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Synthesis of a New Ligand for Transition Metal–Fullerene Supramolecular Systems

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A new ligand has been designed that provides a relatively simple framework to build supramolecular systems containing both fullerene and transition-metal moieties. The modular framework of the ligand allows for the easy design of more complex systems. Analysis of absorption and emission spectra suggests significant photoinduced charge transfer between the two moieties. More complex systems and the excited-state photophysics of the presented systems are being studied.

Since their discovery some 20 years ago,[1] fullerenes have garnered significant interest in the field of photochemistry and molecular electronics for their ability to reversibly undergo multiple one-electron reductions and their large absorption cross area. The former property would make the fullerene a potential "energy dump" for electrons in a supramolecular system following photoinduced electron transfer, while the latter would indicate the fullerene could be used as a light-harvesting antenna with the capability of absorbing a broad range of light (unlike unsensitized inorganic semiconductors). Hence, having fullerene "building blocks" for use in organometallic supramolecular systems would be desirable to the research community. Several research groups have linked fullerene C_{60} to transition-metal (TM) chromophores (e.g., $-Ru^{II}(bpy)_2{}^{2+}$, where bpy = 2,2′-bipyridine)[2−10] and incorporated them into π-conjugated polymers[11−18] using relatively complicated structures.[19,20] While these systems do successfully link these moieties, they provide no convenient electronic pathway between the fullerene and the TM chromophore. Therefore, there is little advantage from a purely electronic standpoint as to their linkage.

Our research group has recently developed a new methodology to provide a simple, rigid, and relatively conjugated link between fullerene C_{60} and a TM chromophore. This linkage is demonstrated by the synthesis of ligand **1** and rhenium complex **Re-1** (Scheme 1). The center of ligand **1** is a basic ethynyl-substituted bipyridine (**5**) commonly used as a TM ligation point in supramolecular systems.[21] Substituted fullerene **4** is inspired by previously reported fullerene substitution chemistry.[8,22−24] The resulting substituted fullerene **4** following a Diels−Alder reaction can be used as a new supramolecular "building block" that could be readily

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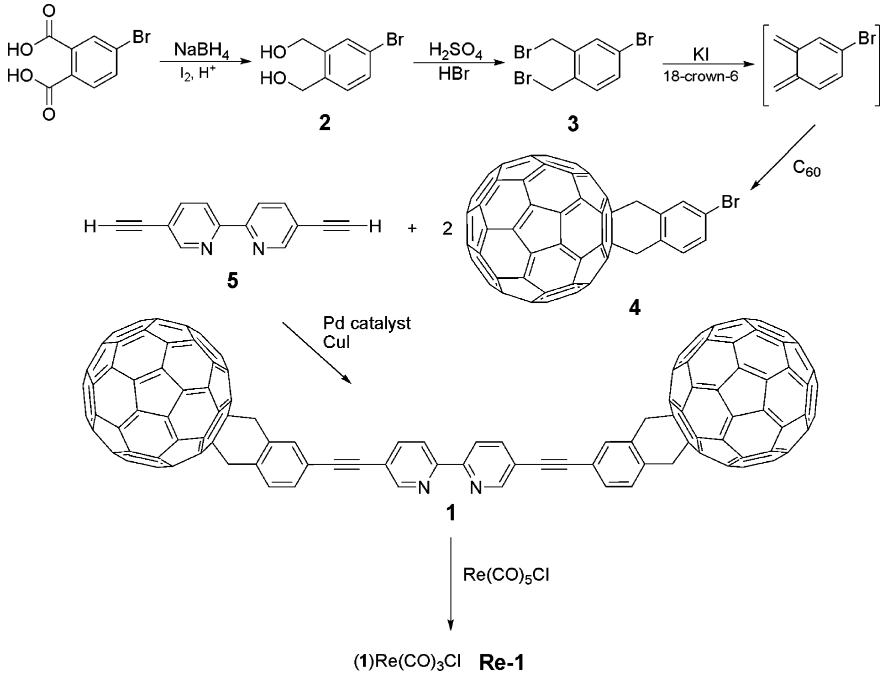
Scheme 1. Synthesis of **1** and **Re-1**



incorporated with other moieties and be utilized as a molecular electronics device. The two subunits are linked via standard Sonogashira coupling techniques.[21,25−27] As expected from the nature of the Diels−Alder reaction, the preparation of **4** can lead to multiply functionalized fullerenes.[28] We have recently reported a novel high-performance liquid chromatography separation methodology to isolate the singly substituted fullerene,[29] although we have subsequently discovered that thorough Soxhlet extraction produces similar results. TM complex **Re-1** was then prepared using standard coordination techniques.[30] NMR and IR spectra confirm the successful synthesis of these systems (see the Supporting Information for full synthetic and spectroscopic details).

