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Synthesis of a Trinuclear Tropolone–Palladium(II) Macrocycle and Its C_{60} Inclusion Properties

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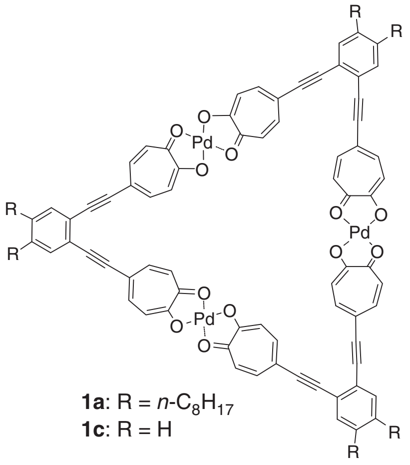
4,5-Dialkyl-1,2-bis(5-tropolonylethynyl)benzenes **5a** and **5b** were synthesized, and dioctyl derivative **5a** was converted into the corresponding trinuclear palladium(II) macrocycle **1a** by reacting it with $Pd(OAc)_2$. Macrocyclic supramolecular coordination complex **1a** has an inner cavity just large enough to include C_{60}. Although trinuclear palladium complex **1a** incompletely incorporated C_{60} in solution owing to weak interactions between the bis(tropolono)palladium(II) moieties and C_{60}, it formed an inclusion complex with C_{60} in the solid state. The inclusion complex showed a moderate charge-transfer absorption in the UV–vis–NIR spectra.

Study of self-assembled supramolecular coordination complexes with well-defined inner cavities has become important for gaining specific information concerning structural, electronic, and optical properties, especially in relation to "inner" and "outer" domains.[1,2] Macrocyclic metal complexes with shape-persistent, noncollapsible backbones are useful for building porous surface networks and inclusion complexes.

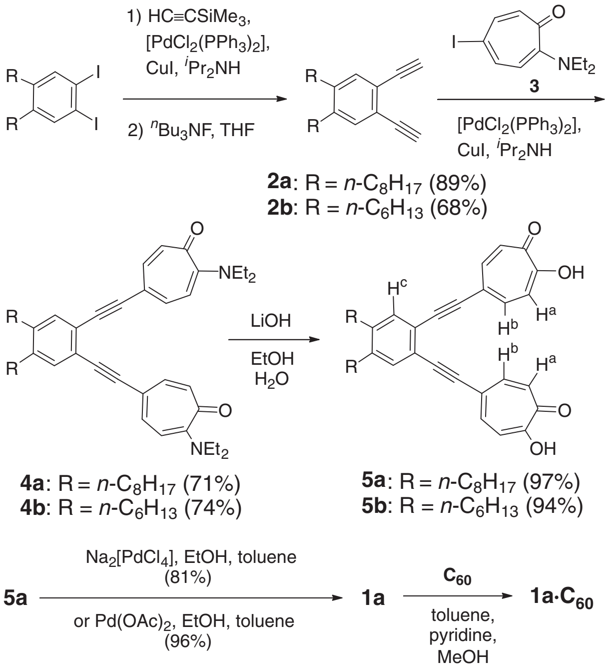
Tropolone and related 2-substituted tropones act as versatile ligands in inorganic and organometallic chemistry.[3] They form chelate complexes with various metal ions via the carbonyl oxygen and vicinal substituents. In this respect, the metal complexes formed with tropolone and related 2-substituted tropones have been employed as catalysts for polymerization,[4] building blocks for supramolecular coordination complexes,[5] stable liquid crystals,[6] and magnetic units for molecular-based magnetic materials.[7] However, only a limited number of tropolone–metal macrocycles have been reported, presumably due to the difficulty in forming cyclic structures among common octahedral tropolone–metal complexes.[5] Recently, we found that a square-planar bis(tropolono)palladium(II) complex can be employed in constructing a macrocyclic framework, which has an inner cavity just large enough to include C_{60} as a guest. Herein, we report the synthesis of large triangular tropolone–palladium complex **1a** (Figure 1). Moreover, we also report the complexation of **1a** with C_{60}.

