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Coronene Nanophase within Coordination Spheres: Increased Solubility of C_{60}

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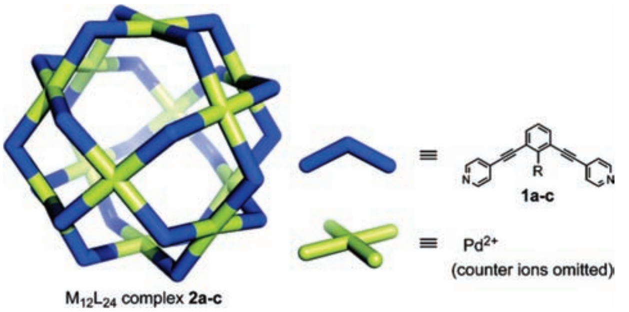
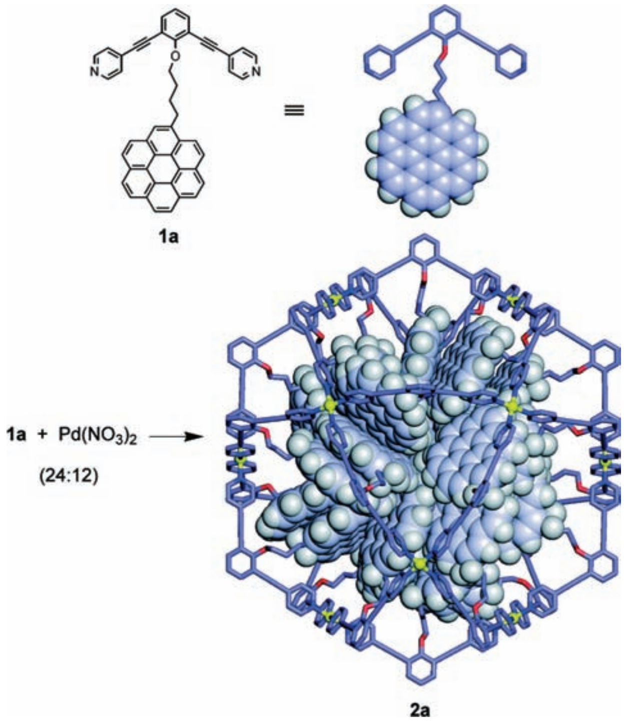
C_{60} and related fullerenes are sparingly soluble in most solvents, and aromatic solvents such as toluene or halobenzenes are typically used.[1] Increasing the size of the aromatic system increases the solubility of C_{60}, but this approach is quickly limited by the rapidly rising melting points.[2] Polycyclic aromatic hydrocarbons such as anthracene and coronene possess extended aromatic systems and are thus intriguing potential solvents for fullerenes, but they exist as solids at room temperature. Self-assembled $M_{12}L_{24}$ coordination spheres **2**[3,4] are useful for generating persistent, nanoscopic phases within the shell framework; hydrophobic[5] and fluorous[6] nanophases have been created by attaching alkyl and perfluoralkyl chains, respectively, to the inner face of ligand **1**. Here we report that use of ligand **1a** with coronene attached generates a nanoscopic coronene pseudosolvent phase that cannot exist under standard conditions. Within the coronene pseudosolvent phase, C_{60} is ~30 times more soluble than in toluene. The ability to generate aromatic nanophases within sphere **2a** allows large π-conjugated molecules to be used as solvents and their solvent properties to be explored.



Bidentate ligand **1a** with pendant coronene (Scheme 1) was prepared from 2,6-dibromophenol in two steps [see the Supporting Information (SI)]. When ligand **1a** (0.0070 mmol) was treated with $Pd(NO_3)_2$ (0.0042 mmol) in DMSO-d_6 (0.7 mL) for 4 h at 70 °C, the quantitative formation of $M_{12}L_{24}$ spherical complex **2a** (Scheme 1) was confirmed by ^1H NMR spectroscopy (1D and DOSY[3,5,6]). Cold-spray ionization mass spectrometry (CSI-MS)[7] confirmed the $M_{12}L_{24}$ composition of **2a′**, in which NO_3^- is replaced by BF_4^- (see the SI), with a molecular weight of 18 892 Da ($[\mathbf{2a'} - (BF_4^-)_n + (DMSO)_m]^{n+}$, where $n = 5-13$, $m = 0-3$; see Figure S3 in the SI).

