

Luminescence Enhancement Induced by Aggregation of Alkoxy-Bridged Rhenium(I) Molecular Rectangles

Bala. Manimaran,[†] P. Thanasekaran,[†] T. Rajendran,[†] Ren-Jay Lin,[‡] I-Jy Chang,[‡] Gene-Hsiang Lee,[§] Shie-Ming Peng,[§] S. Rajagopal,^{†,||} and Kuang-Lieh Lu^{*†}

Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, Department of Chemistry, National Taiwan Normal University, Taipei 117, Taiwan, Department of Chemistry, National Taiwan University, Taipei 107, Taiwan, and School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

Received May 23, 2002

Self-assembly of rhenium(I)-based molecular rectangles containing long alkyl chains has been achieved in one-pot synthesis by solvothermal methods. An enormous enhancement in the emission intensity, quantum yield, and lifetime of the rectangles has been observed when the solvent medium is changed from organic to aqueous. Addition of water favors the aggregation of Re(I) molecular rectangle resulting in the luminescence enhancement, and this phenomenon has been traced out using light scattering techniques.

Tremendous interest has been shown in recent years in the design and fabrication of transition-metal-based supramolecules containing multichromophoric ligands because of their potential applications in molecular recognition and as sensors.^{1–5} A variety of Re(I)-containing molecular cyclo-

phanes have been synthesized partly because of their photophysical and photochemical properties.^{1d,4c,6–8} The photoluminescent supramolecules have the advantage of allowing researchers to study the electronic excited-state reactivity and to detect guest inclusion.^{4c,5} Several strategies have been developed to improve the luminescence quantum yield, the most prominent being the suitable design of ligands.^{4,5} It is worthwhile to mention that amphiphilic molecules carrying long alkyl chains can undergo aggregation in aqueous solution to form micelles and vesicles.⁹ The aggregation may affect, sometimes drastically, the luminescence of the molecule and thus lead to interesting properties.¹⁰ Though the aggregation of organic macromolecules such as aza-crown ethers, cryptand-based amphiphiles, calixarenes, and octopus-type cyclophanes has been achieved and extensively used as receptors, such aggregates carrying metal ions such as Re(I) have not been reported so far.¹¹ To assess the aggregation effect of inorganic molecules, we have accomplished the self-assembly of Re(I) molecular rectangles 1–3 containing long-chain alkyl groups (Figure 1) in one-

* To whom correspondence should be addressed. E-mail: lu@chem.sinica.edu.tw. Fax: international code + (2)27831237.

[†] Academia Sinica.

[‡] National Taiwan Normal University.

[§] National Taiwan University.

^{||} Madurai Kamaraj University.

- (1) (a) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (c) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483 and references therein. (d) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (e) Sun, S. S.; Lees, A. J. *Coord. Chem. Rev.* **2002**, *230*, 171.
- (2) (a) Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185 and references therein. (b) MacGillivray, L. R.; Atwood, J. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1018.
- (3) (a) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53. (b) Constable, E. C.; Schofield, E. *Chem. Commun.* **1998**, 403. (c) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417 and references therein.
- (4) (a) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133. (b) Dixon, F. M.; Eisenberg, A. D.; Farrell, J. R.; Mirkin, C. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 3432. (c) Sun, S. S.; Lees, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 8956.
- (5) (a) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (b) Keefe, M. H.; Benkstein, K. D.; Hupp, J. T. *Coord. Chem. Rev.* **2000**, *205*, 201. (c) Slone, R. V.; Benkstein, K. D.; Belanger, S.; Hupp, J. T.; Guzei, I. A.; Rheingold, A. L. *Coord. Chem. Rev.* **1998**, *171*, 221. (d) De Silva, A. P.; Gunaratne, H. Q. N.; Gunnaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.
- (6) (a) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2891. (b) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 12982. (c) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *Inorg. Chem.* **1998**, *37*, 5404. (d) Slone, R. V.; Yoon, D. I.; Calhoun, R. M.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 11813.
- (7) (a) Woessner, S. M.; Helms, J. B.; Shen, Y.; Sullivan, B. P. *Inorg. Chem.* **1998**, *37*, 5406. (b) Sun, S. S.; Lees, A. J. *Inorg. Chem.* **1999**, *38*, 4181.
- (8) (a) Manimaran, B.; Rajendran, T.; Lu, Y. L.; Lee, G. H.; Peng, S. M.; Lu, K. L. *J. Chem. Soc., Dalton Trans.* **2001**, 515. (b) Rajendran, T.; Manimaran, B.; Lee, F. Y.; Lee, G. H.; Peng, S. M.; Wang, C. M.; Lu, K. L. *Inorg. Chem.* **2000**, *39*, 2016.
- (9) (a) Buntton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. *Acc. Chem. Res.* **1991**, *24*, 357. (b) *Kinetics and Catalysis in Microheterogeneous Systems*; Kalyanasundaram, K., Gratzel, M., Eds.; Marcel Dekker: New York, 1991.
- (10) 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.
- (11) (a) Schenning, A. P. H. J.; Escuder, B.; van Nenen, J. L. M.; de Bruin, B.; Lowik, D. W. P. M.; Rowan, A. E.; van der Gaast, S. J.; Feiters, M. C.; Nolte, R. J. M. *J. Org. Chem.* **2001**, *66*, 1538 and references therein. (b) Murakami, Y.; Kikuchi, J.; Ohno, T.; Hayashida, O.; Kojima, M. *J. Am. Chem. Soc.* **1990**, *112*, 7672.