Building blocks **5a** and **5b** for synthesizing tropolone–palladium(II) macrocycle **1** were synthesized by modifying our previously reported procedure (Scheme 1). The reaction of dialkyldiethynylbenzenes **2a** and **2b** with 2-diethylamino-5-iodotropone (**3**) under Sonogashira coupling conditions proceeded smoothly to afford bis(aminotropone) compounds **4a** (71%) and **4b** (74%). **4a** and **4b** were hydrolyzed with LiOH in aq. EtOH to afford bis(tropolone) compounds **5a** and **5b**, respectively. Although **5a** and **5b** could not be purified by using



1a: R = n-C_8H_{17}
1c: R = H

Figure 1. Molecular structure of trinuclear tropolone–Pd complexes **1a** and **1c**.



Scheme 1. Synthesis of **5a**, **5b**, **1a**, and **1a·C_{60}**.

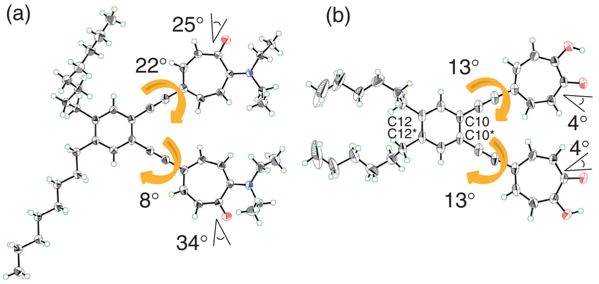


Figure 2. X-ray crystal structures of (a) **4a** and (b) **5b**. The yellow curved arrows show the dihedral angle between the central benzene and terminal tropone rings. Wedges represent the bend angles between the carbonyl groups and C^3–C^4–C^5–C^6 carbons in the tropone and tropolone rings.

column chromatography on silica gel due to their high polarity, they could be purified by recrystallization from CH_2Cl_2–hexane to give pure **5a** (97%) and **5b** (94%) as yellow prisms. Both **5a** and **5b** are stable and can be stored in air at room temperature for more than 1 year.

The crystal structures of **4a** and **5b**, single crystals of which were obtained by recrystallization from $CHCl_3$–hexane and THF–hexane, respectively, were determined by using X-ray analysis.[8] As shown in Figure 2a, the two tropone rings in **4a** are twisted toward the central benzene ring presumably due to packing effects of the bulky diethylamino groups. The dihedral angles between the central benzene and terminal tropone rings in **4a** are 8 and 22°. Furthermore, to decrease steric congestion, the carbonyl groups in the tropone rings are bent by 34 and 25° to form an envelope-like conformation of the tropone ring. The molecular structure of **5b** has crystallographic C_2 symmetry with a twofold axis passing through the midpoints of C(10)–C(10*) and C(12)–C(12*) (Figure 2b). In contrast to the structure of **4a**, the dihedral angles between the central benzene and terminal tropone rings in **5b** are 13°, and the carbonyl groups in the tropone ring in **5b** are almost planar (bend angle: 4°) because there is only a small amount of steric repulsion between the carbonyl and hydroxy groups.

To construct a macrocyclic supramolecular coordination complex composed of benzene rings, acetylene linkages, and bis(tropolono)metal moieties, a square-planar metal-complex unit is indispensable, although most bis(tropolono)metal complexes adopt nonplanar octahedral structures.[3c,3d,3f] We chose a diamagnetic bis(tropolono)palladium(II) complex as a metal unit to prepare supramolecular coordination complex **1**. The coordination sphere around the palladium(II) ions in bis(tropolono)palladium(II) moieties is almost square planar (O–Pd–O angles are 81.83–99.28°), and there are no steric interactions among the atoms in **1**.[9] The palladium complexes could be easily characterized by using ^{1}H NMR analysis.

Complex **1b** with hexyl substituents is much less soluble than **1a** with octyl substituents. Therefore, further studies on the synthesis of macrocyclic palladium complexes and their incorporation of C_{60} in the inner cavity were performed only using **1a**. Trinuclear tropolone–palladium(II) complex **1a** was prepared by mixing a solution of **5a** in toluene with a solution of $Na_2[PdCl_4]$ in ethanol and with a solution of $Pd(OAc)_2$ in ethanol in 81% and 96% yields, respectively, as a dark brown solid. Although **1a** is hardly soluble in common organic solvents except for pyridine, **1a** could be characterized by using spectroscopic analysis. MALDI-TOF MS showed $[M + H]^+$ at 2085.51 with the correct isotopic ratio (Figure S2). In the ^{1}H NMR spectra acquired in pyridine-d_5 (Figure 3), the tropolone protons were shifted downfield (δ 7.96 (H^a), 7.46 (H^b)) compared to those of **5a** (δ 7.75 (H^a), 7.40 (H^b)), whereas the benzene proton (H^c) was shifted slightly upfield (**5a**: δ 7.69; **1a**: δ 7.66). In the UV–vis absorption spectra in pyridine, **1a** showed a small red shift (**5a**: 380 and 418(sh) nm; **1a**: 397 and 430(sh) nm; (sh): shoulder).

