Organometallics **2001,** *20,* 2353−2358

Synthesis and Photophysical Properties of Dinuclear Organometallic Rhenium(I) Diimine Complexes Linked by Pyridine-Containing Macrocyclic Phenylacetylene Ligands

Shih-Sheng Sun and Alistair J. Lees*

Department of Chemistry, State University of New York at Binghamton,
Binghamton, New York 13902-6016

Received February 15, 2001

Two novel pyridine-containing hexagonal phenylacetylenic macrocyclic ligands have been synthesized from Pd-catalyzed cross-coupling or Cu-catalyzed oxidative coupling reactions. These ligands have been subsequently used to prepare dinuclear 4,4′-di-*tert*-butyl-2,2′-bipyridine Re(I) tricarbonyl complexes. Both ligands and complexes show strong luminescence in room-temperature solution. There is no concentration dependence in the ^{1}H NMR spectra for these ligands and complexes, which rules out ground-state self-association. However, both of the free ligands exhibit concentration-dependent fluorescence. The fluorescence bands of the ligands are red-shifted with increasing concentration, and this behavior is ascribed to the formation of excimers in the excited states. In contrast, both of the organometallic complexes do not exhibit any concentration-dependent luminescence.

Introduction

The design and synthesis of structurally well-defined supramolecular transition-metal complexes with interesting photochemical, photophysical, and/or redox properties is an area of considerable current interest.[1] Transition-metal complexes exhibiting metal-to-ligand charge transfer (MLCT) luminescence are particularly attractive for studying these photoinduced dynamical processes and for their possible applications in solar energy conversion.[2] The redox and optical properties of these complexes are usually influenced by the ligands used to link the individual chromophore.[2] Among the various types of ligands used to build multinuclear transition-metal complexes, the ones that comprise conjugated alkynyl spacers in the backbones have been shown to be very promising candidates for constructing a variety of novel molecular structures with potential applications in optical electronics.[3]

In particular, macrocyclic phenylacetylenes with defined shapes and geometries have drawn a great deal of attention in the past few years.[4] Several macrocyclic phenylacetylenes have been shown to have especially interesting properties, such as self-association in solution,[5] the existence of liquid crystalline phases,[6] formation of hydrogen-bonding solids with large internal voids,[7] and the capability to bind small guest molecules.[5c,7,8] These different properties can be easily modified by varying the size and shape of the molecules as well as the electronic and steric character of the substituents on the macrocyclic framework. To the best of our knowledge, however, the utilization of a macrocyclic phenylacetylenic unit to link transition-metal chromophores has not been reported yet,[9] although transition-metal complexes linked by linear conjugated acetylenic ligands are well-known now.[10]

For several years, we have been interested in the photophysical properties of rhenium(I) tricarbonyl complexes containing polypyridyl bridging ligands.[11] We have also found that in many cases the photophysical behaviors of the rhenium(I) tricarbonyl complexes are

---

* Corresponding author. Fax: (+1)607-777-4478. E-mail: alees@binghamton.edu.

[1] Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chihester, U.K., 1991.

[2] (a) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711. (b) Balzani, V.; Juris, A.; Venturi, M.; Campagna S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

[3] Ziessel, R. F. *J. Chem. Edu.* **1997**, *74*, 673, and references therein.

[4] (a) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402, and references therein. (b) Haley, M. M.; Pak, J. J.; Brand, S. C. *Top. Curr. Chem.* **1999**, *201*, 81, and references therein. (c) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294. (d) Kahr, M.; Xu, Z.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537. (e) Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 11600. (f) Wu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 297. (g) Ge, P.-H.; Fu, W.; Herrmann, W. A.; Herdtweck, E.; Campana, C.; Adams, R. D.; Bunz, U. H. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3607.

[5] (a) Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019. (b) Tobe, Y.; Utsumi, N.; Kawabata, K.; Naemura, K. *Tetrahedron Lett.* **1996**, *37*, 9325. (c) Tobe, Y.; Utsumi, N.; Nagano, A.; Naemura, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1285. (d) Tobe, Y.; Nagano, A.; Kawabata, K.; Sonoda, M.; Naemura, K. *Org. Lett.* **2000**, *2*, 3265.

[6] (a) Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2655. (b) Mindyuk, O. Y.; Stetzer, M. R.; Heiney, P. A.; Nelson, J. C.; Moore, J. S. *Adv. Mater.* **1998**, *10*, 1636. (c) Collins, S. K.; Yap, G. P. A.; Fallis, A. G. *Org. Lett.* **2000**, *2*, 3189.

[7] Venkataraman, D.; Lee, S.; Moore, J. S. *Nature* **1994**, *371*, 591.

[8] (a) Anderson, H. L.; Bashall, A.; Hendrick, K.; Mcpartlin, M.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 429. (b) Morrison, D. L.; Höger, S. *Chem. Commun.* **1996**, 2313.

[9] Hupp and co-workers have reported a series of Re(I) tricarbonyl complexes linked by cyclic crown-ether based pyridyl or bipyridyl ligands which exhibit interesting intramolecular electron-transfer properties. See: (a) Yoon, D. I.; Berg-Brennan, C. A.; Lu, H.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 3192. (b) Berg-Brennan, C. A.; Yoon, D. I.; Hupp, J. T. *J. Am. Chem. Soc.* **1993**, *115*, 2048. (c) Berg-Brennan, C. A.; Yoon, D. I.; Slone, R. V.; Kazala, A. P.; Hupp, J. T. *Inorg. Chem.* **1996**, *35*, 2032.

