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Self-Assembly of Octarhenium-Based Neutral Luminescent Rectangular Prisms

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Self-assembly of rhenium-based nanoscale rectangular prismatic boxes has been achieved in quantitative conversion. The *fac*-rhenium corner provided three mutually perpendicular coordination sites and served as a good candidate for the construction of 3-D boxes. These are the first Re-based, neutral, luminescent prisms of $M_8L_2L'_8$ type that has been characterized crystallographically. Their luminescent properties and molecular recognition capabilities make these molecular prisms interesting supramolecules.

Self-assembled supramolecules with precisely designed shape, geometry, and functionality have paved the route toward the use of a “bottom-up” approach toward the design and fabrication of nanoscale devices and molecular machinery.[1−3] The underlying principles of self-assembly reside in suitably designed, information-encoded precursor building blocks that fulfill the requirements for recognition, orientation, and termination during the highly precise assembly process.[1,2,4] Many successful examples are now found in the literature. Mostly they have been synthesized using transition-metal-based metallo-corner building blocks such as *cis*-[Pt(en)]$^{2+}$ by Fujita et al.,[5] *cis*-[Pt(phosphine)$_2$]$^{2+}$ by Stang et al.,[6] and *fac*-Re(CO)$_3$X by Hupp et al.[7,8] that provide predesigned ∼90° coordination geometry as well as 1,8-bis(*trans*-Pt(PEt$_3$)$_2$(NO$_3$))-anthracene by Stang et al. with two parallel aligned coordination sites that behave as a metalloclip.[9]

For some of the metallo-corner precursor systems, a more sophisticated preparation procedure is required. Nevertheless, Sullivan and co-workers accomplished the self-assembly of alkoxy-bridged molecular rectangles using the precursor Re(CO)$_5$(CF$_3$SO$_3$).[8a] In our own work on the construction of molecular prisms via the self-assembly process by using the *fac*-Re(CO)$_3$ corner system, we have prepared a new class of rhenium-based, neutral, luminescent octametallic prismatic supramolecules. We report herein the synthesis, crystal structure, spectral, and molecular recognition studies on this new class of supramolecules.

The synthesis was accomplished by a one-pot process with quantitative conversion based on a rudimentary Re$_2$(CO)$_{10}$ precursor. Octametallic prismatic boxes, $[\{(CO)_3Re(\mu_2\text{-}OR)_2\text{-}Re(CO)_3\}_4(\mu_4\text{-tpeb})_2]$ (**1**, R = C$_8$H$_{17}$, 88%; **2**, R = C$_{12}$H$_{25}$, 98%; **3**, R = C$_7$H$_7$, 72%), were obtained in excellent yields at elevated temperatures by mixing Re$_2$(CO)$_{10}$ and the tetradentate ligand 1,2,4,5-tetraethynyl(4-pyridyl)benzene (tpeb)[10] in a 2:1 ratio in the alcohol of interest (Scheme 1). Compounds **1**−**3** are the first examples of $M_8L_2L'_8$ type supramolecules possessing eight octahedral Re(I) centers and two different kinds of ligands, characterized crystallographically. Molecular weights of **1**−**3** are around 4000, and the compounds are soluble in common organic solvents.

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(1) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995.
(2) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry: a Concise Introduction*; John Wiley & Sons: Chichester, 2000.
(3) Miller, J. S. *Adv. Mater.* **1990**, *2*, 495.
(4) (a) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (b) Parac, T. N.; Caulder, D. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 8003.
(5) (a) Takeda, N.; Umemoto, K.; Yamaguchi, K.; Fujita, M. *Nature* **1999**, *398*, 794. (b) Yamanoi, Y.; Sakamoto, Y.; Kusukawa, T.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 980.
(6) (a) Leninger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Olenyuk, B.; Whiteford, J. A.; Fechtenkotter, A.; Stang, P. J. *Nature* **1999**, *398*, 796.
(7) (a) Slone, R. V.; Yoon, D. I.; Calhoun, R. M.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 11813. (b) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2891 and references cited therein.
(8) For other recent examples see: (a) Woessner, S. M.; Helms, J. B.; Shen, Y.; Sullivan, B. P. *Inorg. Chem.* **1998**, *37*, 5406. (b) Sun, S. S.; Lees, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 8956. (c) Rajendran, T.; Manimaran, B.; Lee, F. Y.; Peng, S. M.; Wang, C. M.; Lu, K. L. *Inorg. Chem.* **2000**, *39*, 2016. (d) Manimaran, B.; Rajendran, T.; Lu, Y. L.; Lee, G. H.; Peng, S. M.; Lu, K. L. *Eur. J. Inorg. Chem.* **2001**, 633. (e) Manimaran, B.; Rajendran, T.; Lu, Y. L.; Lee, G. H.; Peng, S. M.; Lu, K. L. *J. Chem. Soc., Dalton Trans.* **2001**, 515.
(9) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.
(10) Amoroso, A. J.; Cargill Thompson, A. M. W.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 4828.

