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First Light-Emitting Neutral Molecular Rectangles

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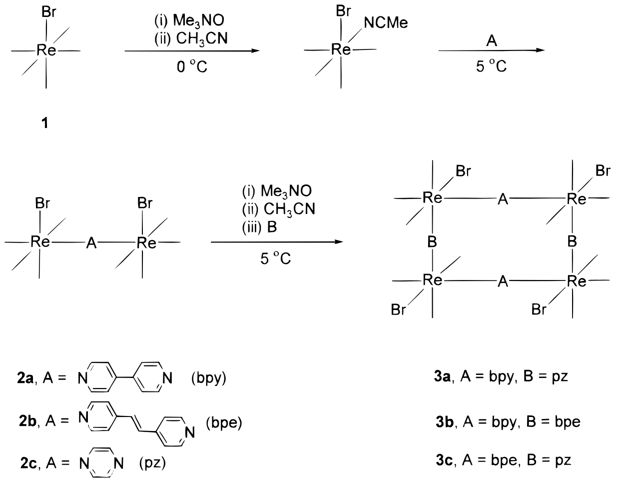
Supramolecular structures containing transition metal ions with potential inclusion and host−guest applications have been extensively explored in recent years.[1−4] Stang and co-workers contributed to the formation of a combinatorial library of cyclic molecular polygons via the systematic combination of building blocks with predetermined angles.[5] The initial focus was directed toward molecular squares, i.e., macrocycles fabricated by cis-coordinated transition metal corners and rigid or semirigid bifunctional ligand edges.[6−8] Subsequent efforts were devoted to the synthesis of molecular rectangles to improve selectivity and sensitivity in molecular recognition and separation.[9−12] Hupp et al. were the first to report the preparation of rhenium thiolate-based rectangles that exhibited interesting electrochemistry.[9,10] Subsequent work by the same group led to the synthesis, characterization, and preliminary binding properties of a new class of tetracationic rectangular molecules with triflate as counterion.[10] To tune the cavity size, Sullivan et al. recently also reported the preparation of a series of molecular rectangles based on fac-Re(CO)$_3$ corners containing 4,4′-bipyridine as one side and two η^2-alkoxy or hydroxy bridges as the other.[12]

Scheme 1



We report herein the synthesis and characterization of a new class of molecular rectangles **3** (Scheme 1) that exhibit luminescence in solution at room temperature. Unlike earlier “rectangles”, compounds **3** are neutral, possess larger cavities, and have no counterions inside the channels.

Activation of Re(CO)$_5$Br (**1**) with Me$_3$NO at 0 °C followed by addition of 0.5 equiv of 4,4′-bipyridine in toluene gave a pale-yellow, shiny product {Re(CO)$_4$Br}$_2$(μ-bpy) (**2a**) in 58% yield. Further treatment of **2a** at 5 °C in CH$_2$Cl$_2$ with 2 equiv of Me$_3$NO and a required amount of acetonitrile yielded intermediate-{(Re(CO)$_3$(NCMe)Br}$_2$(μ-bpy), which produced the molecular rectangle **3a** (14% yield) after subsequent titration with pyrazine. Following a similar strategy, the bimetallic edges **2b** and **2c** were synthesized from *trans*-1,2-bis(4-pyridyl)ethylene and pyrazine, respectively. Compounds **2a** and **2b** were then converted into **3b** and **3c** by reacting with *trans*-1,2-bis-(4-pyridyl)ethylene and pyrazine, respectively.

Rectangles **3** and their corresponding edges **2** were characterized spectroscopically. The FAB-MS analyses of **3a** and **2a** exhibit signals corresponding to the molecular ions at $m/z = 1880$ and $m/z = 916$, respectively, with the experimental isotope pattern matching the calculated values. The ^{1}H NMR spectrum of **3a** shows the presence of two predominant isomeric forms in solution at room temperature, most likely due to the orientation of the CO/Br trans-ligand pairs with respect to the plane containing the Re atoms.