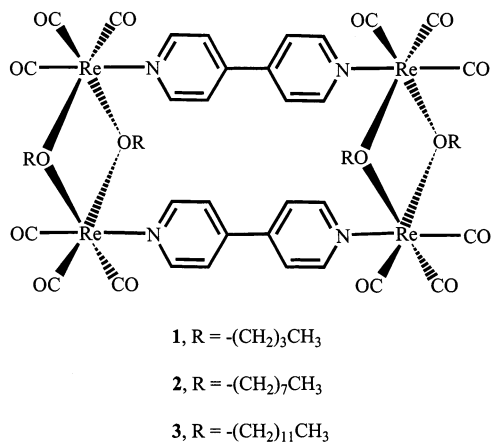


Figure 1. Structures of complexes **1–3**.

pot synthesis and studied their photophysical properties under various organic solvent–water mixtures.

When $\text{Re}_2(\text{CO})_{10}$ is treated with 4,4'-bipyridine (bpy) in the presence of higher aliphatic alcohols (i.e., 1-butanol, 1-octanol, and 1-dodecanol), the alkoxy-bridged molecular rectangles $[\{(\text{CO})_3\text{Re}(\mu\text{-OR})_2\text{Re}(\text{CO})_3\}_2(\mu\text{-bpy})_2]$ (**1–3**) are obtained by using solvothermal methods.^{8a} Rectangles **1–3** have been spectroscopically characterized. Single crystals were obtained, and the X-ray diffraction study was carried out for rectangle **1**. The ORTEP diagram of **1** shows a rectangular architecture with a rhenium atom at each corner. The planar bipyridine ligands coordinated to two rhenium atoms are perpendicular to the rhenium plane. Each rhenium is bonded to two butoxy groups perpendicular to each side of the rhenium plane. Although only rectangle **1** has an X-ray structure, the IR spectra of compounds **1–3** exhibit identical CO stretching patterns and are similar to the previous reports.^{7,8a,12,13} The ^1H and ^{13}C NMR spectra and FAB-MS data of **1–3** are in agreement with the rectangular structures.

The rectangles containing long alkyl chains are not soluble in water but are soluble in organic solvents and are weakly emissive.^{8a} The absorption spectrum of **3** in acetonitrile shows an intense band at 241 nm with a shoulder at 266 nm and a broad band at 385 nm which have been assigned to the ligand-centered (LC) (241 and 266 nm) and metal-to-ligand charge transfer (MLCT) (385 nm) transitions. Addition of water into 6×10^{-6} M of **3** in CH_3CN changes the absorption spectrum. In 10% water content, the LC band at 241 nm has reduced intensity while the shoulder at 266 nm becomes more pronounced. When the water content is increased from 20% to 90%, the bands at 241 and 266 nm are shifted to 248 and 272 nm, respectively, with concomitant increase in the intensity. The solutions were macroscopically homogeneous with no precipitation, even on standing for long periods of time, up to 1×10^{-5} M concentration of **3**. The MLCT band at 385 nm has been red-shifted by 5 nm on the addition of water while there is an abrupt increase in absorbance at 20% water content although it remains mostly unchanged during any further increase in water (Figure 2).

(12) Jiang, C.; Wen, Y. S.; Liu, L. K.; Hor, T. S. A.; Yan, Y. K. *Organometallics* **1998**, *17*, 173.

(13) El-Sayed, M. A.; Kaesz, H. D. *Inorg. Chem.* **1963**, *2*, 158.