Sphere **2a** contains 24 large aromatic coronene molecules located inside the 4.6 nm-sized shell framework. Despite the strong tendency of aromatic molecules to stack, the hydrogens of the 24 coronenes remained equivalent in the ^1H NMR spectrum, and the signals were not considerably broadened (see Figure S1 in the SI). This indicates that within the sphere the 24 coronene molecules behave as a liquid "nanodroplet" rather than a solid "nanocrystal".[8,9]

Scheme 1. Self-Assembly of $M_{12}L_{24}$ Coordination Sphere **2a** with 24 Pendant Coronene Molecules



A remarkable property of the coronene nanophase in **2a** is its ability to dissolve C_{60} with much higher solubility than bulk aromatic solvents. After excess ^{13}C-enriched C_{60}[10] was suspended in a DMSO solution of **2a** and the mixture was stirred for 3 days at 50 °C, the ^{13}C NMR spectrum showed the appearance of a new C_{60} signal ($\delta = 141.2$ ppm) in addition to the signal of free C_{60} ($\delta = 142.5$ ppm) (Figure 1a,b). In view of the poor solubility of C_{60} in DMSO, the new C_{60} signal was quite intense and indicated the high solubility of C_{60} within **2a**. Shielding by the coronene molecules resulted in an upfield shift for the new C_{60} signal, supporting the dissolution of C_{60} in the coronene nanophase of **2a**. Quantitative ^{13}C NMR measurements with a sufficient repetition delay time (110 s, which is 5 times longer than the spin−lattice relaxation time T_1 of C_{60} with no noticeable nuclear Overhauser effect) showed that 0.4 molecules of C_{60} are accommodated per sphere **2a**, i.e., that 40% of the spheres **2a** contain one C_{60} molecule. The local concentration of C_{60} in the $C_{60}\cdot\mathbf{2a}$ complex is 128 mM, which is much higher than in the standard aromatic solvents benzene (2.4 mM) and toluene (3.9 mM).[2] On the other hand, sphere **2c** ($R = CH_3$)[3b] lacks an aromatic inner phase and could not dissolve C_{60}, indicating that the coronene molecules of sphere **2a** are essential for the inclusion of C_{60} (Figure 1d).

The pseudosolution state within sphere **2a** implied by the random alignment and the mobility of the confined coronene moieties allows the dissolution of other guest molecules with various shapes and sizes. To illustrate, the planar aromatic molecule naphthalenediimide (**3**) was dissolved within sphere **2a**. When 6 equiv of **3** was added

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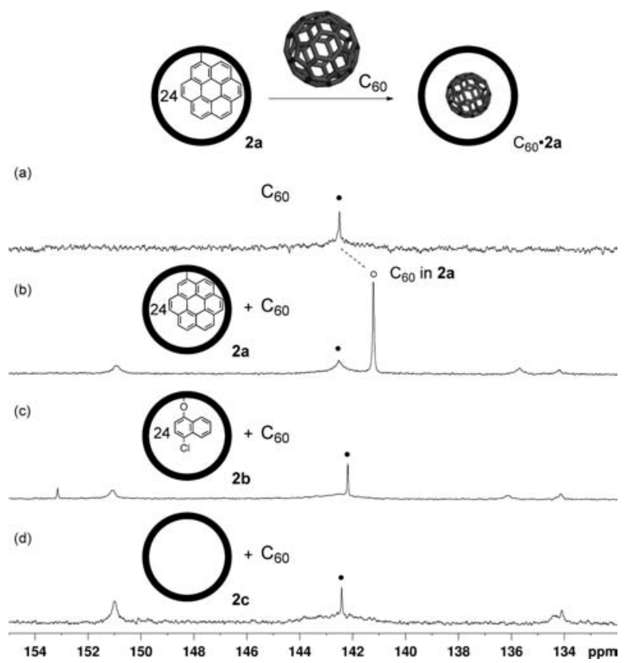