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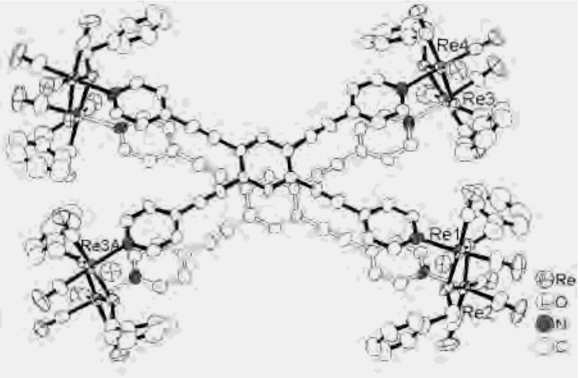
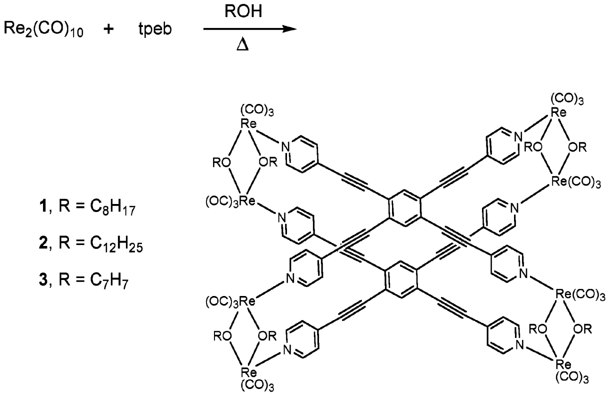


Figure 1. The crystal structure of **3** at 40% ellipsoids. Solvent molecules and hydrogen atoms are omitted for clarity.

Scheme 1



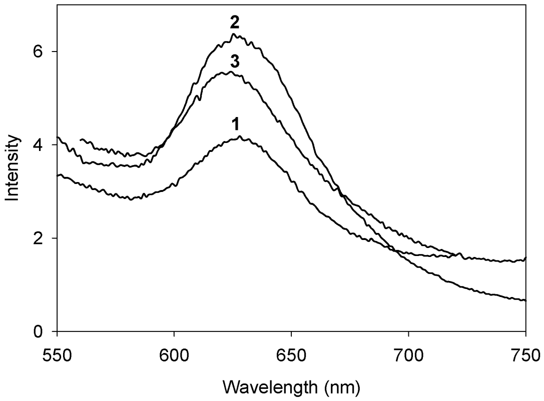


Figure 2. Emission spectra of **1**−**3** at 77 K.

Table 1. Spectral and Photophysical Data of **1**−**3** in H_2O−Organic Solvent Mixture

compd	absorption[a] λ_{max}, nm	emission[a] λ_{max}, nm	quantum yield[a] (Φ) × 10^{-4}	lifetime[a] (τ) ns	emission (77 K)[b] λ_{max}, nm
1	208, 321, 369 (sh)	655	2.88	52	628
2	208, 320, 357 (sh)	645	9.77	66	624
3	208, 321, 360 (sh)	667	1.40	26	624

[a] For **1** and **2**, 20% THF−80% H_2O was used, and for **3**, 20% DMF−80% H_2O was used. [b] For **1** and **2**, THF was used, and for **3**, DMF was used.