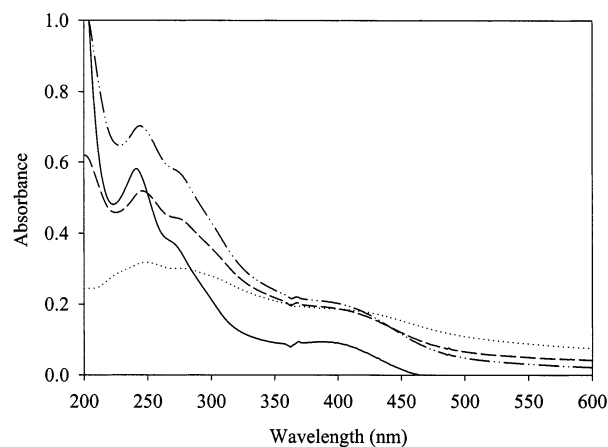


Figure 2. Absorption spectra of **3** in CH_3CN (—), 80% CH_3CN –20% H_2O (···), 50% CH_3CN –50% H_2O (---), and 10% CH_3CN –90% H_2O (— · —) (v/v) mixtures.

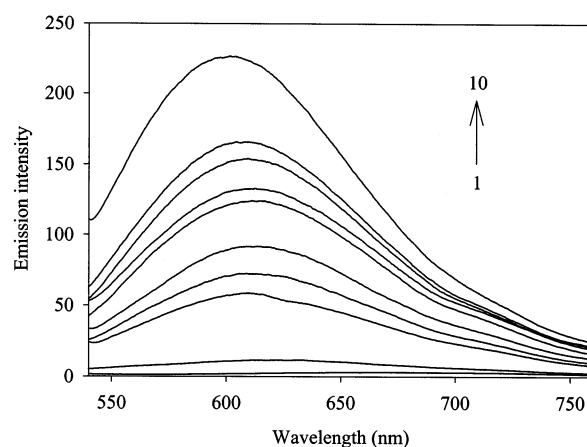


Figure 3. Emission enhancement of **3** in CH_3CN upon increasing water content: (1) 0%, (2) 10%, (3) 20%, (4) 30%, (5) 40%, (6) 50%, (7) 60%, (8) 70%, (9) 80%, and (10) 90% ($\lambda_{\text{ex}} = 390$ nm).

Similar behavior has been observed when the concentration of rectangle **3** is increased in a 50% water–acetonitrile (v/v) mixture. The absorption spectra shown in Figure 2 hint at a scattered light pattern as a function to the fourth of the frequency that tails down to 600 nm, and these results strongly indicate nanoparticle suspensions.¹⁴ Molecular aggregation seems to be the best explanation for these observed spectral changes.

Addition of water leads to enormous enhancement in the emission intensity (Figure 3) of rectangle **3** while the effect is moderate with rectangles **1** and **2**. The emission quantum yield values for **3** in CH_3CN and in 10% CH_3CN –90% H_2O are 0.39×10^{-3} and 6.5×10^{-3} , respectively, and the lifetimes are 11 and 212 ns, respectively. Although the shift in the MLCT absorption band is small, the corresponding emission maximum is substantially blue-shifted with higher quantum yield (Table 1). These results indicate less solvent exposed and less distorted excited-state environments. Molecular aggregation seems to be the most appropriate explanation for these experimental observations, while alkyl chain aggregates expel the solvent molecules and the

(14) Tang, B. Z.; Geng, Y.; Lam, J. W. Y.; Li, B.; Jing, X.; Wang, X.; Wang, F.; Pakhomov, A.; Zhang, X. X. *Chem. Mater.* **1999**, *11*, 1581.

Table 1. Wavelength of Emission Maximum ($\lambda_{\text{max}}^{\text{em}}$), Emission Quantum Yield (Φ), and Lifetime (τ) of Rectangle **3** in Various $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (v/v) Mixtures

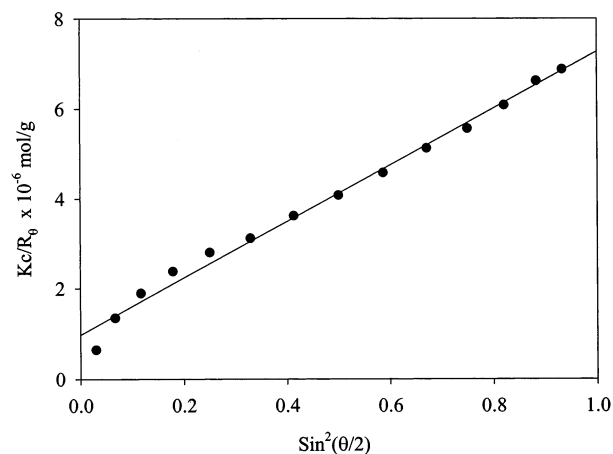
serial number	solvent composition		$\lambda_{\text{max}}^{\text{em}}$ (nm)	Φ ($\times 10^{-3}$) ^a	τ (ns)
	CH_3CN (%)	H_2O (%)			
1	100	00	666	0.39	11
2	90	10	634	0.46	13
3	80	20	612	1.64	120
4	70	30	611	1.73	124
5	60	40	613	2.06	135
6	50	50	613	2.37	137
7	40	60	612	2.58	140
8	30	70	611	3.10	167
9	20	80	604	4.74	176
10	10	90	602	6.54	212