Figure 1. ^{13}C NMR spectra (125 MHz, DMSO-d_6, 300 K) of (a) free C_{60} and (b−d) C_{60} in the presence of (b) **2a**, (c) **2b**, and (d) **2c** (●, free C_{60}; ○, C_{60} in **2a**).

to a 10:1 DMSO-d_6/D_2O solution of **2a** (0.38 mM), the accommodation of **3** within **2a** was evidenced by the large upfield shifts in the signals of **3** ($\Delta\delta_{CH_a} = 2.96$ ppm) in the ^{1}H NMR spectrum (Figure 2). Only one band (with $D = 3.3 \times 10^{-11}$ m^2 s^{-1}) was observed in the DOSY NMR spectrum, showing that **3** was completely dissolved in sphere **2a** and that free **3** ($D = 2.9 \times 10^{-10}$ m^2 s^{-1}) no longer remained in solution.

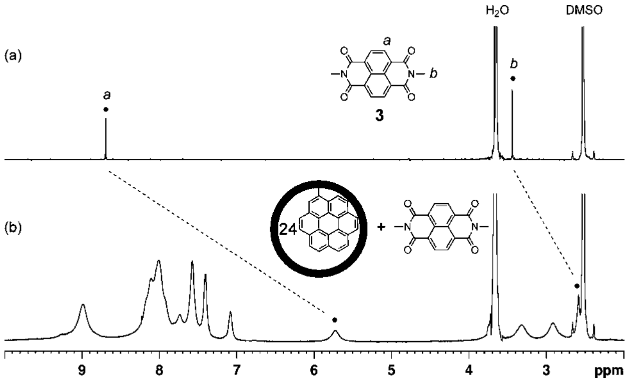

Figure 2. ^{1}H NMR spectra (500 MHz, 10:1 DMSO-d_6/D_2O, 300 K) of (a) free **3** and (b) **3** in the presence of sphere **2a** (●, **3**).

This method of generating aromatic pseudosolution phases is general, and various aromatic molecules can be used. To demonstrate, ligand **1b** with pendant chloronaphthalene and sphere **2b** containing 24 molecules of chloronaphthalene were obtained. However, the interaction of sphere **2b** with C_{60} was weak, and only a slightly upfield-shifted, averaged ^{13}C NMR signal for free and enclathrated C_{60} was observed ($\delta = 142.2$ ppm). Presumably, the total aromatic surface area of the 24 chloronaphthalenes was not enough to efficiently dissolve C_{60} within the sphere (Figure 1c).

In summary, we prepared 4.6 nm-sized coordination spheres with 24 coronene molecules concentrated inside. Within the rigid shell framework, the confined coronene molecules remain fluid and form a coronene aromatic "nanophase" whose formation would be impossible under standard conditions. The increased solubility of aromatic molecules within this aromatic nanophase enables the exploration and expansion of the chemistry of poorly soluble aromatic molecules.

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Supporting Information Available: Experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The local concentration of coronene in the sphere was estimated to be 3.1 M, which is ~2000 times higher than in a saturated DMSO solution. The effective volume of the sphere (13.0 nm^3) was calculated using Accelrys Materials Studio software, version 4.4, by assuming an inscribed sphere. The 24 coronene moieties occupied 65% of the inner void, leaving sufficient space for other guest molecules.

(9) The concentration of coronene in a saturated DMSO solution was determined to be 1.6 mM using ^{1}H NMR analysis with 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt (TSP-d_4) as an internal standard.

(10) ^{13}C-enriched C_{60} was obtained from MTR Ltd. The ^{13}C content was 20−30%, as determined by MALDI-TOF MS.

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