A single-crystal X-ray crystallographic study of the dark-red crystal **3** revealed a rectangular prismatic architecture with a core geometry consisting of a heavy atom prism made up of eight Re atoms with the formula $C_{148}H_{92}N_8O_{32}Re_8(C_6H_5CH_3)_2$ (Figure 1).[11] Two tpeb ligands were coordinated to four $\{(CO)_3Re(\mu_2\text{-}OCH_2C_6H_5)_2Re(CO)_3\}$ edge moieties thereby forming a tetragonal prism. The size of the octanuclear rectangular prism **3** as measured from the rhenium centers was about 18.070(6) Å (Re1−Re3A) × 10.150(7) Å (Re1−Re4) × 3.390(2) Å (Re1−Re2). Compound **3** consisted of 18 aromatic rings, with 10 aromatic rings of the two tpeb moieties oriented in an approximately planar array with effective $\pi-\pi$ stacking.

The ^1H and ^{13}C NMR spectra of compounds **1**−**3** exhibited signals for the presence of tpeb ligand, alkoxy moiety, and CO groups. The UV−vis spectra of **1**−**3** showed a sharp absorption near 318 nm and a shoulder at 363 nm in THF. The sharp intense absorption at 318 nm might be assigned to the $\pi-\pi^*$ transition of the highly conjugated bridging ligand tpeb, and the shoulder at 363 nm to the MLCT transition (Re → tpeb) in line with the previous reports.[12]

Since some Re(I) containing rectangles are emissive,[7b,8a,c] we have attempted to record the emission spectrum of **1** and **2** in THF and **3** in DMF. Though we could not detect the emission in the above solvents at room temperature, **1**−**3** are emissive at 77 K and the emission maxima were observed at 628 nm for **1** and 624 nm for **2** and **3** (Figure 2). Previously, Sullivan et al. have also reported that the alkoxy-bridged molecular rectangles luminesce in the solid state, but not in solution.[8a] Note that the ligand tpeb itself is luminescent with emission maxima at 400 and 770 nm and a lifetime of 0.6 ns.[13]

It is interesting to note that **1** and **2** were weakly emissive at room temperature when pyridine was used as the solvent. The emission maximum occurred at 636 nm for **1** and 641 nm for **2**; an emission spectrum could not be obtained for **3**, as it was insoluble in pyridine. The emission lifetimes of **1** and **2** in pyridine at room temperature are 22 and 37 ns, respectively.

To improve the luminescence property of **1**−**3**, we have recorded the emission spectra in organic solvent−water mixtures, and the results are presented in Table 1. Interestingly, on excitation of **1**−**3** at their MLCT bands, a significant improvement was observed in the emission intensity in a 80% H_2O−20% organic solvent mixture compared to that in the pure organic solvent. The enhanced emission in the presence of water might be due to the formation of self-aggregates.[14]

Molecular recognition studies revealed that these rectangular prisms could engage in host−guest interactions with

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(11) Crystal data for **3**: $(CO)_{24}Re_8(C_{34}H_{18}N_4)_2(C_7H_7O)_8 \cdot 2(C_7H_8)$, triclinic, space group $P\bar{1}$, $a = 14.4754(6)$ Å, $b = 15.8560(7)$ Å, $c = 19.0493(8)$ Å, $\alpha = 89.979(1)°$, $\beta = 68.328(1)°$, $\gamma = 64.207(1)°$, $V = 3590.6(3)$ Å^3, $Z = 1$, R1 = 0.0444 [$I > 2\sigma(I)$], wR2 (all data) = 0.1230.

(12) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439 and references therein.

(13) For emission lifetime measurements, a time-correlated single photon counting FL 920 nanosecond spectrometer (Edinburgh instrument) was used.

(14) (a) Manimaran, B.; Thanasekaran, P.; Rajendran, T.; Lin, R. J.; Chang, I. J.; Lee, G. H.; Peng, S. M.; Rajagopal, S.; Lu, K. L. *Inorg. Chem.* **2002**, *41*, 5323. (b) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L. Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740. (c) Yam, V. W.-W.; Wong, K. M.-C.; Zhu, N. *J. Am. Chem. Soc.* **2002**, *124*, 6506.