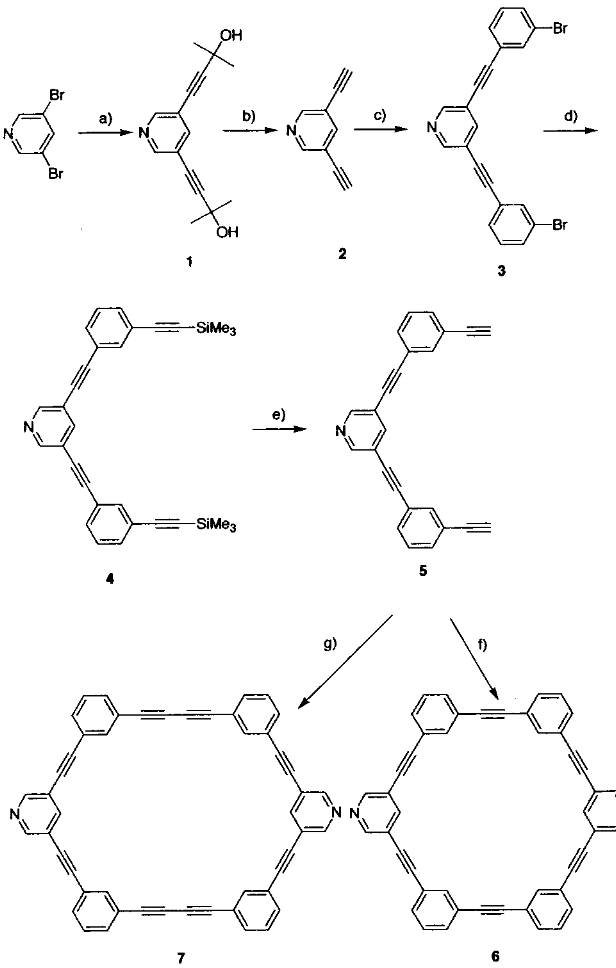
10.1021/om010125s CCC: $20.00
Publication on Web 05/02/2001

mainly determined by the electronic properties of the bridging ligands.[11c–g] As an extension of this ongoing research interest, we report herein the preparation, characterization, and photophysical properties of two diimine Re(I) tricarbonyl based dimeric complexes that are bridged by novel pyridine-containing hexagonal phenylacetylenic macrocyclic ligands.

Results and Discussion

Synthesis. Stepwise synthetic procedures for the macrocyclic ligands **6** and **7** are illustrated in Scheme 1. Precursor **1** was readily synthesized from 3,5-dibromopyridine and 2-methyl-3-butyn-2-ol by a Sonogashira–Hagihara cross-coupling reaction[12] catalyzed by $Pd(PPh_3)_2Cl_2$ and CuI. Subsequent deprotection of **1**, leading to precursor **2**, can be achieved using KOH in refluxing benzene. We used 2-methyl-3-butyn-2-ol as the coupling reagent to synthesize precursor **2** instead of the more commonly used but also more expensive trimethylsilyl acetylene. It was found out that the yield is comparable to the published procedure using trimethylsilyl acetylene.[13] Precursor **3** was synthesized by selective coupling of **2** with 1-bromo-3-iodobenzene. Further coupling of **3** with trimethylsilylacetylene afforded precursor **4**. Deprotection of the trimethylsilyl group using KF in MeOH solution afforded precursor **5**. The yield when using 2-methyl-3-butyn-2-ol to synthesize precursor **4** was low (~20%). The subsequent deprotection step afforded only mixtures of products, and we were unable to separate them to get pure precursor **5**. Precursor **5** was then used to synthesize cyclic ligands **6** and **7** using Sonogashira–Hagihara cross-coupling and oxidative coupling with a Hay catalyst,[14] respectively. The cyclic ligand **6** can be easily purified by recrystallization from CH_2Cl_2/hexane. No other oligomers or cyclic compounds were isolated as minor products. The solubility of ligand **6** is fair in polar solvent, ca. 8 mg/mL in CH_2Cl_2. Cyclic ligand **7** exhibits very low solubility in common organic solvents, ca. <1 mg/mL in CH_2Cl_2. The preparation of **7** has been performed under a high dilution condition to reduce the formation of some higher order macrocycles and diacetylene polymers.[15] However, while elemental analysis of ligand **7** is satisfactory, it does suggest that there are still impurities in ligand **7** and presumably these are higher order oligomers or polymers. Solids **6** and **7** are relatively stable in the air for a few weeks without any sign of decomposition, although they are quite air sensitive in solution.

Scheme 1[a]



[a] (a) $PdCl_2(PPh_3)_2$, CuI, NEt_3/THF (1:1), 2-methyl-3-butyn-2-ol, 75 °C, 12 h, 91%; (b) KOH, benzene, refluxed, 5 h, 82%; (c) 1-bromo-3-iodobenzene, $PdCl_2(PPh_3)_2$, CuI, NEt_3/THF (1:1), 35 °C, 20 h, 76%; (d) $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, trimethylsilylacetylene, 70 °C, 48 h, 59%; (e) KF, MeOH, room temperature, 24 h, 99%; (f) **3**, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, 70 °C, 16 h, 54%; (g) CuCl, pyridine, O_2, room temperature, 30 h, 32%.

