

Self-Assembly Molecular Architectures Incorporating Fluorene- and Carbazole-Based Bichromic Oligopyridines. Novel Photoactive Materials

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Fluorene- and carbazole-bridged dipyriddy ligands potentially useful for the construction of supramolecules by self-assembly processes have been synthesized by palladium-catalyzed cross-coupling reactions. They undergo facile ring closure reactions with $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) to form molecular geometries of varied dimensions. Fluorene-bridged ditopic ligands facilitate the formation of trimetallic triangles, while the angular carbazole-bridged ligands led to the formation of cyclic dimers. The ligands are strongly emitting in the blue region, and the supramolecules display emission of different origins triggered by the bridging aromatic segment. Carbazole-containing cyclic dimers emit green light that probably originates from a ligand-localized excited state. However, in the fluorene-based triangles emission was observed only at low temperature, and it displayed $^3\pi-\pi^*$ and $^3\text{MLCT}$ -based emissions with prolonged lifetimes.

Introduction

Metal-containing supramolecules and coordination polymers is an area of expanding development because these compounds not only provide useful models for molecular recognition and light harvesting but also have potential application in various materials.¹ Self-assembly inorganic cyclophane molecules have emerged as an important class of supramolecules in the past decade.² Such macrocycles are attractive in sensing technology: (a) the cavity inside these molecules offers

the feasibility of accommodation of guest molecules; (b) the detection of guest molecules is possible through the photoluminescence characteristics or changes in redox potential values of the incorporated metal centers.

Macrocycles in which metals are all linked by conjugated spacers appear to be very interesting because molecular wire type spacers are expected to enhance the sensitivity of chemosensors, similar to conjugated polymer-based chemical sensors.³ Furthermore, such compounds may find applications in other aspects, such as (a) third-order nonlinear optical materials;⁴ (b) electrochromic materials tunable through the redox of the metal center;⁵ and (c) electrochemical sensing materials.⁶

We have been interested in metal-containing macrocycles in which metals are linked by conjugated spacers only. Transition metal complexes generally suffer from very low luminescent quantum efficiencies due to the presence of heavy atom effects.⁷ It was thought that use of strongly emissive spacers would partially overcome this problem. The prerequisite for the construction of self-assembly metal-containing macrocycles is the avail-

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(1) (a) Lehn, J.-M. *Supramolecular Chemistry*, VCH Publishers: New York, 1995. (b) Fyfe, M. C. T.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393. (c) Fujita, M. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Lehn, J. M., Eds.; Pergamon: Oxford, 1996; Vol. 9, p 253. (d) Constable, E. C. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Lehn, J. M., Eds.; Pergamon: Oxford, 1996; Vol. 9, p 213. (e) Baxter, P. N. W. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Lehn, J. M., Eds.; Pergamon: Oxford, 1996; Vol. 9, p 165. (f) Balzani, V.; Scandola, F. *Pure Appl. Chem.* **1990**, *8*, 1457.

(2) (a) Sun, S.-S.; Lees, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 8956. (b) Leniniger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (c) Takeda, N.; Umemoto, K.; Yamaguchi, K.; Fujita, M. *Nature* **1999**, *398*, 794. (d) Fujita, M.; Yu, S.-Y.; Kusukawa, T.; Funaki, H.; Ogura, K.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2082. (e) Slone, R. V.; Benkstein, K. D.; Bélanger, S.; Hupp, J. T.; Guzei, I. A.; Rheingold, A. L. *Coord. Chem. Rev.* **1998**, *171*, 221. (f) Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289. (g) Olenyuk, B.; Fechtenkötter, A.; Stang, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1707. (h) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (i) Slone, R. V.; Hupp, J. T.; Stern, C. L.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *35*, 4096. (j) Slone, R. V.; Yoon, D. I.; Calhoun, R. M.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 11813.

(3) (a) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537. (b) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201.

(4) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349.

(5) (a) Zhu, Y.; Wolf, M. O. *J. Am. Chem. Soc.* **2000**, *122*, 10121. (b) McDonagh, A. M.; Bayly, S. R.; Riley, D. J.; Ward, M. D.; McCleverty, J. A.; Cowin, M. A.; Morgan, C. N.; Varrazza, R.; Penty, R. V.; White, I. H. *Chem. Mater.* **2000**, *12*, 2523. (c) Barthram, A. M.; Cleary, R. L.; Kowallick, R.; Ward, M. D. *Chem. Commun.* **1998**, 2695. (d) Lee, S.-M.; Marcaccio, M.; McCleverty, J. A.; Ward, M. D. *Chem. Mater.* **1998**, *10*, 3272.

(6) Bélanger, S.; Hupp, J. T.; Stern, C. L.; Slone, R. V.; Watson, D. F.; Carrell, T. G. *J. Am. Chem. Soc.* **1999**, *121*, 557.

(7) Turro, N. J. Ed. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978.

ability of ditopic (or oligotopic) ligands, and oligo- and polypyridyl ligands are probably the most widely used ligands for this purpose. We therefore set out to synthesize highly emissive, conjugated dipyrindine. A fluorene or carbazole moiety is incorporated into the conjugated spacers for the following reasons: (a) fluorene and carbazole are rigid entities which may avoid nonradiative decay of the electronic excited state; (b) fluorene and carbazole have relatively high thermal stability; (c) fluorene-⁸ and carbazole-based⁹ polymers or small molecules have been widely used in organic light-emitting materials. Here we describe the preparation and characterization of a series of *fac*-tricarboxyl rhenium(I)-based self-assembly macrocyclic compounds constructed from conjugated dipyrindines containing a fluorene or carbazole moiety.

Experimental Section

General Procedures. All reactions and manipulations were carried out under N₂ with the use of standard inert-atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed under N₂ with the use of silica gel (230–400 mesh, Macherey-Nagel GmbH & Co.) as the stationary phase in a column of 30 cm in length and 2.0 cm in diameter. 2,7-Dibromo-9,9-diethylfluorene,¹⁰ 2,7-bis(trimethylsilylethynyl)-9,9-diethylfluorene,¹¹ 3,6-dibromo-9-ethyl-carbazole,¹² (*E*)-1-(4-ethynylphenyl)-2-(4-pyridyl)ethylene,¹³ (4-ethynylphenyl)(4-pyridyl)acetylene,¹³ and Re(CO)₅Cl¹⁴ were prepared by published procedures with modifications. Infrared measurements were measured on a Perkin-Elmer Paragon-2000 FTIR spectrometer. The ¹H NMR spectra were measured by using Bruker AC300 spectrometers. Electronic absorption spectra were obtained on a Perkin-Elmer lambda 9 spectrometer.

Emission spectra were recorded in deoxygenated solvent solution at 293 K with an SLM 48000S lifetime fluorescence spectrophotometer equipped with a red-sensitive Hamamatsu R928 photomultiplier tube. The emission spectra were collected on samples with OD ~0.1 at the excitation wavelength. Low-temperature emission spectra were performed using an Oxford Instruments DN1740K liquid-nitrogen cryostat equipped with an external Oxford Instruments Model 3120 temperature controller. In all emission experiments, the sample solutions were filtered through 0.22 μm Millipore filters prior to measurement. UV–visible spectra were checked before and after irradiation to monitor possible sample degradation. Emission maxima were reproducible to within 2 nm. Luminescence quantum yields (Φ_{em}) were calculated relative to [Ru^{II}(bpy)₃]Cl₂ in air-equilibrated aqueous solution (Φ_{em} =

0.028).¹⁵ Luminescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%.

