

## Metal-Directed Assembly of Triple-Layered Fluorescent Metallophthalocyanes

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Over the past decade, researchers in the area of supramolecular photochemistry have made impressive progress toward the development of molecular sensors and light-harvesting materials. This is due in part to the rapid growth of synthetic techniques, which enable one to construct complex molecular architectures.<sup>1</sup> The synthesis and study of cyclophanes has been a particularly active area of research.<sup>2</sup> These compounds allow one to align and stack chromophores and redox-active groups within a macrocyclic cavity, which often leads to host–guest structures with novel photophysical properties. Considerable effort has been dedicated to the synthesis of cyclophanes that contain both electron donor (D) and acceptor (A) moieties so that D–A interactions can be explored in the context of a structure with fixed and well-defined D–A orientations and distances.<sup>3</sup> To date, advances in this field have involved impressive, but often tedious, low-yielding, covalent synthetic methods.

Our group recently reported a new high-yield approach for preparing binuclear metallocyclophanes from flexible ligands and readily available metal precursors.<sup>4</sup> This synthetic strategy involves two elementary steps, the initial preparation of a condensed intermediate held together via weak metal–oxygen links followed by the expansion of that structure via its reaction with small molecules that can break the metal–oxygen bonds, Scheme 1. Since all of the ligands that are used in this approach are derived from simple quinone precursors, a large number of binuclear macrocyclic structures with synthetically tailorable chemical and physical properties can be prepared easily. Herein, we demonstrate that the “weak-link” synthetic approach can be used to design and prepare novel fluorescent metallocyclophanes with the appropriate cage dimensions and reactivity for sequestering and aligning bifunctional “A” molecules in virtually quantitative fashion.

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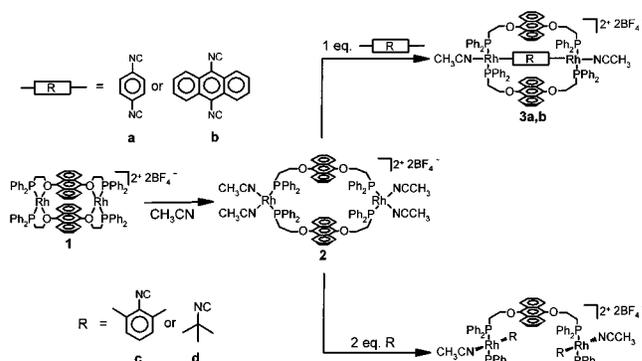
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### Scheme 1



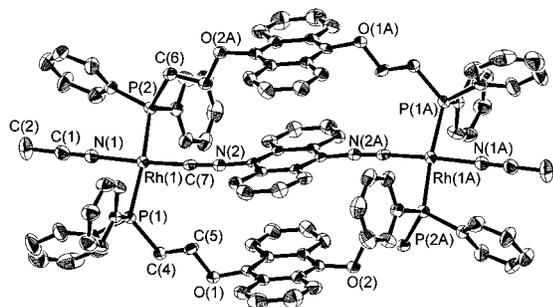
The new ligand, 9,10-bis[2-(diphenylphosphino)ethoxy]anthracene, was prepared in two steps by modifications of literature procedures for alkylating quinones<sup>5</sup> and nucleophilic substitution.<sup>4a</sup> The “condensed” rhodium macrocycle **1** (Scheme 1) was prepared in >99% yield by reaction of 9,10-bis[2-(diphenylphosphino)ethoxy]anthracene with  $[\text{RhCl}(\text{COT})_2]_2$  (COT = cyclooctene).<sup>4</sup> Upon addition of acetonitrile to a methylene chloride solution of **1**, the weak Rh–O linkages of **1** are selectively broken resulting in the quantitative formation of open macrocycle **2**, Scheme 1. Significantly, the conversion of the condensed macrocycle **1** into **2** is accompanied by a 10-fold increase in the fluorescence intensity of an emission band at 442 nm (excitation at 390 nm). The increase in fluorescence is due to two factors: (1) the breaking of the Rh–O bonds, which results in a large decrease in the through-bond communication between the metal center and the anthracenyl fluorophores and (2) the “opening” of the macrocycle which causes a decrease in the through-space interactions between the two fluorophores and the metal centers and fluorophores.<sup>6</sup>