Dinuclear complexes **8** and **9** were prepared in a similar manner by refluxing the cyclic ligand and (*t*-Bu_2bpy)$Re(CO)_3(CH_3CN)(PF_6)$ (*t*-Bu_2bpy is 4,4′-di-*tert*-butyl-2,2′-bipyridine) in THF (see Scheme 2) and subsequent recrystallization from CH_2Cl_2/hexane solution. In contrast to ligand **7**, complex **9** is soluble in most polar organic solvents due to the presence of *tert*-butyl groups and positive charges imparted by the structure. As noted above, there is the indication of a small amount of impurties in ligand **7**, and this may contribute to the lower yield of complex **9** (26%) compared to complex **8** (62%).

Photophysical Properties. The obtained photophysical data, including absorption, emission spectral data, emission quantum yields, and lifetimes of com-

---

(10) (a) Lin, J. T.; Sun, S.-S.; Wu, J. J.; Lee, L.; Lin, K.-J.; Huang, Y.-F. *Inorg. Chem.* **1995**, *34*, 2323. (b) Lin, J. T.; Sun, S.-S.; Wu, J. J.; Liaw, Y.-C.; Lin, K.-J. *J. Organomet. Chem.* **1996**, *517*, 217. (c) Ley, K. D.; Whittle, C. E.; Bartberger, M. D.; Schanze, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3423. (d) Hissler, M.; El-ghayoury, A.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1717. (e) Harriman, A.; Hissler, M.; Trompette, O.; Ziessel, R. *J. Am. Chem. Soc.* **1999**, *121*, 2516.

(11) (a) Kotch, T.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I. *Chem. Mater.* **1992**, *4*, 675. (b) Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I.; Snyder, R. W. *Inorg. Chem.* **1993**, *32*, 2570. (c) Sun, S.-S.; Lees, A. J. *Inorg. Chem.* **1999**, *38*, 4181. (d) Sun, S.-S.; Silva, A. S.; Brinn, I. M.; Lees, A. J. *Inorg. Chem.* **2000**, *39*, 1344. (e) Sun, S.-S.; Robson, E.; Dunwoody, N.; Silva, A. S.; Brinn, I. M.; Lees, A. J. *Chem. Commun.* **2000**, 201. (f) Sun, S.-S.; Lees, A. J. *Chem. Commun.* **2000**, 1687. (g) Sun, S.-S.; Lees, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 8956. (h) Sun, S.-S.; Lees, A. J. *Chem. Commun.* **2001**, 103.

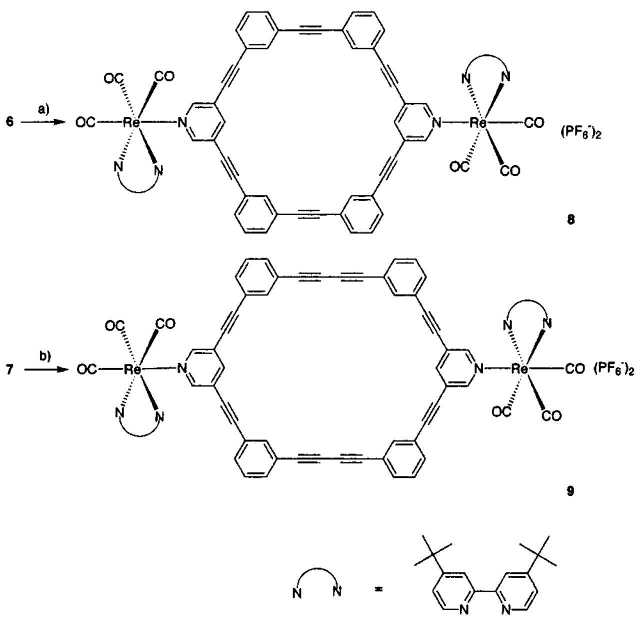
(12) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467. (b) Takahashi, S. N.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(13) Bosch, E.; Barnes, C. L. *Organometallics* **2000**, *19*, 5522.

(14) (a) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320. (b) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614. (c) Anthony, J.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 406.

(15) (a) Höger, S.; Enkelmann, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2713. (b) Höger, S.; Meckenstock, A.-D.; Müller, S. *Chem. Eur. J.* **1998**, *4*, 2423.

Scheme 2[a]



[a] (a) $(CH_3CN)Re(CO)_3(4,4'\text{-}t\text{-}Bu_2bpy)(PF_6)$, THF, 60 °C, 18 h, 62%; (b) $(CH_3CN)Re(CO)_3(4,4'\text{-}t\text{-}Bu_2bpy)(PF_6)$, THF, 60 °C, 3 days, 26%.