aromatic hydrocarbons. To investigate the binding capability of these rectangular prisms, the absorption and emission spectra of pyrene in the absence and presence of **1**−**3** were recorded in aerated THF and DMF. Interestingly, an increase in the absorbance of pyrene due to complex formation was observed with increasing concentration of the prisms. On the basis of absorption/emission spectral measurements, a linear Benesi−Hildebrand plot[15] indicated 1:1 complex formation between **1** and pyrene, and the binding constants were found to be in the range 2.2−9.2 × 10^4 M^{-1}. Efficient quenching of the emission from the pyrene was also noted with increasing concentration of **1**−**3**. The Stern−Volmer plot[16] was linear at low concentrations giving quenching rate constants of 2.1−2.6 × 10^{13} M^{-1} s^{-1}; but at higher concentrations deviation from linearity[17] was observed. This behavior indicated that the quenching occurred after the binding of pyrene with **1**−**3**. Also, from the quenching constants, we suggest that standard static quenching is responsible for the efficient quenching. This type of quenching has been reported for conjugated macromolecules and bipyridinium derivatives[17a] and porphyrin unit with diimide.[18]

^{1}H NMR studies of **1** with increasing concentrations of pyrene in d_6-acetone revealed an upfield shift of the signals corresponding to the pyridyl (H^3, from δ 8.57 to 8.55 ppm; H^2, from δ 7.70 to 7.61 ppm) and phenyl hydrogens (from δ 8.08 to 8.06 ppm) of the tpeb ligand, when 0.08 M pyrene was used. In contrast, the chemical shifts of the alkoxy protons were unaffected upon the addition of pyrene. These observations suggest that pyrene is recognized as a guest molecule by the tpeb ligand of the rectangular prisms. Since the separation of the two tpeb ligands is about 4 Å, the mode of recognition of the pyrene involves presumably not an intracavity but the surface of tpeb ligand of the sandwich compound.

For the sake of comparison, the M_4L compound [$\{(CO)_4$-$ReBr\}_4(\mu_4$-tpeb)] (**4**), a nonsandwich analogue of the $M_8L_2L'_8$ prisms, was prepared and similar binding studies were carried out. Compound **4** exhibited a similar binding property (binding constant with pyrene = 5.8 × 10^4 M^{-1}) supporting the fact that both $M_8L_2L'_8$ and M_4L systems possessed similar binding sites. The extended conjugation present in tpeb drives it to recognize the guest molecules on the surface of **1**−**3** as well as **4** (due to $\pi-\pi$ interactions). However, the $M_8L_2L'_8$ type rectangular prisms (**1**−**3**) are considered to be a more superior system than the M_4L compound (**4**) for the following reasons: (i) **1**−**3** are air and moisture stable, whereas **4** is air and moisture sensitive; (ii) **1**−**3** are synthesized by the self-assembly process in quantitative conversion, but **4** is obtained by a stepwise procedure in low yield; (iii) **1** and **2** exhibit better photoemissive properties (τ = 22 and 37 ns, respectively) than **4** (τ = 10 ns) in pyridine.

In conclusion, we have accomplished the self-assembly of 18 components into an octametallic rectangular prism bearing octahedral Re centers in a one-pot synthesis. To the best of our knowledge, this is the first neutral luminescent Re-based octanuclear rectangular prism that is structurally characterized. The presence of lengthy alkoxy groups increases the solubility of supramolecules dramatically. The “on−off switching” of emission of the prisms is regulated by the presence−absence of aqueous solvent, respectively. The luminescence and host−guest interaction capabilities of these prismatic boxes endow these supramolecular systems with interesting properties.

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Supporting Information Available: Synthetic procedure and spectral data for compounds **1**, **2**, and **3**. Crystallographic file for compound **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (b) Murakami, Y.; Kikuchi, J. I.; Suzuki, M.; Matsuura, T. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1289.

(16) (a) Stern, O.; Volmer, M. *Phys. Z.* **1919**, *20*, 183. (b) Eftink, M. R.; Ghiron, C. A. *J. Phys. Chem.* **1976**, *80*, 486. (c) Rajendran, T.; Rajagopal, S.; Srinivasan, C.; Ramamurthy, P. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3155.

(17) (a) Wang, D.; Wang, J.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Langmuir* **2001**, *17*, 1262. (b) Harrison, B. S.; Ramey, M. B.; Reynolds, J. R.; Schanze, K. S. *J. Am. Chem. Soc.* **2000**, *122*, 8561.

(18) Flamigni, L.; Johnston, M. R. *New J. Chem.* **2001**, *25*, 1368.