Room-temperature luminescence lifetimes were recorded on a SLM 48000S phase-modulation lifetime fluorescence spectrophotometer. The excitation light passed through a monochromator and was then intensity modulated at a different frequency by a Debye-Sears ultrasonic modulator. The sample and reference solutions were placed in a two-chamber turret. The emission intensities of each at the observation wavelength were approximately balanced by neutral density filters. The phase shift and modulation of each sample was measured alternately 25 times. The results were averaged and analyzed by an interfaced IBM computer. The errors for fitted lifetimes are estimated to be within 10%. Luminescence lifetimes at 77 K were determined on a PRA System 3000 time-correlated pulsed single-photon counting apparatus.¹⁶ Samples were excited with light from a PRA 510 nitrogen flashlamp transmitted through an Instruments SA Inc. H-10 monochromator, and emission was detected at 900 via a second Hamamatsu R995 photomultiplier tube. The resulting photon counts were stored on a Tracer Northern 7200 microprocessor-based multichannel analyzer. The instrument response function was then deconvoluted from the emission data to yield an undisturbed decay, which was fitted by an iterative least-squares procedure on an IBM-PC. The reported lifetimes were found to be within 10% over at least three measurements.

2,7-Bis(4'-pyridylethynyl)-9,9-diethylfluorene (**4a**) and 2,7-bis(4'-pyridylethynyl)-9,9-dihexylfluorene (**4b**) were obtained by a similar procedure, and so a detailed description is provided only for **4b**.

Synthesis of 4b. 2,7-Dibromo-9,9-dihexylfluorene (4.92 g, 10.0 mmol), Pd(PPh₃)₂Cl₂ (140 mg, 0.20 mmol), CuI (20 mg, 0.10 mmol), triphenylphosphine (104 mg, 0.40 mmol), trimethylsilyl acetylene (2.35 g, 24.0 mmol), and diethylamine (50 mL) were charged sequentially in a two-neck flask under nitrogen atmosphere and heated to reflux for 12 h. The volatiles were removed under vacuum, and the resulting solid was extracted into diethyl ether. The organic extract was washed with brine solution, dried over anhydrous MgSO₄, and evaporated to leave a pale yellow viscous oil. It was further purified by column chromatography on silica gel to obtain 9,9-dihexyl-2,7-bis(trimethylsilylethynyl)fluorene as a colorless viscous oil (4.75 g, 90%). ¹H NMR (CDCl₃): 0.25(s, 18 H, SiMe₃), 0.50–0.58 (m, 4 H, CH₂), 0.75 (t, *J* = 7.3 Hz, 6 H, CH₃), 1.00–1.10 (m, 12 H, –CH₂CH₂CH₂–), 1.88–1.94 (m, 4 H, CH₂), 7.39 (s, 2 H, aromatic), 7.43 (dd, *J* = 7.5, 1.2 Hz, 2 H, aromatic), 7.57 (d, *J* = 7.5 Hz, 2 H, aromatic). It was quantitatively converted into the 2,7-diethynyl-9,9-dihexylfluorene (**3b**) by treatment with methanolic sodium hydroxide in CH₂Cl₂ at room temperature for 6 h. ¹H NMR (CDCl₃): 0.50–0.57 (m, 4 H, CH₂), 0.75 (t, *J* = 7.3 Hz, 6 H, CH₃), 0.99–1.08 (m, 12 H, –CH₂CH₂CH₂–), 1.88–1.94 (m, 4 H, CH₂), 3.13 (s, 2 H, =CH), 7.44 (s, 2 H, aromatic), 7.46 (dd, *J* = 7.4, 1.2 Hz, 2 H, aromatic), 7.61 (d, *J* = 7.5 Hz, 2 H, aromatic). MS (EI): *m/e* 382 (M⁺).

A mixture of **3b** (1.91 g, 5.0 mmol), Pd(PPh₃)₂Cl₂ (70 mg, 0.10 mmol), CuI (10 mg, 0.05 mmol), triphenylphosphine (52 mg, 0.20 mmol), 4-bromopyridine hydrochloride (2.13 g, 11 mmol), and diethylamine (30 mL) was refluxed for 12 h. The cooled mixture was evaporated to dryness under vacuum. The resulting yellow solid was triturated with water and extracted with diethyl ether. The organic layer was collected, washed with saturated sodium chloride solution, and dried over anhydrous MgSO₄, and volatiles were removed by rotary evaporation. After column chromatography over silica gel, **4b**

(8) (a) Donat-Bouillud, A.; Lévesque, I.; Tao, Y.; D'Iorio, M.; Beaupré, S.; Blondin, P.; Ranger, M.; Bouchard, J.; Leclerc, M. *Chem. Mater.* **2000**, *12*, 1931. (b) Weinfurter, K.-H.; Fujikawa, H.; Tokito, S.; Taga, Y. *Appl. Phys. Lett.* **2000**, *76*, 2502. (c) Klärner, G.; Davey, M. H.; Chen, W.-D.; Scott, J. C.; Miller, R. D. *Adv. Mater.* **1998**, *10*, 993.

(9) (a) Maruyama, S.; Tao, X.-T.; Hokari, H.; Noh, T.; Zhang, Y.; Wada, T.; Sasabe, H.; Suzuki, H.; Watanabe, T.; Miyata, S. *J. Mater. Chem.* **1999**, *9*, 893. (b) Romero, D. B.; Nüesch, F.; Benazzi, T.; Adès, D.; Siove, A.; Zuppiroli, L. *Adv. Mater.* **1997**, *9*, 1158. (c) Romero, D. B.; Schaer, M.; Leclerc, M.; Adès, D.; Siove, A.; Zuppiroli, L. *Synth. Met.* **1996**, *80*, 271. (d) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *App. Phys. Lett.* **1993**, *63*, 2627.

(10) Tsuiue, B.; Reddinger, J. L.; Sotzing, G. A.; Soloduchko, J.; Katritzky, A. R.; Reynolds, J. R. *J. Mater. Chem.* **1999**, *9*, 2189.

(11) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112.

(12) Park, M.; Buck, J. R.; Rizzo, C. J. *Tetrahedron* **1998**, *54*, 12707.

(13) Wu, I.-I.; Lin, J. T.; Sun, S.-S.; Li, C.-S.; Lin, K. J.; Tsai, C.; Hsu, C.-C.; Lin, J.-L. *Organometallics* **1997**, *16*, 2038.

(14) King, R. B., Ed. *Organometallic Synthesis, Transition-Metal Compounds*; Academic Press: New York, 1965; Vol. 1.