Table 1. Photophysical Data of Ligands (6 and 7) and Complexes (8 and 9) in Deoxygenated CH_2Cl_2[a]

compd	λ_{max}, nm ($\epsilon \times 10^{-3}$, $M^{-1}cm^{-1}$)	λ_{em}, nm	τ, ns	Φ_{em}[b]
6[c]	252 (54), 262 (60), 288 (41.2), 303 (32.9)	337	1.2	0.19
7[c]	240 (43.2), 249 (46.1), 275 (sh, 35.0), 287 (42.2), 300 (33.4)	336	1.1	0.15
8	251 (116), 272 (121), 281 (120), 305 (102), 316 (sh, 81.3), 344 (sh, 23.1), 380 (sh, 9.31)	542	1060	0.026
9	251 (156), 261 (154), 283 (sh, 111), 303 (94.9), 316 (sh, 80.6), 346 (sh, 24.9), 380 (sh, 9.31)	540	1010	0.026

[a] λ_{ex} = 350 nm. sh = shoulder. [b] Quantum yield is calculated relative to $[(bpy)Re(CO)_3(4\text{-}Etpy)](PF_6)$ (Φ_{em} = 0.027 in CH_3CN) for dimers **8** and **9** or calculated relative to aniline (Φ_{em} = 0.10 in EtOH) for ligands **6** and **7**. [c] λ_{ex} = 310 nm.

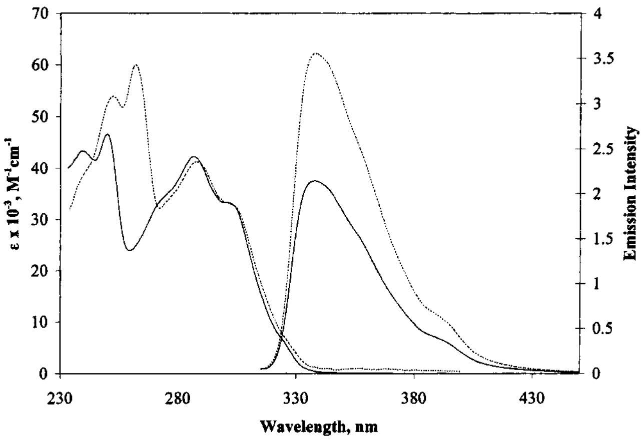


Figure 1. Electronic absorption and emission spectra of cyclic ligands **6** (dashed line) and **7** (solid line) in deoxygenated CH_2Cl_2 solution.

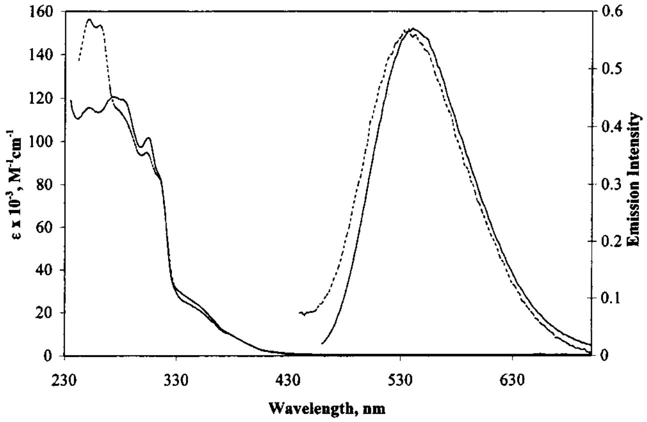


Figure 2. Electronic absorption and emission spectra of complexes **8** (solid line) and **9** (dashed line) in deoxygenated CH_2Cl_2 solution.

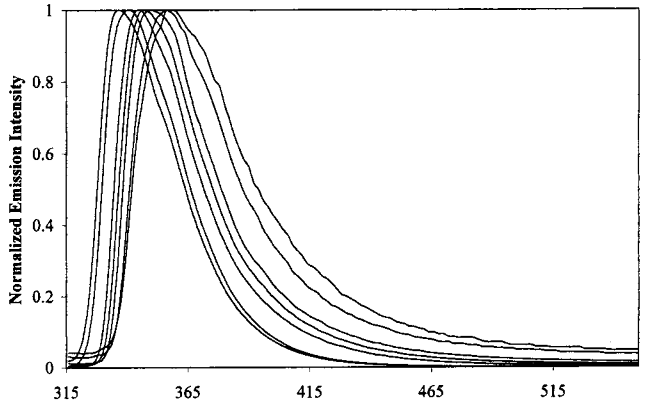


Figure 3. Concentration-dependent fluorescence spectra of cyclic ligands **6** in deoxygenated CH_2Cl_2. The spectra from left to right are recorded at concentrations of 1×10^{-5}, 1×10^{-4}, 1×10^{-3}, 2×10^{-3}, 4×10^{-3}, 8×10^{-3}, and 1×10^{-2} M, respectively.

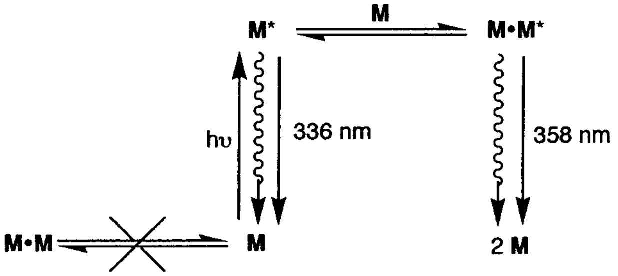
plexes **8** and **9**, as well as ligands **6** and **7**, are summarized in Table 1. Figures 1 and 2 present the absorption and emission spectra recorded from ligands **6** and **7** and complexes **8** and **9** in deoxygenated CH_2Cl_2 solution. The bands that appear below 320 nm for complexes **8** and **9** are assigned to the vibrational progression of $\pi-\pi^*$ absorptions, as evidenced from the similar vibrational structures in the corresponding ligands **6** and **7**. It is noted that, although the frameworks of ligands **6** and **7** are extended, the colors of **6** and **7** are only pale yellow because of the interruption of conjugation at the meta-connection.[15b] The absorption bands that extend from 350 to 430 nm in complexes **8** and **9** are assigned to the combination of Re (dπ) to t-Bu_2bpy (π^*) and Re (dπ) to cyclic ligand (π^*) charge-transfer transitions with the Re (dπ) to t-Bu_2bpy (π^*) charge-transfer band at slightly higher energy.