Yellow single crystals of **3a** were grown from acetone, and X-ray diffraction studies were carried out.[13] An ORTEP diagram of **3a** is shown in Figure 1. The structure consists of a molecular rectangle in which two Br(CO)$_4$Re−bpy−Re(CO)$_4$Br edges are

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(13) Crystal data for **3a**: monoclinic, space group = $P2_1/c$, $a = 12.0890(2)$ Å, $b = 24.2982(2)$ Å, $c = 12.8721(2)$ Å, $\beta = 107.923(1)°$, $V = 3597.57(9)$ Å^3, $\rho = 2.051$ Mg/m^3, $Z = 2$, $T = 150$ K; of 18 370 reflections ($2\theta < 52°$) measured, 7285 with $I > 2\sigma(I)$ were used to refine 451 parameters. $R = 0.0356$ and $wR(F^2) = 0.0693$.

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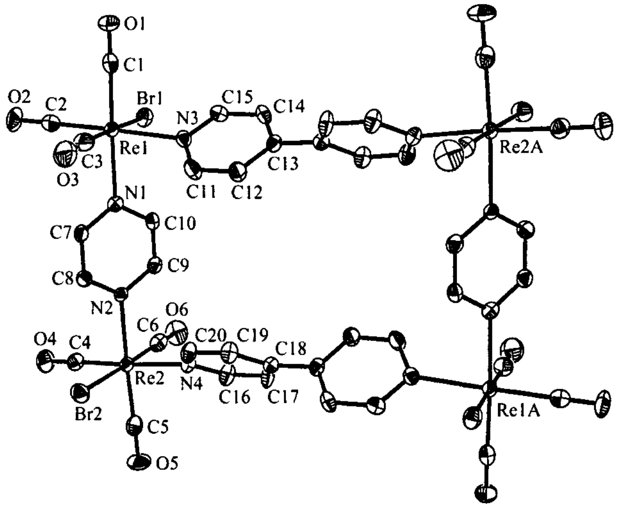

Figure 1. ORTEP diagram of **3a**. Selected bond distances (Å) and angles (deg) are the following: Re(1)−N(1) 2.212(5), Re(1)−N(3) 2.221(5), Re(1)−C(1) 1.929(7), Re(1)−C(2) 1.922(6), Re(1)−C(3) 1.92(2), Re(2)−N(2) 2.212(4), Re(2)−N(4) 2.218(5), Re(2)−C(4) 1.919(6), Re(2)−C(5) 1.924(7), Re(2)−C(6) 1.92(1), N(1)−Re(1)-N(3) 84.5(2), N(2)−Re(2)-N(4) 82.4(2).

bridged by two pyrazine moieties. In each bipyridine moiety, one of the aromatic rings is found to have a canted configuration with respect to the plane of other rings. The Br(1) and Br(2) are disordered with the CO group in 73/27 occupancy, which is substantiated by the isomeric ^{1}H NMR spectral pattern of **3a**. Average bond distances are as follows: Re−C(CO), 1.92 Å; Re−N(4,4′-bpy), 2.22 Å; Re−N(pz), 2.21 Å. They are similar to those found for a number of other Re(I) complexes.[7a,b,12] The molecular rectangle **3a** consists of a cavity with the dimensions of 11.44 Å × 7.21 Å. Since no steric hindrance exists between the Re metal centers, fine-tuning of the cavity size is possible. For example, in **3b**, a cavity with dimensions of 11.38 Å × 13.17 Å could be achieved, as revealed by molecular modeling. The packing diagram of **3a** shows the effective π staking of the aromatic rings that ensures the close packing of the molecules to form an infinite number of open-end channels.