(15) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

(16) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: London, 1984.

was obtained as a pale yellow solid in 72% yield. Anal. Calcd for $C_{39}H_{40}N_2$: C, 87.27; H, 7.51; N, 5.22. Found: C, 87.03; H, 7.36; N, 5.08. 1H NMR ($CDCl_3$): 0.62 (m, 4 H, CH_2), 0.75 (t, $J = 7.3$ Hz, 6 H, CH_3), 1.05–1.11 (m, 12 H, $-CH_2CH_2CH_2-$), 2.12–2.18 (m, 4 H, CH_2), 7.48–7.50 (m, 4 H, pyridyl H *meta* to N), 7.62 (d, $J = 8.0$ Hz, 2 H, aromatic), 7.73 (s, 2 H, aromatic), 7.93 (d, $J = 8.0$ Hz, 2 H, aromatic), 8.62 (d, $J = 5.6$ Hz, 4 H, pyridyl H *ortho* to N). MS (FAB): m/e 538 ($M^+ + 2$).

3a: Yield: 82%. 1H NMR ($CDCl_3$): 0.29 (t, $J = 7.2$ Hz, 6 H, CH_3), 1.99 (q, $J = 7.2$ Hz, 4 H, CH_2), 3.12 (s, 2 H, $=CH$), 7.44 (s, 2 H, aromatic), 7.45–7.48 (dd, $J = 7.5$; 1.1 Hz, 2 H, aromatic), 7.62 (d, $J = 7.5$ Hz, 2 H, aromatic). MS (EI): m/e 270 (M^+).

4a: Yield: 76%. Anal. Calcd for $C_{31}H_{24}N_2$: C, 87.70; H, 5.70; N, 6.60. Found: C, 87.63; H, 5.58; N, 6.47. 1H NMR ($CDCl_3$): 0.30 (t, $J = 7.3$ Hz, 6 H, CH_3), 2.18 (q, $J = 7.3$ Hz, 4 H, CH_2), 7.51 (m, 4 H, pyridyl H *meta* to N), 7.64 (d, $J = 8.0$ Hz, 2 H, aromatic), 7.71 (s, 2 H, aromatic), 7.95 (d, $J = 8.1$ Hz, 2 H, aromatic), 8.66 (br s, 4 H, pyridyl H *ortho* to N). MS (FAB): m/e 425 ($M^+ + 1$).

Synthesis of 5a. 2,7-Dibromo-9,9-diethylfluorene (5.85 g, 15.4 mmol), 4-vinylpyridine (3.2 g, 30.8 mmol), palladium(II) acetate (0.112 g, 0.5 mmol), tri(*o*-tolyl)phosphine (0.304 g, 1 mmol), triethylamine (8 mL), and benzene (10 mL) were charged in a Schlenk-type tube under N_2 atmosphere and sealed. The mixture was heated at 100 °C for 2 days, poured into ice water, extracted with dichloromethane, washed with brine solution, and dried over anhydrous $MgSO_4$. Evaporation of the solvent left a yellow solid, which was purified by column chromatography (SiO_2 , dichloromethane/ethyl acetate (10:1)) to yield 3.58 g (83.5%) of a pale yellow solid. Anal. Calcd for $C_{31}H_{28}N_2$: C, 86.88; H, 6.59; N, 6.54. Found: C, 86.73; H, 6.39; N, 6.38. 1H NMR (acetone- d_6): 0.35 (t, $J = 7.3$ Hz, 6 H, CH_3), 2.08 (q, $J = 7.3$ Hz, 4 H, CH_2), 7.06 (d, $J = 16.3$ Hz, 2 H, vinyl), 7.35–7.41 (m, 6 H, vinyl and pyridyl H *meta* to N), 7.49–7.54 (m, 4 H, aromatic), 7.70 (d, $J = 7.8$ Hz, 2 H, aromatic), 8.56 (d, $J = 5.6$ Hz, pyridyl H *ortho* to N). MS (FAB): m/e 429 ($M^+ + 1$).

Synthesis of **5b** was accomplished by a procedure similar to that described above for **5a**. Yield: 78%. Anal. Calcd for $C_{39}H_{44}N_2$: C, 86.62; H, 8.20; N, 5.18. Found: C, 86.51; H, 8.30; N, 4.97. 1H NMR (acetone- d_6): 0.65 (m, 4 H, CH_2), 0.73 (t, $J = 7.3$ Hz, 6 H, CH_3), 1.04–1.12 (m, 12 H, $-CH_2CH_2CH_2-$), 1.98–2.04 (m, 4 H, CH_2), 7.05 (d, $J = 16.3$ Hz, 2 H, vinyl), 7.35–7.41 (m, 6 H, vinyl and pyridyl H *meta* to N), 7.49 (s, 2 H, aromatic), 7.52 (d, $J = 8.0$ Hz, 2 H, aromatic), 7.69 (d, $J = 7.9$ Hz, 2 H, aromatic), 8.57 (d, $J = 5.7$ Hz, 4 H, pyridyl H *ortho* to N). MS (FAB): m/e 542 ($M^+ + 2$).

Synthesis of Triangles. Essentially the same procedure was used to obtain the triangles, so a detailed description is given below only for **6**. Equimolar quantities of **5b** and $Re(CO)_5Cl$ were dissolved in benzene/tetrahydrofuran (4:1, 100 mL) and heated at 60 °C for 8 h. The yellow solution was cooled, filtered, and evaporated to dryness to yield a yellow residue. It was redissolved in dichloromethane, layered with hexane, and cooled at 0 °C overnight to obtain the title compound as a yellow powder in 85% yield (0.72 g). Anal. Calcd for $C_{126}H_{132}Cl_3N_6O_9Re_3$: C, 59.59; H, 5.24; N, 3.31. Found: C, 59.19; H, 5.01; N, 2.98. 1H NMR ($CDCl_3$): 0.58–0.73 (m, 10 H), 0.86–0.98 (m, 12 H), 1.98 (m, 4 H), 7.02 (d, $J = 15.6$ Hz, 2 H), 7.30–7.57 (m, 10 H), 7.70 (d, $J = 7.8$ Hz, 2 H), 8.67 (m, 4 H). IR ($\nu(CO)$, cm^{-1}): 2024 s, 1921 s, 1887 m. MS (FAB): m/e 2539 ($M^+ + H$, ^{187}Re ; ^{35}Cl), 2504 ($M^+ - Cl$, ^{187}Re ; ^{35}Cl).

7: Yield: 92%. Anal. Calcd for $C_{126}H_{120}Cl_3N_6O_9Re_3$: C, 59.88; H, 4.79; N, 3.33. Found: C, 60.02; H, 4.64; N, 3.07. 1H NMR ($CDCl_3$): 0.57 (m, 4 H), 0.73 (q, $J = 7.2$ Hz, 6 H), 1.02 (m, 12 H), 1.97 (m, 4 H), 7.35–7.48 (m, 4 H), 7.53 (d, $J = 7.9$ Hz, 2 H), 7.56 (d, $J = 8.0$ Hz, 2 H), 7.72 (d, $J = 7.9$ Hz, 2 H), 8.70–8.75 (m, 4 H). IR ($\nu(CO)$, cm^{-1}): 2026 s, 1921 s, 1887 m. MS (FAB): m/e 2526 (M^+ , ^{187}Re ; ^{35}Cl), 2491 ($M^+ - Cl$, ^{187}Re ; ^{35}Cl).