^aEmission quantum yield measured at 298 K with reference to $\text{Ru}(\text{bpy})_3^{2+}$, $\Phi_{\text{em}} = 0.042$ (Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617); $\lambda_{\text{ex}} = 409$ nm.

aggregation leads to less vibrational motion. Similar spectral changes have been observed for the aggregation of siloles by Tang and co-workers.¹⁰

To realize the molecular recognition capability of this luminescent rectangle, we studied the reaction of **3** with various quinones by a luminescence quenching technique. Our preliminary results show that the quenching reaction is efficient and the quenching rate constant, k_q , values are in the range 2.0×10^8 to $3.8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ (calculated from a Stern–Volmer plot at lower concentration of quencher). Most of the k_q values are well above the values for diffusion-controlled quenching. The Stern–Volmer plot based on the luminescence intensity data for the quenching of **3** by quinones at high concentrations shows clear upward curvature. This type of deviation from linearity can be explained because only a certain fraction of the excited state of **3** is actually quenched with quinones by a collisional process. The remaining is associated with quinones, and quenching is by a static process. This luminescence quenching study clearly indicates that rectangle **3** binds with quinones. From the nonlinear Stern–Volmer plots, Aoyama et al.¹⁵ have concluded that static quenching dominates the quenching of porphyrins by various quinones. The detailed quenching studies of rectangles **1–3** with several quinones will be reported separately.

The binding constants have been evaluated using the Benesi–Hildebrand equation for the 1:1 host–guest interaction. A good linear correlation with respect to the double reciprocal plot of the extent of fluorescence intensity change (ΔI) upon the addition of the guest against the total concentration of the guest molecule is obtained.¹⁵ Analysis of the data for **3** with methyl-*p*-benzoquinone gives a binding constant of $4.1 \times 10^2 \text{ M}^{-1}$. ¹H NMR studies of **3** with increasing concentration of methyl-*p*-benzoquinone in a 50% (v/v) THF-*d*₆/D₂O mixture lead to downfield shifts of H³ and H² protons of pyridyl group of **3** from δ 8.434 to 8.446 ppm and 7.581 to 7.605 ppm, respectively, when 0.075 M concentration of methyl-*p*-benzoquinone is used. The chemical shifts of the alkoxy protons did not exhibit a noticeable change upon the addition of quinone. This study indicates that quinone interacts closely with the pyridyl group of **3**.

**Figure 4.** Average molecular mass determination by SLS using Zimm plot approach for aggregated Re(I) molecular rectangle **3** in 50:50 (v/v) $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solvent mixture.

Light scattering studies¹⁶ provide a good method to detect aggregation. A static light scattering (SLS) study of Re(I)-oxo-bridged rectangle **3** shows the existence of large aggregates present in solution. The average molecular mass of the Re(I) rectangle **3** in 50% aqueous CH_3CN (v/v) by a Zimm plot is 1.43×10^6 as shown in Figure 4. To gain insight into the particle size of aggregates, the aggregation of the Re(I) rectangle was monitored by dynamic light scattering technique. The Cumulant and Histogram analysis of aggregated Re(I) rectangle **3** indicated a diameter value of 262 and 265 nm, respectively. All these experiments support that the addition of water favors the aggregation of Re(I) rectangle **3** and results in an enormous luminescence enhancement.

In summary, the luminescence enhancement in Re(I) molecular rectangles is achieved by introducing long alkyl chains in the ligand and changing the medium from organic to aqueous solution. To the best of our knowledge, this is the first report on emission enhancement due to self-aggregation of supramolecules containing metal ions. These luminescent neutral molecular rectangles act as hosts for quinones and find applications in molecular recognition studies.

Acknowledgment. We thank Academia Sinica and the National Science Council of the Republic of China for financial support.

Supporting Information Available: Synthetic and characterization information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC020364N

- (15) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1991**, *113*, 6233.
- (16) Laser light scattering experiments were performed using a DLS-7000 light scattering photometer (Photal Otsuka Electronics, Japan) with an LS-71 control unit using a 10 mW He–Ne laser light source operating at 632.8 nm. DLS was conducted at a scattering angle of 90° using both Cumulant and Histogram software. The refractive index increment (dn/dc) of the molecular aggregation of this system was determined to be -10.13 mL/g at 20 °C using double beam differential refractometer, model DRM-1021 (Photal Otsuka Electronic, Japan). The SLS measurements were made in the angle of 20–150° with an interval of 10° at 20 °C. For light scattering experiments, the concentration of the **3** used was $1 \times 10^{-6} \text{ M}$.