Absorption spectra of **4**, **1**, and **Re-1** are shown in Figure 1. The spectra for all three species are dominated by a significant π,π^* absorption band at 330 nm. The π,π^* band is similar in position and intensity to those of other fullerene absorption studies.[31,32] The high absorptivity values for these systems (including the rhenium complex) suggest the dominance of the ground-state absorption manifold by the fullerene moiety. Indeed, there is no significant metal-to-ligand charge-transfer (MLCT) absorption observed in the **Re-1** spectrum, although it might be obscured by the tail of the fullerene absorption. The extended absorption observed in the visible region is again similar to that observed in fullerene systems, although extended molecular aggregation cannot be ruled out. Additional studies are underway to examine this phenomenon.[33]

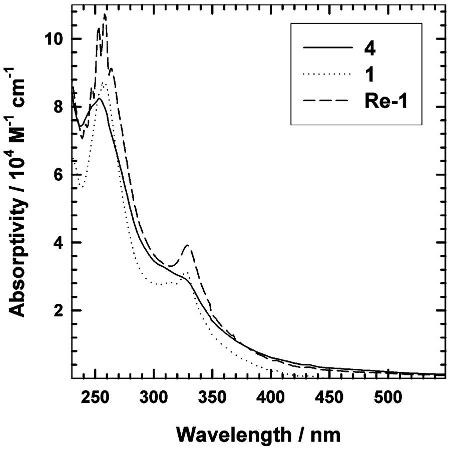


Figure 1. UV−visible absorption of **4** (CH_2Cl_2), **1** (CH_2Cl_2), and **Re-1** (THF).

Emission spectra of **1** and **Re-1** at 298 and 80 K are shown in Figure 2. As measured previously,[34] the quantum yield of C_{60} fullerene is very low ($\phi_{em} = 3 \times 10^{-4}$). However, the observed emission is considerably higher ($\phi_{em} = 0.02$ and 0.01 for **1** and **Re-1**, respectively), suggesting the addition of emissive excited states following substitution. This emission quantum yield is still quite low, however, for these types of supramolecular systems. The emission of **1** is

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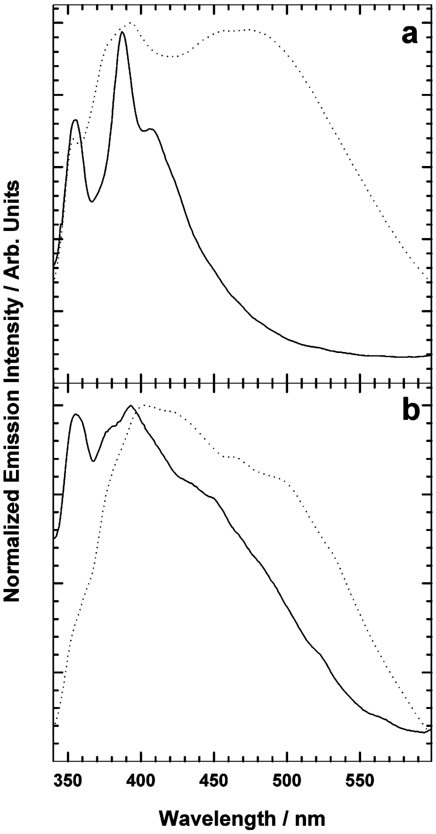

Figure 2. Emission of **1** (solid line) and **Re-1** (dotted line) in 2-methyltetrahydrofuran at (a) 298 K and (b) 80 K. Samples are freeze−pump−thaw degassed and excited at 320 nm.

dominated by a π,π* 360 nm fluorescence following photoexcitation into the primary fullerene absorption band. The band shape is typical for π-conjugated bipyridine systems but is blue-shifted 60 nm from systems without fullerene.[21] This shift is due to the fullerene's electron-withdrawing nature and the expected presence of additional "dark" excited states (fullerenes have considerably high triplet yields). While the same fluorescence is also observed in the **Re-1** spectrum, an additional luminescence is observed at 500 nm (again blue-shifted 50 nm from non-fullerene-containing systems). This luminescence becomes highly structured at lower temperatures and is absent from the **1** spectrum at both temperatures (although some red shifting in **1** is observed, again likely to aggregation).[33] This emission has been assigned as a Re → bipyridine MLCT state. While the same emission spectra for both molecules can be obtained at longer excitation wavelengths, the fact that these spectra are observed following excitation into the primary fullerene absorption indicates significant interaction between the excited-state manifolds of the fullerene, π-conjugated bipyridine, and rhenium moieties. Furthermore, the presence of both emission bands in **Re-1** suggests some equilibrium between the π,π* and MLCT excited states.

The presented systems illustrate the possibility of creating a relatively simple substituted fullerene (**4**) that can be used in supramolecular systems containing TM moieties (**Re-1**). While absorption spectra indicate dominance by the fullerene moiety, emission is largely based on the TM and linkage moieties, suggesting significant photoinduced charge transfer in the system. Further excited-state studies, including flash photolysis and Stark measurements,[35] are currently underway on these molecules because more advanced supramolecular systems are being developed.

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Supporting Information Available: Full synthetic details of all compounds, IR data, and variable-temperature emission data. This material is available free of charge via the Internet at http://pubs.acs.org.

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