9-Hexyl-3,6-bis[4-(2-pyridin-4-ylvinyl)phenylethynyl]-9H-carbazole (8). 3,6-Dibromo-9-hexylcarbazole (2.05 g, 5.0 mmol), (*E*)-1-(4-ethynylphenyl)-2-(4-pyridyl)ethylene (2.26 g, 11.0 mmol), $PdCl_2(PPh_3)_2$ (140 mg, 0.20 mmol), CuI (19.2 mg, 0.10 mmol), and diisopropylamine (30 mL) were charged in a Schlenk-type tube under an N_2 atmosphere. The cooled mixture was evaporated to dryness under vacuum, and the residue was extracted with a mixture of dichloromethane and water. The organic layer was collected and dried over anhydrous $MgSO_4$. Evaporation of the solvent left a yellow solid, which was purified by column chromatography (SiO_2 , ethyl acetate) to yield 1.38 g (42%) of a pale yellow solid. Anal. Calcd for $C_{48}H_{39}N_3$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.98; H, 5.91; N, 6.08. 1H NMR ($CDCl_3$): 0.85 (t, $J = 6.8$ Hz, 3 H, CH_3), 1.15–1.48 (m, 6 H, CH_2), 1.75–1.90 (m, 2 H, CH_2), 4.30 (t, $J = 6.8$ Hz, 2 H, NCH_2), 7.05 (d, $J = 16.3$ Hz, 2 H, $=CH$), 7.26 (d, $J = 16.3$ Hz, 2 H, $=CH$), 7.31 (d, $J = 6.2$ Hz, 4 H, $NCHCH$), 7.32 (d, $J = 8.5$ Hz, 4 H, C_6H_4), 7.50 (d, $J = 8.5$ Hz, 4 H, C_6H_4), 7.54 (d, $J = 8.5$ Hz, 2 H, C_6H_3), 7.65 (dd, $J = 8.5$; 1.4 Hz, 2 H, C_6H_3), 8.28 (d, $J = 1.4$ Hz, 2 H, C_6H_3), 8.55 (d, $J = 6.2$ Hz, 4 H, NCH). MS (EI): m/e 657 (M^+).

9-Hexyl-3,6-bis[4-(pyridin-4-ylethynyl)phenylethynyl]-9H-carbazole (9). Compound **9** was synthesized by the same procedure as for the synthesis of **8**, except that (4-ethynylphenyl)(4-pyridyl)acetylene was used instead of (*E*)-1-(4-ethynylphenyl)-2-(4-pyridyl)ethylene. The yellow **9** was isolated in 45% yield. Anal. Calcd for $C_{48}H_{35}N_3$: C, 88.18; H, 5.40; N, 6.43. Found: C, 88.16; H, 5.29; N, 6.45. 1H NMR ($CDCl_3$): 0.87 (t, $J = 6.8$ Hz, 3 H, CH_3), 1.20–1.47 (m, 6 H, CH_2), 1.75–1.92 (m, 2 H, CH_2), 4.30 (t, $J = 6.8$ Hz, 2 H, NCH_2), 7.20 (d, $J = 6.2$ Hz, 4 H, $NCHCH$), 7.39 (d, $J = 8.4$ Hz, 4 H, C_6H_4), 7.55 (d, $J = 8.4$ Hz, 4 H, C_6H_4), 7.63 (d, $J = 8.4$ Hz, 2 H, C_6H_3), 7.66 (dd, $J = 8.4$; 1.3 Hz, 2 H, C_6H_3), 8.27 (d, $J = 1.3$ Hz, 2 H, C_6H_3), 8.62 (d, $J = 6.2$ Hz, 4 H, NCH). MS (EI): m/e 653 (M^+).

9-Hexyl-3,6-bis(2-pyridin-4-ylvinyl)-9H-carbazole (**10**) and 9-phenyl-3,6-bis(2-pyridin-4-ylvinyl)-9H-carbazole (**11**) were obtained by a similar procedure, and so a detailed description is provided only for **11**.

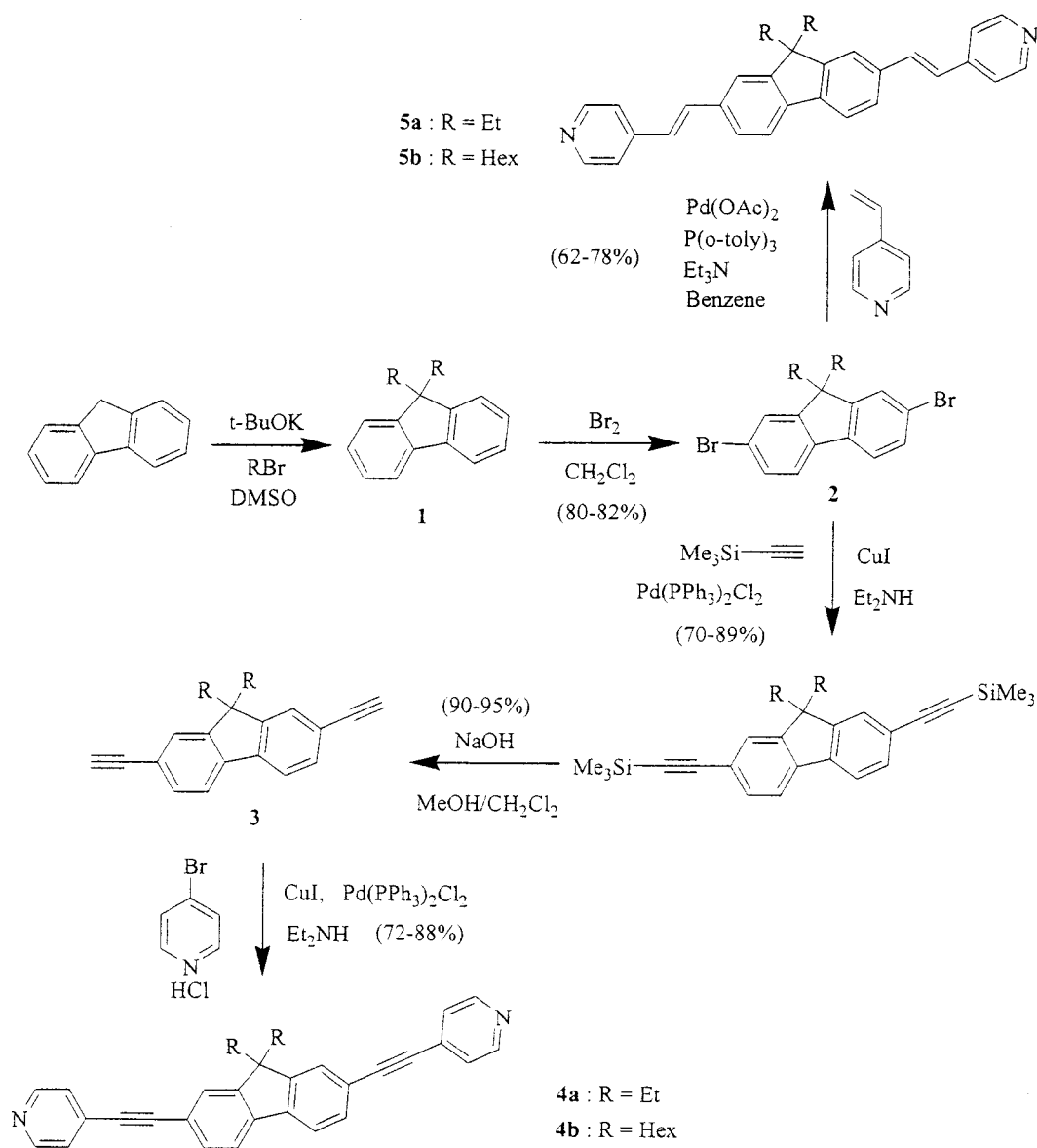
Synthesis of 11. A mixture of 3,6-dibromo-9-phenyl-9H-carbazole (4.01 g, 10.0 mmol), 4-vinyl pyridine (2.52 g, 24.0 mmol), palladium acetate (45 mg), tri-*o*-tolylphosphine (121 mg), triethylamine (3.03 g, 30.0 mmol), and toluene (10 mL) were charged successively in a pressure tube under a nitrogen atmosphere and closed using a screw cap. The contents were heated at 100 °C for 12 h. After cooling, the volatiles were removed to yield a pale yellow solid. This was chromatographed on silica using ethyl acetate as eluent to afford **11** in 76% yield (3.42 g). Anal. Calcd for $C_{32}H_{23}N_3$: C, 85.50; H, 5.16; N, 9.35. Found: C, 85.32; H, 4.98; N, 9.42. 1H NMR ($CDCl_3$): 7.06 (d, $J = 16.3$ Hz, 2 H, $=CH$), 7.36–7.65 (m, 15 H, aromatic and $=CH$), 8.32 (d, $J = 1.1$ Hz, 2 H, aromatic), 8.56 (d, $J = 6.5$ Hz, 4 H, NCH). MS (FAB): m/e 450 ($M + 1$).