Ligands **6** and **7** both exhibit strong blue fluorescence with similar band maxima and comparable lifetimes and quantum yields to each other. The emission data of complexes **8** and **9** in deoxygenated CH_2Cl_2 solution resemble one another in that each exhibits structureless bands and long lifetimes. The emissions are assigned to Re (dπ) to cyclic ligand (π^*) charge-transfer transitions in the complexes. Ligand **6** exhibits concentration-dependent fluorescence in CH_2Cl_2 solution (see Figure 3). The fluorescence maximum shifts from 336 nm in 10^{-6} M solution to 358 nm in 10^{-2} M solution. There is no further spectral change observed below 10^{-6} M, and precipitation occurs when the solution concentration is raised higher than 10^{-2} M. The fluorescence lifetime of **6** is best fitted to a biexponential decay (1.1 and 3.2 ns) when it is monitored at 460 nm, where the emission comprises contributions from both monomer and excimer. The emission is best fitted as a single-exponential decay (1.1 ns) when it is monitored at 320 nm, where the emission is solely from the monomer. Cyclic ligand **7** exhibits a similar red shift in the fluorescence with the maximum moving from 336 nm at 10^{-6} M solution to 342 nm at $\sim 5 \times 10^{-4}$ M, which is near the point of saturation. The fluorescence decay of **7** also exhibits a biexponential process (1.1 and 3.6 ns) when it is monitored at 420 nm, where the emission comprises contributions from both monomer and excimer. In contrast, the emission spectra and lifetimes are observed to be concentration independent for both complexes **8** and **9**.

Several cyclic phenylacetylenes have been shown to aggregate at high concentration in solution, and this is thought to be mainly due to a favorable $\pi-\pi$ stacking interaction.[5] Ligand **6** and complexes **8** and **9** do not exhibit any concentration dependence in the ^{1}H NMR spectra recorded in CD_2Cl_2, ruling out the existence of any significant degree of ground-state aggregation. We were unable to test the associative nature of ligand **7** by ^{1}H NMR spectra due to the low solubility of this species. However, the lack of aggregation in solution of complexes **8** and **9** is thought to be due to the bulky *tert*-butyl groups which surely prevent close association. In ligand **6**, the electrostatic repulsion between the nitrogen atoms would seem to be responsible for the non-association behavior, as evidenced by the electrostatic potential plot based on an AM1 calculation.[16] The same reasoning can also be applied to ligand **7**, and it is, therefore, plausible to assume that there is no self-association for ligand **7** in solution either. Thus, the concentration-dependent fluorescence bands observed in CH_2Cl_2 solution for ligands **6** and **7** cannot be attributed to ground-state association.

Consequently, the concentration-dependent fluorescence is best to be ascribed to an excited-state aggregation process. Polyaromatic compounds are already known to exhibit excimer emission that is highly concentration dependent.[17] Indeed, the first reported example for aromatic excimer formation was the concentration-dependent fluorescence of pyrene in solution.[18] Recently, Kopelman et al. have found the formation of excimers from some phenylacetylene dendrimers;[19a] the excimer formation is observed in some solvents even at concentrations as low as 7.0×10^{-8} M. Excimer emission is also observed for some poly(*p*-phenyleneethynylene) polymers in solution and thin films.[19b,c] We have also recently found some linear alkynyl bipyridines that exhibit concentration-dependent excimeric emission.[20]

Scheme 3



Scheme 3 depicts a qualitative diagram of the excited-state processes for ligands **6** or **7** and portrays the lack of any ground-state association. The biexponential decay of the emission at higher concentration for ligands **6** and **7** in CH_2Cl_2 confirms that there are indeed two distinct excited states present. The longer lifetime observed at the higher concentrations is, therefore, attributed to the excimer species.

Conclusion

We have successfully synthesized two pyridine-containing hexagonal phenylacetylenic macrocyclic ligands with Pd-catalyzed cross-coupling or Cu-catalyzed oxidative coupling reaction in moderate yields. These macrocyclic ligands can then be used to synthesize dimeric Re(I) complexes in relatively good yields. There is no concentration dependence in the ^{1}H NMR spectra for both the macrocyclic ligands and the metal complexes, which rules out ground-state self-association. Both metal complexes and their macrocyclic ligands show strong emission in room-temperature solution. While the metal complexes do not show any concentration-dependent emission, the macrocyclic ligands exhibit concentration-dependent emissions that are ascribed to the formation of excimers.

Experimental Section

Materials and General Procedures. All starting chemicals were commercially available and used without further purification unless otherwise noted. 1-Bromo-3-iodobenzene was degassed by freeze−pump−thaw cycle (three times) and kept in the dark before use. (t-Bu$_2$bpy)Re(CO)$_3$(CH$_3$CN)(PF$_6$) was prepared according to a published method.[11f] Nitrogen used for the synthesis and purging experiments was dried and deoxygenated according to a previously reported procedure.[11g]

Equipment and Procedures. NMR spectra were obtained using Brücker AM 360 or AC 300 spectrometers. Infrared spectra were measured on a Nicolet 20SXC Fourier transform infrared spectrophotometer. Elemental analysis was performed by Oneida Research Service, Whitesboro, NY. Electrospray mass spectra were obtained using a Finnigan MAT TSQ700 triple quadrupole mass spectrometer equipped with a Finnigan electrospray interface. Absorption spectra were obtained using a HP 8450A diode array spectrophotometer interfaced to an IBM computer.

