar evaluation system was then applied to explore the interaction between the hosts **5**, **6** and C_{70}. K_a value was

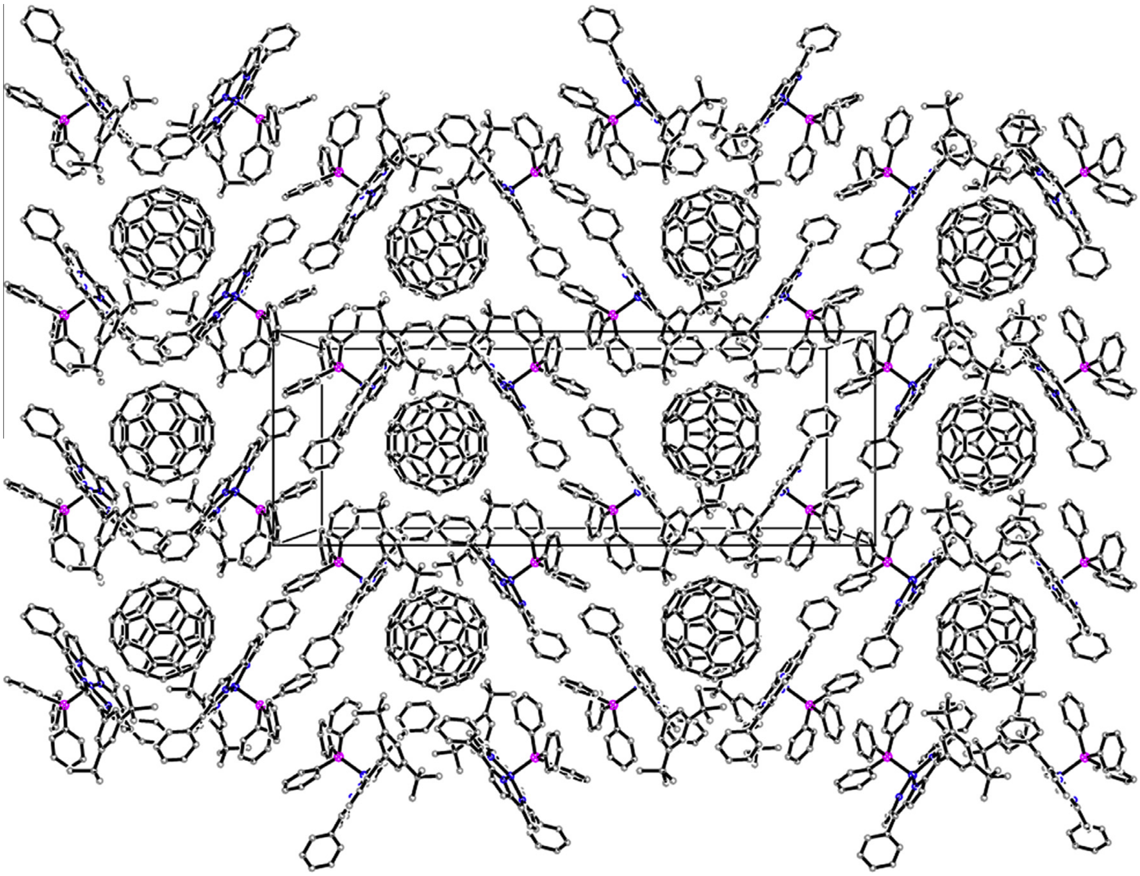


Figure 1. Stereoview of packing diagram for **4**·C_{60} with 50% thermal ellipsoids. Solvents and hydrogen atoms are omitted for clarity.