10: Yield: 58%. Anal. Calcd for $C_{32}H_{31}N_3$: C, 83.99; H, 6.83; N, 9.18. Found: C, 83.56; H, 6.76; N, 9.16. 1H NMR (acetone- d_6): 0.83 (t, $J = 6.8$ Hz, 3 H, CH_3), 1.23–1.41 (m, 6 H, CH_2), 1.84–1.95 (m, 2 H, CH_2), 4.34 (t, $J = 6.8$ Hz, 2 H, NCH_2), 7.19 (d, $J = 16.3$ Hz, 2 H, $=CH$), 7.51 (d, $J = 6.2$ Hz, 4 H, $NCHCH$), 7.59 (d, $J = 8.6$ Hz, 2 H, C_6H_3), 7.70 (d, $J = 16.3$ Hz, 2 H, $=CH$), 7.81 (dd, $J = 8.6$; 1.7 Hz, 2 H, C_6H_3), 8.44 (d, $J = 1.7$ Hz, 2 H, C_6H_3), 8.53 (d, $J = 6.2$ Hz, 4 H, NCH). MS (EI): m/e 457 (M^+).

Synthesis of Cyclic Dimers. Complexes **12–14** were synthesized by a procedure similar to that described above for **6b** except that **8–10** were used instead of **4b** and the reaction time was 24 h.

The yellow complex **12** was isolated with a yield of 48%. Anal. Calcd for $C_{102}H_{78}Br_2N_6O_6Re_2$: C, 60.77; H, 3.90; N, 4.17. Found: C, 59.59; H, 3.54; N, 4.39. 1H NMR (CD_2Cl_2): 0.88 (t, $J = 6.8$ Hz, 6 H, CH_3), 1.20–1.52 (m, 12 H, CH_2), 1.78–1.95 (m, 4 H, CH_2), 4.33 (t, $J = 6.8$ Hz, 4 H, NCH_2), 7.07 (d, $J = 16.0$ Hz, 4 H, $=CH$), 7.30 (d, $J = 16.0$ Hz, 4 H, $=CH$), 7.37 (d,

Scheme 1



$J = 6.5$ Hz, 8 H, NCHCH), 7.39 (d, $J = 8.5$ Hz, 8 H, C₆H₄), 7.59 (d, $J = 8.5$ Hz, 8 H, C₆H₄), 7.60 (d, $J = 8.4$ Hz, 4 H, C₆H₃), 7.70 (dd, $J = 8.4; 1.4$ Hz, 4 H, C₆H₃), 8.30 (d, $J = 1.4$ Hz, 4 H, C₆H₃), 8.70 (d, $J = 6.5$ Hz, 8 H, NCH). IR (ν (CO), cm⁻¹): 2025 s, 1922 s, 1886 m. MS (FAB +ve): 2018 (M⁺, ¹⁸⁷Re; ⁸¹Br), 1937 (M⁺ - Br, ¹⁸⁷Re; ⁸¹Br).

The golden yellow complex **13** was isolated with a yield of 65%. Anal. Calcd for C₁₀₂H₇₀Br₂N₆O₆Re₂: C, 61.01; H, 3.51; N, 4.19. Found: C, 60.80; H, 3.56; N, 4.62. ¹H NMR (CD₂Cl₂): 0.89 (t, $J = 6.8$ Hz, 6 H, CH₃), 1.32–1.52 (m, 12 H, CH₂), 1.87–1.95 (m, 4 H, CH₂), 4.34 (t, $J = 6.8$ Hz, 4 H, NCH₂), 7.41 (d, $J = 6.2$ Hz, 8 H, NCHCH), 7.45 (d, $J = 8.4$ Hz, 8 H, C₆H₄), 7.60 (d, $J = 8.4$ Hz, 8 H, C₆H₃), 7.67 (d, $J = 8.4$ Hz, 4 H, C₆H₃), 7.70 (dd, $J = 8.4; 1.3$ Hz, 4 H, C₆H₃), 8.32 (d, $J = 1.3$ Hz, 4 H, C₆H₃), 8.77 (d, $J = 6.2$ Hz, 8 H, NCH). IR (ν (CO), cm⁻¹): 2028 s, 1927 s, 1892 m. MS (FAB +ve): 2010 (M⁺, ¹⁸⁷Re; ⁸¹Br), 1929 (M⁺ - Br, ¹⁸⁷Re; ⁸¹Br).