The coordinatively labile rhodium(I) centers in **2** facilitate the binding of a variety of A molecules with para-ligating moieties within the metallocyclophane cavity. Herein, we provide two different examples involving aryl diisocyanides, and in principle this reactivity allows one to study many different acceptor molecules without complicated synthetic manipulation. For comparison purposes, the reactions between macrocycle **2** and several mono- and diisocyanides have been explored by titration experiments, Scheme 1. Upon addition of 1 equiv of a para-substituted aromatic diisocyanide such as 1,4-phenylene- and 9,10-anthracenediisocyanide to a  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (100:1) solution of compound **2**, the “three-tiered” structures, **3a**, **b** are formed in quantitative yields, respectively. Both **3a** and **3b** have been fully characterized in solution, and the solid-state structure of **3b** has been determined by a single-crystal X-ray diffraction study,<sup>7</sup> Figure 1. This

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(7) Single crystals for X-ray diffraction study were grown by slow diffusion of pentane into a saturated solution of **3b** in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (10:1). Crystal data for **3b**:  $\{[\mu^2\text{-}9,10\text{-bis[2-(diphenylphosphino)ethoxy]anthracene}]_2\text{-}(\mu^2\text{-}9,10\text{-anthracenediisocyanide})(\text{CH}_3\text{CN})_2\text{Rh}_2\}[\text{BF}_4]_2 \cdot 6 \text{CH}_2\text{Cl}_2 \cdot \text{CH}_3\text{CN}$ , MW = 2509.70, monoclinic,  $C2/c$ ,  $a = 35.3676(3) \text{ \AA}$ ,  $b = 14.3486(2) \text{ \AA}$ ,  $c = 21.8735(2) \text{ \AA}$ ,  $\beta = 95.6070(7)^\circ$ ,  $V = 11047.2(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 173(2) \text{ K}$ ,  $D_{\text{calc}} = 1.509 \text{ g cm}^{-3}$ , orange blade,  $0.40 \times 0.25 \times 0.2 \text{ mm}$ ,  $\mu(\text{Mo K}\alpha) = 7.15 \text{ cm}^{-1}$ ,  $R_I$  (based on  $F_o^2$ ) = 6.86% for 8635 observed independent reflections ( $3.54^\circ \leq 2\theta \leq 48.00^\circ$ ). The asymmetric contains half of the rhodium cation, a tetrafluoroborate anion, three molecules of dichloromethane, and half a molecule of an acetonitrile residing along a 2-fold axis.



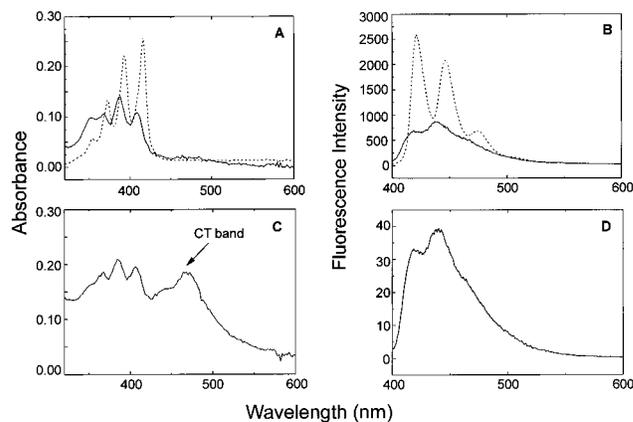
**Figure 1.** ORTEP drawing of complex **3b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and anions are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)–Rh(1a) = 11.64(12), Arene–Arene = 4.197(5); Rh(1)–P(1) = 2.3199(14), Rh(1)–P(2) = 2.3422(14), Rh(1)–N(1) = 2.034(5), Rh(1)–C(7) = 1.884(5), P(1)–Rh(1)–P(2) = 172.50(5), P(1)–Rh(1)–N(1) = 88.18(13), P(1)–Rh(1)–C(7) = 90.68(15), P(2)–Rh(1)–N(1) = 85.80(13), P(2)–Rh(1)–C(7) = 95.71(15), N(1)–Rh(1)–C(7) = 174.8(2).

structure shows that the metallocyclophane fluorophores are separated by 4.197 Å from the sequestered aryl diisocyanide and aligned with it in a cofacial fashion. Monoisocyanides, such as *tert*-butylisocyanide and 2,6-dimethylphenylisocyanide, form 2:1 complexes **4c**, **d**, with the concomitant release of acetonitrile; a *cis* to *trans* rearrangement of the phosphine ligands around the Rh(I) centers accompanies this transformation.<sup>4b,8</sup>