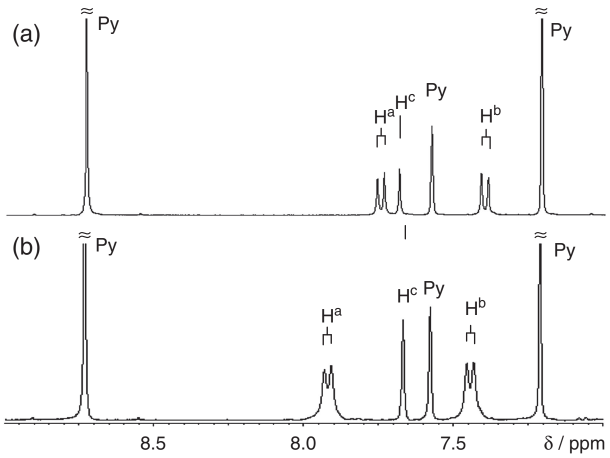


Figure 3. Aromatic region in the ^{1}H NMR spectra (500 MHz) of (a) **5a** and (b) **1a** in pyridine-d_5 at 25 °C.

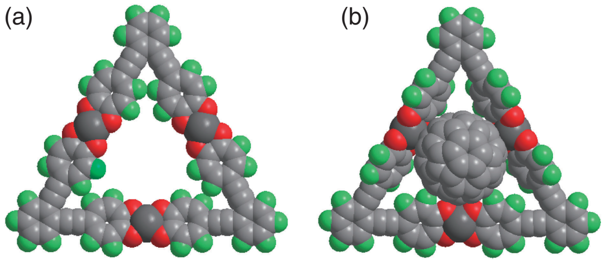


Figure 4. Calculated structures of **1c** and **1c**•C_{60}.[8] (a) Planar **1c** at B3LYP/LAN2DZ level. (b) **1c** with C_{60} in the inner cavity at HF/STO-3G. The diameter of inner cavity is 12.4 Å, which is large enough to fit C_{60} (7.1 Å), considering van der Waals radii.

DFT calculations (B3LYP/LAN2DZ) on unsubstituted macrocyclic trinuclear palladium(II) complex **1c** predicted an almost planar structure with roughly C_2 symmetry (Figure 4a). Since there were two doublets for the tropolone units in the ^{1}H NMR spectrum of **1a**, the bis(tropolono)palladium(II) moiety freely rotates on the NMR time scale. Although the planar structure of **1c** cannot incorporate C_{60} in the inner cavity, the conformation with the bis(tropolono)palladium(II) moieties nearly vertical to the molecular plane (Figure 4b) has an inner cavity size large enough to fit C_{60}. Therefore, we examined the incorporation of C_{60} inside **1a**.[10]

A solution of **1a** in pyridine was mixed with a solution of C_{60} in toluene to afford a dark brown solution, from which a dark brown solid was obtained after evaporation of the solvent.[11] The solubility of the dark brown solid in either toluene or pyridine was greater than those of **1a** and C_{60}, indicating the formation

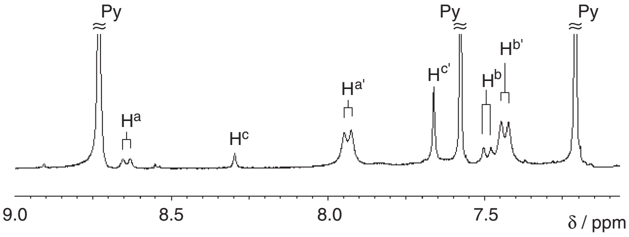


Figure 5. Aromatic region in the ^1H NMR spectrum (500 MHz) measured 1 h after dissolving 1.4 mg of **1a**·C_{60} in pyridine-d_5 (0.5 mL) at 25 °C [**1a**·C_{60} (H^a, H^b, and H^c) and **1a** ($H^{a'}$, $H^{b'}$, and $H^{c'}$)].