The golden yellow complex **14** was isolated with a yield of 76%. Anal. Calcd for C₇₀H₆₂Br₂N₆O₆Re₂: C, 52.04; H, 3.87; N, 5.20. Found: C, 52.43; H, 3.45; N, 4.89. ¹H NMR (CD₂Cl₂): 0.87 (t, $J = 6.8$ Hz, 6 H, CH₃), 1.20–1.53 (m, 12 H, CH₂), 1.82–2.10 (m, 4 H, CH₂), 4.35 (t, $J = 6.8$ Hz, 4 H, NCH₂), 7.14 (d, $J = 16.1$ Hz, 4 H, =CH), 7.45 (d, $J = 6.5$ Hz, 8 H, NCHCH), 7.52 (d, $J = 8.6$ Hz, 4 H, C₆H₃), 7.65 (d, $J = 16.1$ Hz, 4 H, =CH), 7.76 (dd, $J = 8.6; 1.7$ Hz, 4 H, C₆H₃), 8.31 (d, $J = 1.7$

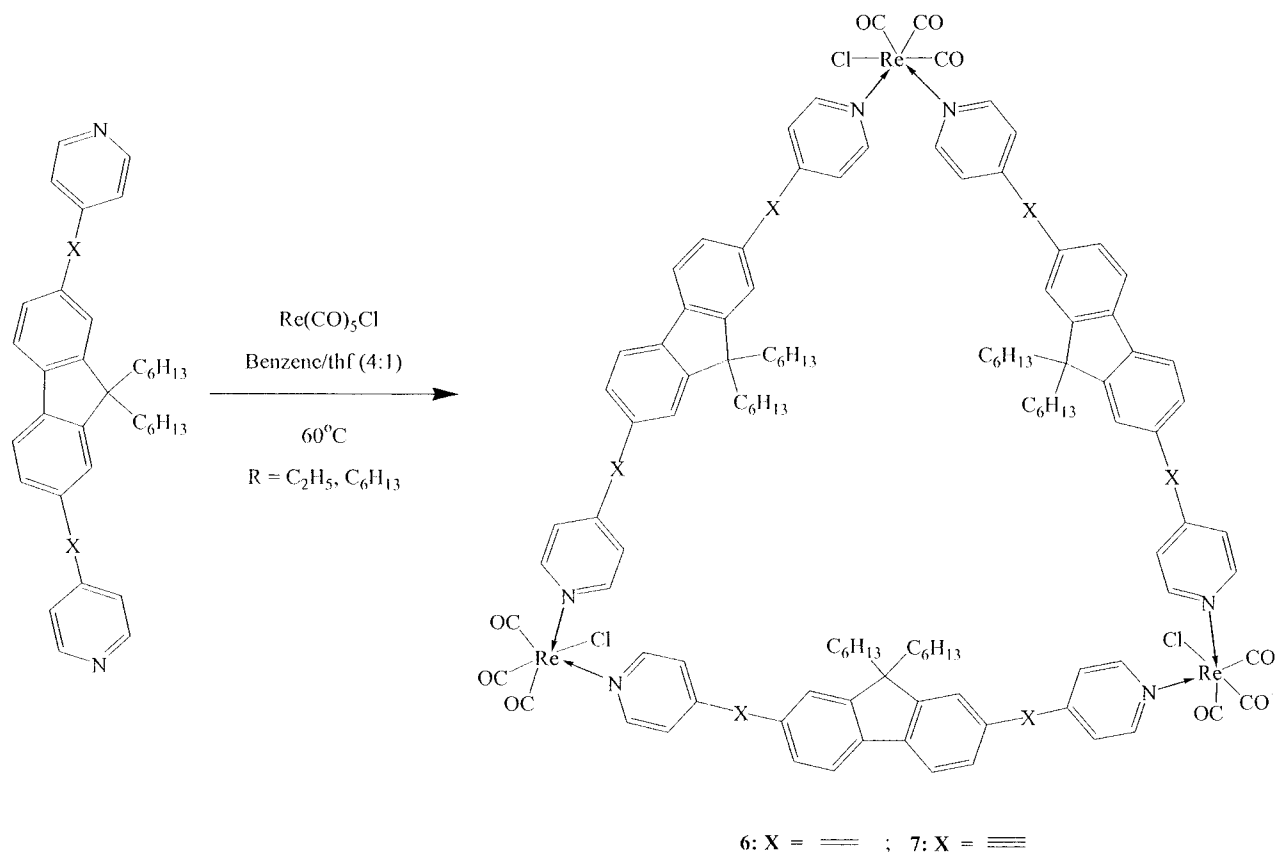
Hz, 4 H, C₆H₃), 8.68 (d, $J = 6.5$ Hz, 8 H, NCH). IR (ν (CO), cm⁻¹): 2024 s, 1921 s, 1890 m. MS (FAB +ve): 1618 (M⁺, ¹⁸⁷Re; ⁸¹Br), 1537 (M⁺ - Br, ¹⁸⁷Re; ⁸¹Br).

Synthesis of 15. The complex Re(CO)₅Cl (362 mg, 1.0 mmol) and **11** (450 mg, 1.0 mmol) were dissolved in a toluene/THF mixture (3:2, 100 mL) and heated at 80 °C for 10 h. A dark yellow precipitate was formed during this time, which was collected by filtration and washed thoroughly with ether, toluene, and hexane. Yield: 715 mg (95%). Anal. Calcd for C₇₀H₄₆Cl₂N₆O₆Re₂: C, 55.66; H, 3.07; N, 5.56. Found: C, 55.48; H, 3.12; N, 5.49. ¹H NMR (CDCl₃): 7.01 (d, $J = 16.2$ Hz, 4 H, =CH), 7.38–7.65 (m, 30 H, aromatic and =CH), 8.23 (s, 4 H, aromatic), 8.68 (d, $J = 6.5$ Hz, 8 H, NCH). IR (ν (CO), cm⁻¹): 2022 s, 1919 s, 1889 m. MS (FAB): m/e 1510 (M⁺, ¹⁸⁷Re; ³⁵Cl), 1475 (M⁺ - Cl, ¹⁸⁷Re; ³⁵Cl).

Results and Discussion

The dipyriddy ligands **4a–c** were conveniently prepared by a three-step reaction (Scheme 1). Fluorene was dialkylated at the 9-position using the corresponding alkyl halide and potassium *tert*-butoxide in dimethyl sulfoxide to yield the 9,9-dialkyl fluorenes (**1b** and **1c**). These fluorenes were brominated at the 2- and 7-posi-

Scheme 2



tion using $\text{Br}_2/\text{CH}_2\text{Cl}_2$ to yield the dibromides **2**. Palladium-catalyzed Sonogashira coupling¹⁷ reaction with trimethyl silyl acetylene and desilylation by KOH in methanol at room temperature lead to the required terminal acetylenes **3**. These terminal acetylenes underwent facile cross-coupling reactions with 4-bromopyridine hydrochloride to provide the dipyrindyl ligands **4a–c** in good yields. The ligands **5a–c** were obtained by the Heck reaction¹⁸ of **2** with 4-vinyl pyridine. Heck coupling of 4-vinylpyridine with 2,7-dibromofluorene or 2,7-dibromo-9-fluorenone was also reported by McCleverty and Ward recently.¹⁹ Similarly, the dipyrindyl ligands **8–11** were also prepared via Sonogashira or Heck coupling reaction of 3,6-dibromo-substituted carbazole with appropriate terminal alkynes or alkene (Scheme 2). All the ligands described here were thoroughly characterized by NMR, mass spectrometry, and elemental analysis. While **15** has decent solubility only in DMSO, other ligands and complexes are soluble in most common organic solvents owing to the incorporation of the alkyl substituents in the fluorene or carbazole moiety. The *trans* configuration of the vinyl ligands, **5**, **8**, **10**, and **11**, was established by the vinyl coupling constant ($^3J_{\text{H-H}} = \sim 16$ Hz) in the ^1H NMR spectra.