Emission spectra were recorded in deoxygenated CH_2Cl_2 solution at 293 K with an SLM 48000S lifetime fluorescence spectrophotometer equipped with a red sensitive photomultiplier tube. The emission quantum yields were calculated relative to [(bpy)Re(CO)$_3$(4-Etpy)](PF$_6$) ($\Phi_{em} = 0.027$ in CH$_3$CN)[21] or aniline ($\Phi_{em} = 0.1$ in EtOH).[22] Luminescence lifetimes

---

(16) *CAChe Work System 3.8*; Oxford Molecular: Oxford, 1995.

(17) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.

(18) (a) Förster, T.; Kasper, K. *Z. Phys. Chem.* **1954**, *1*, 275. (b) Förster, T. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 333.

(19) (a) Swallen, S. F.; Zhu, Z.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B* **2000**, *104*, 3988. (b) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S.; L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655. (c) Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52.

(20) Sun, S.-S.; Lees, A. J. *J. Photochem. Photobiol. A* **2001**, *140*, 157.

(21) Tapolsky, G.; Duesing R.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 2285.

of metal complexes were obtained using a Molectron Pulsed Nd:YAG laser ($\lambda_{ex} = 355$ nm) system as the excitation source, and a Tektronix 7612A digitizer was used for decay data acquisition. Luminescence lifetimes of the free ligands were obtained using an SLM 48000S lifetime fluorescence spectrophotometer. The detailed procedures for the luminescence experiments have been described in a previous paper.[11g]

Synthesis. 4-[5-(3-Hydroxy-3-methylbut-1-ynyl)pyridin-3-yl]-2-methylbut-3-yn-2-ol (1). A 250 mL flask were charged with 3,5-dibromopyridine (5 g, 21.2 mmol), $PdCl_2(PPh_3)_2$ (900 mg, 1.28 mmol), and CuI (484 mg, 2.54 mmol). Subsequently, 50 mL of THF, 100 mL of NEt_3, and 4.5 mL of 2-methyl-3-butyn-2-ol (3.91 g, 46.4 mmol) were added to the flask successively. The resulting mixture was heated to 75 °C for 12 h before the solvent was removed under vacuum. The black residue was extracted with diethyl ether (100 mL × 3) and washed with 100 mL of water. The ether layer was dried over $MgSO_4$ and then filtered through neutral alumina. The ether was rotary evaporated to leave a dark purple oil, which solidified after about 30 min. Approximately 150 mL of hexane was added to the flask, and the solution was vigorously shaken. The resulting white solid was collected on a frit and washed several times with 10 mL of hexane to afford a white powder of **1** (4.7 g, 91%). ^{1}H NMR (360 MHz, $CDCl_3$): 8.54 (d, $^4J_{H-H} = 1.9$ Hz, 2 H, PyH_α), 7.70 (s, 1 H, PyH_γ), 2.89 (s, 2 H, $-OH$), 1.59 (s, 12 H, $-CH_3$). ^{13}C NMR ($CDCl_3$): 150.5, 141.0, 119.6, 98.1, 77.8, 65.2, 31.2. Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.00; H, 7.09; N, 5.69.

3,5-Diethynylpyridine (2). To a 250 mL flask containing **1** (4.4 g, 18.1 mmol) and powdery KOH (1.4 g) was added 100 mL of Ar-degassed benzene, and the resulting solution was refluxed for 5 h. The brown solid was filtered, and the filtrate was dried under vacuum to leave a yellow brown solid in the flask. Recrystallization from ether/pentane afforded **2** as a white solid. Yield: 1.89 g (82%). ^{1}H NMR (360 MHz, $CDCl_3$): 8.63 (d, $^4J_{H-H} = 2.0$ Hz, 2 H, PyH_α), 7.24 (s, 1 H, PyH_γ), 3.22 (s, 2 H, $-C{\equiv}CH$). ^{13}C NMR ($CDCl_3$): 151.9, 141.9, 119.0, 81.4, 79.4. Anal. Calcd for C_9H_5N: C, 85.02; H, 3.96; N, 11.02. Found: C, 85.16; H, 4.01; N, 11.16.