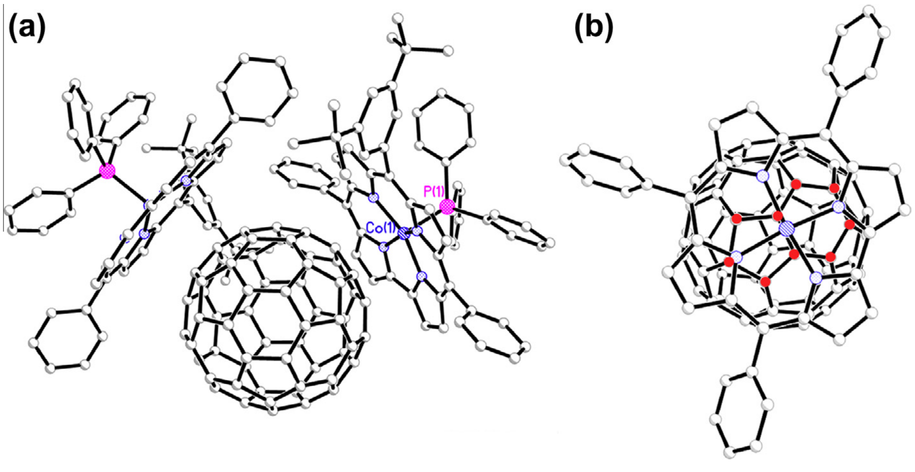


Figure 2. (a) X-ray structure of the 2:1 complex of cobalt corrole **4** with C_{60} with 50% thermal ellipsoids; (b) Illustration of orientation of C_{60} with respect to the corrole plane. Hydrogen atoms are omitted for clarity.

determined to be 3878 M^{-1} for **5** and 4305 M^{-1} for **6**, which indicates a more powerful binding ability for the hosts toward C_{70}. Unlike the result from bis-corrole-C_{60} system, here compound **6** tends to be more effective host toward C_{70} than **5**.

The difference of the cavity size in bis-corroles seems to have some influence on their inclusion ability toward fullerenes. Compound **5** with relatively small cavity size shows stronger binding ability toward C_{60} than compound **6**, whereas C_{70} binds to compound **6** more tightly than **5**. Furthermore, the evidently larger binding ability toward fullerenes was actually observed for bis-corroles **5** and **6** than corrole monomer **4**. So it should be safe to conclude that a cooperative effect must exist in the bis-corroles system, this may endow the corrole system with a probability of the fullerene purification. Although the cooperative effect is much less than the system with hydrogen-bonding-driven pre-organization reported by Professor Li,[14] it is undoubtedly larger than the corresponding jaw-like bis-porphyrins which also present the lack of pre-organization as hosts **5** and **6**.[9d]

In conclusion, the supramolecular interactions between cobalt corroles and fullerenes (C_{60} and C_{70}) have been systematically

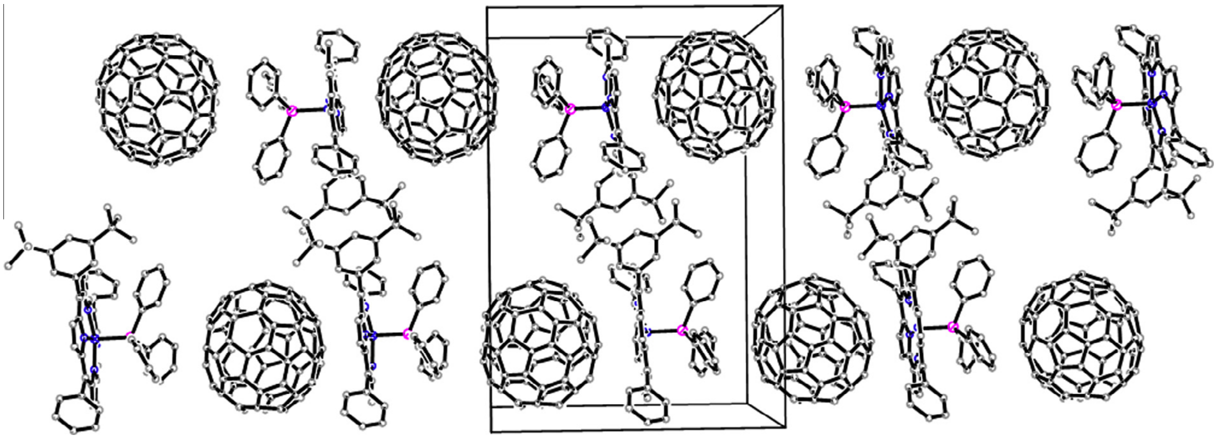
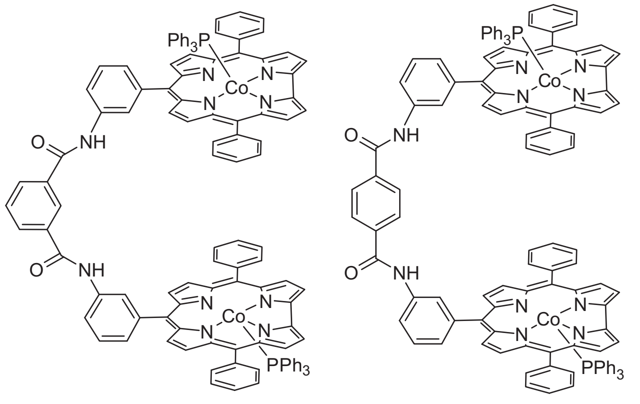