Self-assembly of a linear bipyridine, 1,4-bis(4'-pyridylethynyl)-2,5-dihexyloxybenzene (**BPDB**), and *fac*- $\text{Re}(\text{CO})_3\text{X}$ (X = Cl or Br) was reported to form exclu-

sively molecular triangles instead of square or higher oligomers.^{2a} Such an outcome was attributed to the dominance of the entropy factor over the enthalpy factor. We found that the dipyrindyl ligands **4b** and **5b** with 9-dihexyl substituents, being only slightly deviated from linearity, readily reacted with $\text{Re}(\text{CO})_5\text{Cl}$ in a THF/benzene (4:1) mixture to yield highly soluble molecular triangles **6** and **7** (Scheme 3). The mass spectra confirmed the identity of the triangles and pointed out the absence of square or higher oligomers. The solubility of the intermediates in the solvents was found important for the thermodynamically structure-error correcting process to continue during the self-assembly process.^{2a} Indeed, some uncharacterized species accompanied the formation of molecular triangles from the reaction of **4a** and **5a** with $\text{Re}(\text{CO})_5\text{Cl}$. Being sparingly soluble in THF, the nonalkylated congeners of **4** and **5** were treated with $\text{Re}(\text{CO})_5\text{Cl}$ to form only insoluble products. Furthermore, only insoluble products formed from the reaction of **4a** or **5a** with $\text{Re}(\text{CO})_5\text{Cl}$ in benzene. In contrast to **4a**, **4b**, **5a**, and **5b**, the carbazole-based dipyrindyl ligands **8–11** react with $\text{Re}(\text{CO})_5\text{X}$ (X = Cl, Br) to form cyclic dimers **12–15** (Scheme 4), possibly due to the roughly 90° bonding angle in the dipyrindines. The sole formation of squares was unanimously established by the FAB mass spectra. Figure 1 shows the observed and the calculated isotropic distribution patterns of the parent peak for **14** in the FABMS. Infrared carbonyl stretching frequencies of new molecular cycles in this study exhibit tricarbonyl stretching patterns in the 1886–2028 cm^{-1} region that are typical for *fac*- $\text{Re}(\text{LL})(\text{CO})_3\text{X}$ complexes.²⁰ As ex-

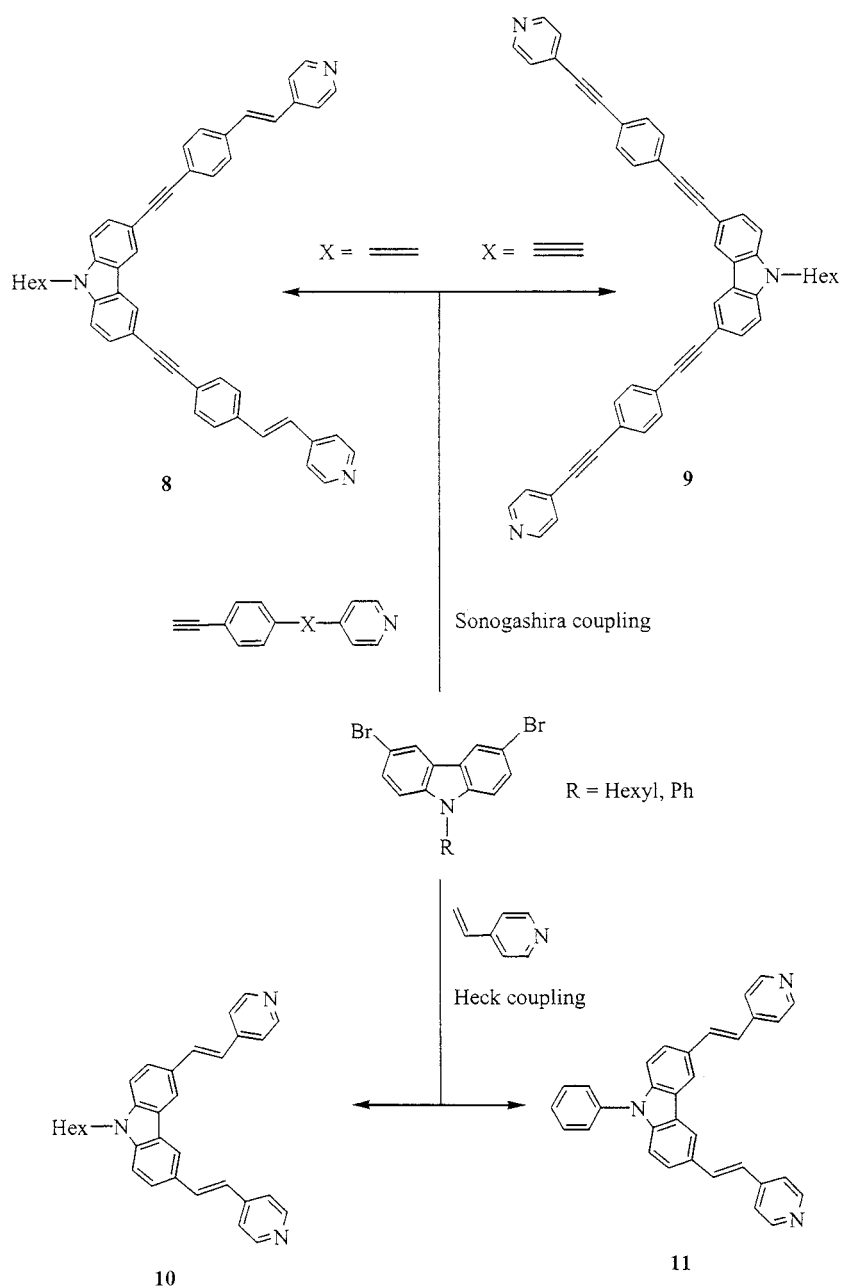
(17) Campbell, I. B. In *Organocopper Reagents*; Tilor, R. J. K., Ed.; Oxford University Press: Oxford, U.K., 1994; Chapter 10.

(18) Cadogan, J. I. G., Ed. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: New York, 1979.

(19) Behrendt, A.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1999**, 4349.

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

Scheme 3



pected, both α - and β -pyridyl protons in these complexes were shifted downfield relative to their free ligands due to the dative bonding nature of the nitrogen lone pair to the Re(I) centers.