3,5-Bis(3-bromophenylethynyl)pyridine (3). Triethylamine (120 mL), THF (50 mL), and 1-bromo-3-iodobenzene (7.99 g, 28.2 mmol) were successively added into a flask containing **2** (1.7 g, 13.4 mmol), $PdCl_2(PPh_3)_2$ (564 mg, 0.8 mmol), and CuI (306 mg, 1.61 mmol). The resulting mixture was gently heated at 35 °C for 20 h. The solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2/H_2O. The CH_2Cl_2 portion was collected, dried over $MgSO_4$, and filtered through neutral alumina. A copious amount of pale yellow solid appeared after the volume of filtrate was reduced under vacuum to ~10 mL. The solvent was carefully decanted, and the residue was washed with hexane and dried in vacuo to afford an off-white powder (4.45 g, 76%). ^{1}H NMR (360 MHz, $CDCl_3$): 8.67 (d, $^4J_{H-H} = 1.6$ Hz, 2 H, PyH_α), 7.90 (s, 1 H, PyH_γ), 7.68 (s, 2 H, Ph-2), 7.50 (d, $^3J_{H-H} = 8.0$ Hz, 2 H, Ph-6), 7.45 (d, $^3J_{H-H} = 7.8$ Hz, 2 H, Ph-4), 7.23 (t, $^3J_{H-H} = 7.9$ Hz, 2 H, Ph-5). ^{13}C NMR ($CDCl_3$): 151.1, 140.7, 134.4, 132.2, 130.3, 129.9, 124.2, 122.3, 119.7, 91.7, 86.3. Anal. Calcd for $Br_2C_{21}H_{11}N$: C, 57.70; H, 2.54; N, 3.20. Found: C, 57.54; H, 2.71; N, 3.27.

3,5-Bis[3-(trimethylsilanylethynyl)phenylethynyl]pyridine (4). To a 100 mL flask containing **3** (0.95 g, 2.17 mmol), $PdCl_2(PPh_3)_2$ (60 mg, 0.087 mmol), and CuI (17 mg, 0.087 mmol) was added 50 mL of *i*-Pr_2NH. The mixture was refluxed for 2 days before the solvent was removed under vacuum. The black residue was extracted with CH_2Cl_2/H_2O. The organic portions were collected, dried over $MgSO_4$, and filtered through neutral alumina. The solvent was removed under reduced pressure. The residue was washed with pentane (10 mL × 2) and dried in vacuo to afford an off-white powder (550 mg, 59%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.65 (d, $^4J_{H-H} = 1.9$ Hz, 2 H, PyH_α), 7.89 (t, $^4J_{H-H} = 1.9$ Hz, 1 H, PyH_γ), 7.65 (s, 2 H, Ph-2), 7.48−7.43 (m, 4 H, Ph-4,6), 7.29 (t, $^3J_{H-H} = 7.7$ Hz, 2 H, Ph-5), 0.24 (s, 18 H, $-CH_3$). ^{13}C NMR ($CDCl_3$): 151.0, 141.0, 135.4, 132.5, 131.8, 128.7, 124.0, 122.7, 120.3, 104.1, 95.6, 92.7, 85.8, 0.11. Anal. Calcd for $C_{31}H_{29}NSi_2$: C, 78.93; H, 6.20; N, 2.97. Found: C, 79.02; H, 5.89; N, 3.25.

3,5-Bis(3-ethynylphenylethynyl)pyridine (5). To a 100 mL flask containing a mixture of **4** (470 mg, 1 mmol) and KF (150 mg, 2.59 mmol) was added 40 mL of MeOH, and the solution was stirred at room temperature for 24 h. The solvent was evaporated under vacuum, and the residue was extracted with CH_2Cl_2/H_2O. The CH_2Cl_2 portion was collected, dried over $MgSO_4$, filtered, and evaporated to dryness. The pale yellow solid was recrystallized from CH_2Cl_2/hexane to afford a white powder in 99% yield (320 mg). ^{1}H NMR (300 MHz, $CDCl_3$): 8.72 (bs, 2 H, PyH_α), 7.94 (bs, 1 H, PyH_γ), 7.65 (s, 2 H, Ph-2), 7.47−7.44 (m, 4 H, Ph-4,6), 7.30 (t, $^3J_{H-H} = 7.8$ Hz, 2 H, Ph-5), 3.10 (s, 2 H, $-C{\equiv}CH$). ^{13}C NMR ($CDCl_3$): 151.2, 140.9, 135.4, 132.8, 132.1, 128.8, 122.92, 122.86, 120.1, 92.5, 86.0, 82.7, 78.3. Anal. Calcd for $C_{25}H_{13}N$: C, 91.72; H, 4.00; N, 4.28. Found: C, 92.01; H, 4.14; N, 4.51.

Cyclic Ligand 6. To a 100 mL flask containing **3** (300 mg, 0.62 mmol), **5** (200 mg, 0.62 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.021 mmol), and CuI (5 mg, 0.026 mmol) was added 50 mL of *i*-Pr_2-NH. The mixture was refluxed for 18 h before the solvent was removed under vacuum. The brown residue was extracted with CH_2Cl_2/H_2O. The organic portions were combined and filtered through a short alumina column (2 cm length). The filtrate was washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was removed under reduced pressure to leave a yellow-brown oil. Recrystallization from CH_2Cl_2/hexane afforded pale yellow powdery **6** (220 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.72 (d, $^3J_{H-H} = 1.8$ Hz, 4 H, PyH_α), 7.91 (t, $^3J_{H-H} = 1.8$ Hz, 2 H, PyH_γ), 7.62 (s, 4 H, Ph-2), 7.46−7.42 (m, 8 H, Ph-4,6), 7.21 (t, $^3J_{H-H} = 7.8$ Hz, 4 H, Ph-5). ^{13}C NMR ($CDCl_3$): 153.2, 142.9, 135.7, 131.8, 131.1, 127.8, 121.94, 121.88, 117.1, 91.5, 85.0, 78.0. EI-MS: *m/z* 602.18 (calcd *m/z* 602.18 for M^+). Anal. Calcd for $C_{46}H_{22}N_2$: C, 91.67; H, 3.68; N, 4.65. Found: C, 92.01; H, 3.69; N, 4.42.