Figure 3. Stereoview of packing diagram for **4**·C_{70} with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.



5 **6**

Scheme 2. Structures of bis-corroles **5** and **6**.

explored both in solution and the solid state for the first time. It is very appealing that cobalt corroles can form stable complexes with fullerenes in solution. Further results from bis-corroles suggest a realizable way to construct powerful complexes of corroles and fullerenes with the aid of cooperative effect. This work will broaden the application of corroles in supramolecular chemistry. The effects of central metal ions and peripheral substitutes of corroles on the interaction of corroles with fullerenes are in progress.

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Supplementary data

Crystallographic data for the structures reported in this Letter have been deposited with the Cambridge Crystallographic Data

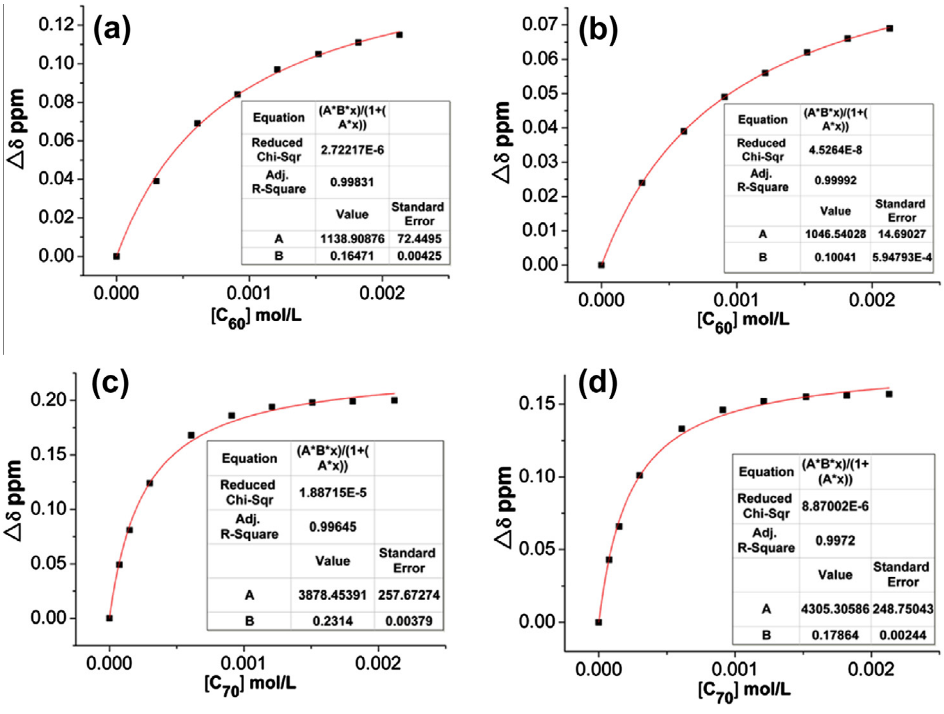

Figure 4. Nonlinear curve fitting of complexation induced chemical shift changes. (a) **5**·C_{60}, (b) **6**·C_{60}, (c) **5**·C_{70}, and (d) **6**·C_{70}.

Centre as supplementary publications CCDC 914118 (**4**·C60) and 915575 (**4**·C70). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.05.083. These data include MOL files and InChiKeys of the most important compounds described in this article.

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