Compounds **2**, **3a**, **b** and **4c**, **d** have been studied by UV–vis, emission, and excitation spectroscopy. Macrocycle **2** displays UV–vis spectra characteristic of 9,10-functionalized anthracene chromophores<sup>9</sup> [**2**]:  $\lambda_{\text{max}} = 390$  nm ( $\epsilon = 37\,200$ ), CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (100:1)] and a broad structureless emission at 442 nm, Figure 2A and B (–). Of the isocyanides explored (mentioned above) only 9,10-anthracenediisocyanide absorbs and emits in the spectral window studied (300–800 nm) [ $\lambda_{\text{max}} = 416$  nm ( $\epsilon = 16\,100$ ),  $\lambda_{\text{max}}$  emission = 420 nm, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (100:1)], Figure 2A and B (– – –).

Interestingly, the electronic spectra of the triple-layered metallocyclophanes **3a** and **3b**<sup>10</sup> display both structured bands similar to **2** and broad, structureless charge-transfer (CT) bands (**3a**, 356 nm; **3b**, 466 nm, Figure 2C) which are characteristic of D–A containing cyclophanes.<sup>2a</sup> These broad absorption bands are attributed to intramolecular CT interactions between the donor anthracenyl group and the sequestered acceptor arene because neither the electronic spectrum of **2** nor that of the acceptor diisocyanide molecules free in solution exhibit a longer wavelength band, Figure 2A.<sup>3d</sup> The CT excited states are non-emissive, and the excitation spectrum of the emission band at 442 nm in each case gives rise to the structured absorption band observed in the electronic spectrum of **3a** and **3b**.

The fluorescence lifetimes of compounds **2**, **3a**, and **3b** were measured in 100:1 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN [**2**:  $\tau_F = 11.5$  ns, **3a**:  $\tau_F = 9.8$  ns, **3b**:  $\tau_F = 7.1$  ns]. The moderate decrease in fluorescent lifetime that accompanies the conversion of **2** to either **3a** or **3b** as well as the continuing existence of both a structured absorption band and CT band in the UV–vis spectra of **3a** and **3b** indicate that the sequestered acceptors in both metallocyclophanes are



**Figure 2.** Electronic absorption and emission spectra ( $\lambda_{\text{excitation}} = 390$  nm) of compounds **2** (–) and 9,10-anthracenediisocyanide (– – –), A and B, and compound **3b**, C and D.

forming CT complexes with only one of the two donor moieties. The remaining donor chromophore is left only slightly perturbed and retains its characteristic electronic, fluorescence emission,<sup>11</sup> and excitation spectra, Figure 2.

Finally, reactions between **2** and either *tert*-butylisocyanide or 2,6-dimethylphenylisocyanide showed no appreciable change in the fluorescence signal of the macrocycle as the 2:1 complexes **4c**, **d** were formed, demonstrating that the photophysical responses associated with **3a**, **b** are not due to a steric shielding of the anthracenyl chromophores from one another or an electronic change at the metal centers brought on by their binding to isocyanide ligands.

This paper is significant for the following reasons. First, it demonstrates that one can use metal-directed assembly to prepare a new class of fluorescent metallocyclophanes in fewer steps and higher yield than conventional methods based on covalent organic synthesis. Second, the ability to systematically introduce different acceptors into a D–A–D triple-layered structure provides a synthetic flexibility that is a major advantage over covalent synthetic methods. Third, the emission properties of these systems are striking as others have found that metal centers within the context of such structures often completely quench the fluorescence associated with the organic chromophoric ligands.<sup>12</sup> The generality of this approach and the novel photophysical properties of these metallocyclophanes will provide insight and some exciting opportunities in the areas of electron transfer and synthetic receptor design.

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**Supporting Information Available:** Experimental details for photophysical measurements, synthesis of all compounds, and X-ray structural data for **3b**, including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) The large decrease in observed fluorescence intensity in **3b** is due to “trivial quenching” (quenching due to the reabsorption of emitted light within the sample, not competing decay processes such as energy or electron transfer) as the CT absorption (466 nm) significantly overlaps with the fluorescence emission (442 nm) of the unperturbed anthracene chromophore.

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(10) (**3a**):  $\lambda_{\text{max}} = 356$  nm ( $\epsilon = 51\,100$ ); (**3b**):  $\lambda_{\text{max}} = 386$  nm ( $\epsilon = 60\,700$ ).