Cyclic Ligand 7. To a 250 mL flask containing CuCl (10 mg, 0.10 mmol) and 150 mL of oxygen-saturated pyridine was slowly added **5** (300 mg, 0.93 mmol) in 50 mL of pyridine over 6 h. The mixture was stirred at room temperature for another 24 h after addition of **5**. The orange-brown solution was poured into 500 mL of water, and the resulting pale yellow precipitate was collected on a frit and washed with water, acetone, and cold CH_2Cl_2 to afford a pale yellow solid (90 mg, 32%). The solubility of **7** is extremely low in common organic solvents, which prevents further spectroscopic characterization. Anal. Calcd for $C_{50}H_{22}N_2$: C, 92.29; H, 3.41; N, 4.30. Found: C, 92.93; H, 3.44; N, 4.16.

[(*t*-Bu$_2$bpy)Re(CO)$_3$]$_2$(*μ*-6)(PF$_6$)$_2$ (8). To a 100 mL flask containing ligand **6** (150 mg, 0.23 mmol) and (*t*-Bu$_2$bpy)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (340 mg, 0.47 mmol) was added 30 mL of THF. The mixture was refluxed for 18 h before the solvent was removed under vacuum. The yellow residue was dissolved in CH_3CN and filtered to remove any insoluble material. Slow diffusion of diethyl ether into CH_3CN filtrate afforded dimer **8** as a yellow solid (280 mg, 62%). IR ($\nu_{C\equiv O}$, CH_2Cl_2): 2034, 1929. ^{1}H NMR (300 MHz, CD_2Cl_2): 8.85 (d, $^3J_{H-H} = 5.9$ Hz, 4 H, $H_{6,6'-bpy}$), 8.28 (d, $^4J_{H-H} = 1.6$ Hz, 4 H, $H_{3,3'-bpy}$), 8.07 (s, 2 H, PyH_γ), 7.72 (s, 4 H, Ph-2), 7.64 (dd, $^3J_{H-H} = 5.9$ Hz, $^4J_{H-H} = 1.5$ Hz, 4 H, $H_{5,5'-bpy}$), 7.53 (m, 12 H, PyH_α, Ph-4,6), 7.29 (t, $^3J_{H-H} = 7.9$ Hz, 4 H, Ph-5), 1.47 (s, 36 H, *t*-Bu). ^{13}C NMR (CD_2Cl_2): 194.3, 191.0, 166.5, 156.6, 153.4, 151.0, 142.9, 135.1, 133.1, 131.2, 130.7, 126.0, 124.3, 122.8, 122.5, 121.9, 93.9, 91.6, 86.8, 86.2, 36.5, 30.4. ES-MS: *m/z* 1824.9 (calcd *m/z* 1825.4 for $(M - PF_6^-)^+$) and *m/z* 840.2 (calcd *m/z* 840.2

---

(22) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

for (M − 2 PF_6^-)$^{2+}$). Anal. Calcd for $C_{88}H_{70}N_6O_6P_2F_{12}Re_2$: C, 53.66; H, 3.58; N, 4.27. Found: C, 53.56; H, 3.47; N, 4.39.

[(*t*-Bu$_2$bpy)Re(CO)$_3$]$_2$(*μ*-7)(PF$_6$)$_2$ (9). Dimer **9** was prepared in a manner similar to that for dimer **8** using ligand **7** (50 mg, 0.08 mmol) and (*t*-Bu$_2$bpy)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (90 mg, 0.17 mmol). The refluxing time was extended to 3 days to ensure the completeness of the reaction. Yield: 32 mg (26%). IR ($\nu_{C\equiv O}$, CH_2Cl_2): 2035, 1931. ^{1}H NMR (300 MHz, CD_2Cl_2): 8.85 (d, $^3J_{H-H}$ = 5.9 Hz, 4 H, $H_{6,6'-bpy}$), 8.28 (d, $^4J_{H-H}$ = 1.4 Hz, 4 H, $H_{3,3'-bpy}$), 7.99 (s, 4 H, PyH_β), 7.66−7.62 (m, 12 H, PyH_α, Ph-2, $H_{5,5'-bpy}$), 7.53−7.46 (m, 8 H, Ph-4,6), 7.35 (t, $^3J_{H-H}$ = 7.7 Hz, 4 H, Ph-5), 1.48 (s, 36 H, *t*-Bu). ^{13}C NMR (CD_2Cl_2): 194.3, 191.0, 166.5, 156.6, 153.4, 151.3, 141.4, 135.5, 132.9, 132.2, 129.2, 126.0, 124.4, 123.1, 122.5, 122.0, 104.2, 96.0, 93.0, 86.1, 36.5, 30.4. ES-MS: *m*/*z* 1873.9 (calcd *m*/*z* 1873.4 for (M − PF_6^-)$^+$) and *m*/*z* 864.1 (calcd *m*/*z* 864.2 for (M − 2 PF_6^-)$^{2+}$). Anal. Calcd for $C_{92}H_{70}N_6O_6P_2F_{12}Re_2$: C, 54.76; H, 3.50; N, 4.16. Found: C, 54.54; H, 3.59; N, 4.43.

Acknowledgment. We are grateful to the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (Grant DE-FG02-89ER14039), for support of this research.

OM010125S