IR spectroscopy showed that the CO stretching (ν_{CO}) shifted bathochromically from 2113 to 2032 cm^{-1} when **2a** was converted into **3a**. This red shift in ν_{CO} indicates that new linkages are formed between the additional π ligands and the metal center. In addition, compounds **2** and **3** exhibit two absorption bands in the near-UV region. We attribute the absorption band at higher energy (251−265 nm) to a $\pi-\pi^*$ transition and the lower one (315−342 nm) to the MLCT transition.[14−16] Control experiments showed that the MLCT bands of **2** or **3** are insensitive to the variation of the halide,[14] whereas a substitution of CO with other ligands would shift the MLCT band bathochromically. Examination of the UV−vis absorption spectra showed that the MLCT maximum of **2a** is centered at 315 nm, whereas for **3a** it is at 324 nm. This spectral difference suggests that the ground state of **2a** has been raised to a higher level after conversion to **3a**.

Table 1. Electronic Absorption Maxima, Excited-State Emission Maxima, Emission Lifetimes, and Emission Quantum Yields

no.	complex	λ_{max} (nm)^a LIG	λ_{max} (nm)^a MLCT	λ_{max} (nm)^a Em	τ (ns)^a	Φ_{em}^{b}
2a	$\{Re(CO)_4Br\}_2(\mu\text{-bpy})$	263	315	412, 563	228	0.0017
2b	$\{Re(CO)_4Br\}_2(\mu\text{-bpe})$	265	320	452	16	0.0031
2c	$\{Re(CO)_4Br\}_2(\mu\text{-pz})$	262	322	541	17	0.0014
3a	$[\{Re(CO)_3(\mu\text{-bpy})Br\}\{Re(CO)_3(\mu\text{-pz})Br\}]_2$	254	324	416, 563	14	0.0010
3b	$[\{Re(CO)_3(\mu\text{-bpy})Br\}\{Re(CO)_3(\mu\text{-bpe})Br\}]_2$	252	329	467	11	0.0014
3c	$[\{Re(CO)_3(\mu\text{-bpe})Br\}\{Re(CO)_3(\mu\text{-pz})Br\}]_2$	251	342	385, 470 558	15	0.0022

[a] Measured in deoxygenated CH$_3$CN at 298 K. [b] Emission quantum yield measured at 298 K. $\lambda_{ex} = 436$ nm with reference to $[Ru(bpy)_3]^{2+}$ ($\Phi_{em} = 0.0420$); error is ±10%.

Because compounds **2** and **3** were brought to their MLCT excited states photochemically, both molecules fluoresced with quantum yield of ca. 0.002 relative to $Ru(bpy)_3{}^{2+}$.[17−19] The lifetimes measured for **2** and **3** are on the order of nanoseconds (Table 1). On the other hand, cyclic voltammetry revealed that electron exchange through an electrode such as glassy carbon occurred near the potential of $E \geq 1.0$ V vs SCE. Therefore, compounds **2** and **3** are expected to be strong reducing agents upon photoexcitation. Combining the energy gap between the ground state and the MLCT excited state as well as the formal potentials of $\mathbf{3}^{+/0}$, we estimated formal potentials for **3** at their excited states of about −1 V vs SCE. Thus, these compounds are capable of reducing methyl viologen (MV^{2+}, $E^{0\prime}{}_1 \approx -0.4$ V; $E^{0\prime}{}_2 \approx -0.7$ V vs SCE) or tetracyanoquinodimethane (TCNQ, $E^{0\prime} \approx -0.3$ V vs SCE). Preliminary results with **3a** are in full accord with this hypothesis. The excited state of **3a** can be oxidatively quenched by TCNQ; the Stern−Volmer quenching rate constant is estimated to be 10^5 M^{-1} s^{-1} at 25 °C.

Further experiments showed that these molecular rectangles can form thin films on many electrodes, such as gold and glassy carbon, and showed interesting ability to differentiate substrates of different sizes. With these unique properties, rectangles **3** should find many applications, including ultrafiltration, molecular separation, and optical rectification.

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Supporting Information Available: Experimental details, tables listing molecular modeling data of interatomic distances (Re···Re), electrochemical data, crystallographic data, isotopic distribution patterns of the M$^+$ peaks for **2a** and **3a**, packing diagram of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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