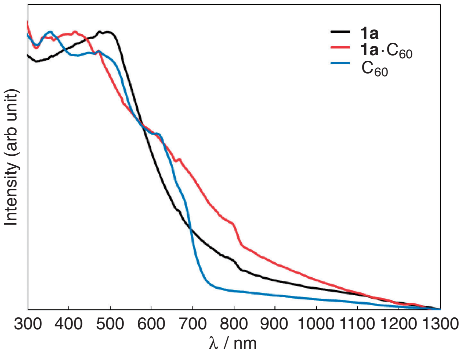


Figure 6. Normalized solid-state UV–vis–NIR spectra of **1a**, C_{60}, and **1a**·C_{60} using integrating spheres.

of **1a**·C_{60}, as shown in Figure 4b. However, C_{60} gradually precipitated from the toluene solution, followed by precipitation of **1a**. In the ^1H NMR spectra of **1a**·C_{60} in pyridine-d_5 (Figure 5), the tropolone protons at δ 8.65 (H^a) and 7.49 (H^b) and the benzene proton at 8.30 (H^c) were markedly downfield-shifted from those of **1a** (δ 7.94 (H^a), 7.44 (H^b), and 7.66 (H^c)). Because of the weak binding constant for **1a**·C_{60} ($K_a = 580$ at 25 °C) in pyridine-d_5,[12,14] **1a**·C_{60} was rapidly dissociated in pyridine-d_5.[15] The large downfield shift of the H^c proton in **1a**·C_{60} indicates that aggregation occurs in pyridine-d_5.[16] Thus, we believe that C_{60} can be incorporated in the cavity of **1a**.

The UV–vis–NIR absorption spectra of **1a**, C_{60}, and **1a**·C_{60} in the solid state are shown in Figure 6. Although the UV–vis–NIR spectra of **1a** and **1a**·C_{60} are similar, a charge-transfer (CT) absorption was observed at 700 nm with tailing up to 1000 nm.[17]

In summary, we synthesized a new supramolecular tropolone–palladium(II) complex, **1a**, with a large inner cavity and investigated its ability to incorporate C_{60}. Although the low solubility of **1a**, C_{60}, and **1a**·C_{60} in common organic solvents made it difficult to characterize them in solution, a peak indicating a CT interaction between **1a** and C_{60} was observed in the solid-state UV–vis–NIR spectrum of **1a**·C_{60}. We believe that our results are important for developing functional supramolecular coordination complexes with new electronic and optical properties.

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Supporting Information is available electronically on J-STAGE.

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8 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 988875 for **4a** and CCDC 988876 for **5b**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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11 XRD analysis of the dark brown solid of **1a**·C_{60} revealed an amorphous pattern.

12 By assuming the formation of 1:1 complex **1a**·C_{60}, the binding constant was determined by the ^1H NMR spectrum of **1a**·C_{60} (1.35 mg) in pyridine-d_5 (0.5 mL) at 25 °C (Figure S5). All **1a**, C_{60}, and **1a**·C_{60} were soluble in pyridine-d_5 under these conditions.[13]

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14 Mixing a solution of **1a** in pyridine with C_{60} in the same solvent at room temperature very slowly formed only a small amount of **1a**·C_{60}.

15 The ratio of **1a**·C_{60} and **1a** was 0.5:1 5 min after dissolving **1a**·C_{60} in pyridine-d_5 at 25 °C. However, the ratio of **1a**·C_{60} and **1a** changed to 0.4:1 1 h after dissolving **1a**·C_{60} under the same conditions (Figure S6).

16 Tropolone–metal complexes easily form a dimeric structure.[3c–3f] Therefore, the formation of a 2:1 **1a**·C_{60} complex or $(\mathbf{1a})_m \cdot (C_{60})_n$ complexes can be expected. However, the low solubility of **1a**, C_{60}, and **1a**·C_{60} in common organic solvents prevented further studies on aggregation behavior in solution.

17 HOMO and LUMO orbitals of **1a**·C_{60} are consistent with the CT absorption (Figure S7).