Table 1 summarizes the photophysical data of dipyrindyl ligands as well as their corresponding self-assembly metal complexes. All dipyrindyl ligands possess intense $\pi-\pi^*$ absorption in the near-UV region. Metal complexes possess two substantially overlapping ligand-localized $\pi-\pi^*$ and MLCT transitions, with the latter appearing at lower energy (see Figure 2 for **10** and **14**). At room temperature the dimeric complexes **12–15** exhibit wavelength-independent luminescence and a single-exponential decay profile with emission lifetime ranging from 0.39 to 4.2 ns. The relatively small Stokes shift and the short lifetime indicate that the emission is mainly ligand-localized $\pi-\pi^*$ fluorescence. The large spin-orbit coupling exerted from Re(I) atoms is expected to dramatically quench the quantum yields and

the lifetimes of **12–15** compared to their parent ligands,^{20b} due to the rapid and efficient intersystem crossing from the $^1\pi-\pi^*$ state to the $^3\text{MLCT}$ or $^3\pi-\pi^*$ states.²¹ Rapid vibration relaxation may result in detrimental quenching of the $^3\text{MLCT}$ state. The emission profiles of **12–15** at 77 K glass are very similar to those at 298 K (see Figure 2 for **10** and **14**), and no MLCT emission could be detected. Photolysis of strained molecular triangles at room temperature results in immediate decomposition of the complexes. Emission was found to be solely originated from the free dipyrindine ligands judging from λ_{em} and the lifetime measurements. However, a weak emission was detected when the photolysis was conducted at 77 K glass. The complex

(21) (a) Ley, K. D.; Li, Y.; Johnson, J. V.; Powell, D. H.; Schanze, K. S. *Chem. Commun.* **1999**, 1749. (b) Ley, K. D.; Walters, K. A.; Schanze, K. S. *Synth. Met.* **1999**, *102*, 1585. (c) Ley, K. D.; Schanze, K. S. *Coord. Chem. Rev.* **1998**, *171*, 287. (d) Ley, K. D.; Whittle, C. E.; Bartberger, M. D.; Schanze, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3423.

Scheme 4

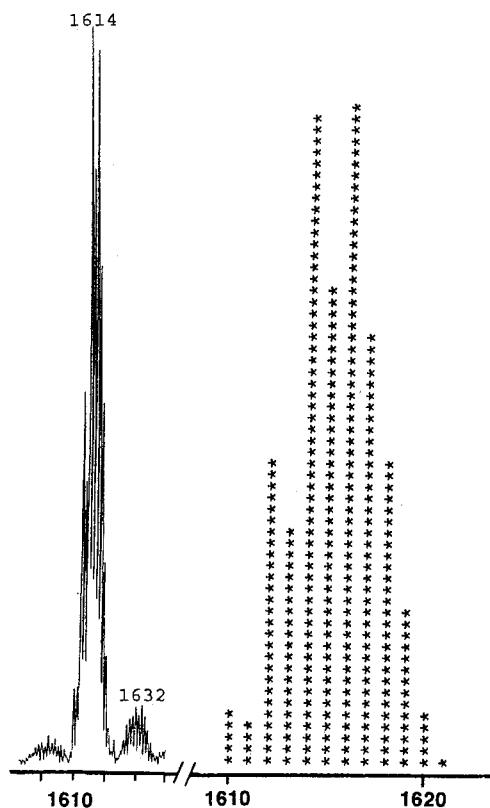
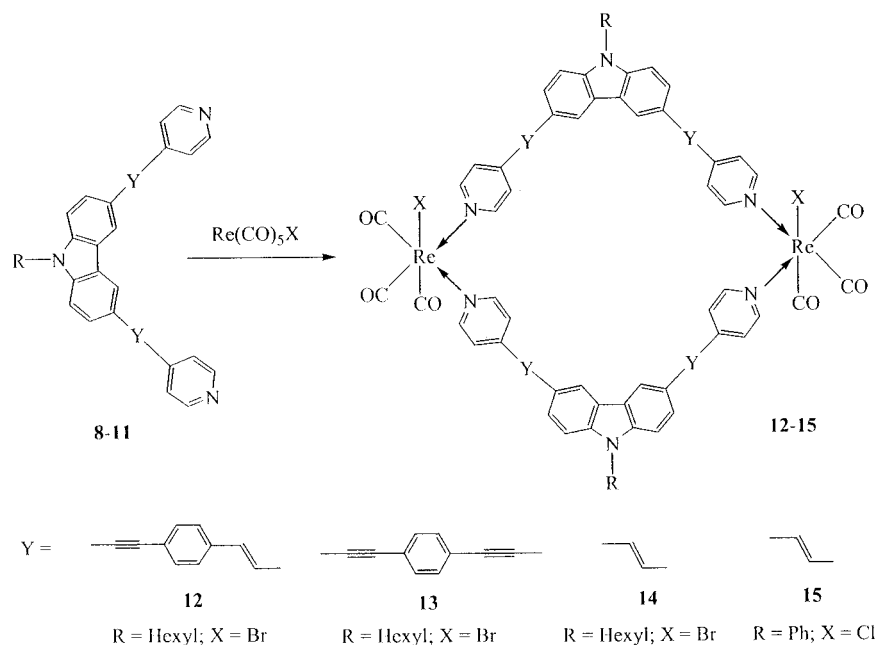


Figure 1. Observed (left) and calculated (right) FABMS for compound **14**.

6 exhibited vibronic structure peaks at 382 and 420 nm, and the single-exponential decay profile indicated a lifetime of 29.1 μ s. This may be attributed to the emission from the ligand-localized $^3\pi-\pi^*$ excited state. On the other hand, the complex **7** exhibited a ligand-localized $^3\pi-\pi^*$ excited state centered at 460 nm and a 3 MLCT excited state centered at 620 nm. The lifetimes for the $^3\pi-\pi^*$ excited state and the 3 MLCT excited state are 14.5 and 1.59 μ s, respectively.

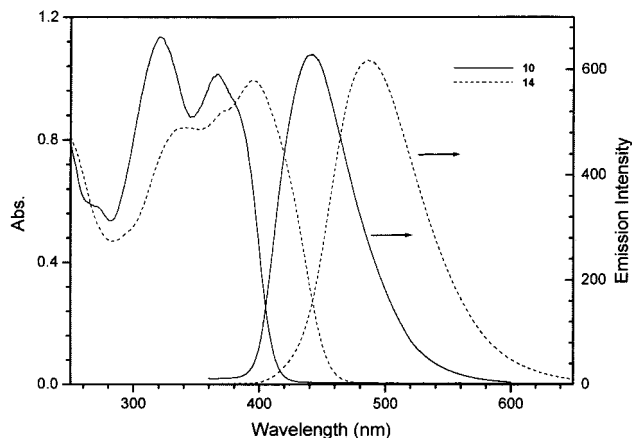


Figure 2. Electronic absorption spectra and emission spectra of **10** (solid line) and **14** (dotted line) in CH_2Cl_2 .

Table 1. Electronic Absorption and Emission Data for the Compounds

compd	absorption spectra		lifetime τ , ns	quantum yield Φ_{em}
	λ_{max} , nm ($10^{-4}\epsilon$, $\text{M}^{-1}\text{cm}^{-1}$)	λ_{max} , nm		
4a	351 (4.36)	372, 396	0.63	0.96
4b	352 (4.42)	375, 395	0.81	0.94
5a	375 (4.36)	407, 430	1.0	0.96
5b	375 (4.52)	408, 430		0.94
6	379 (19.6), 396 sh	382, 420	29.1×10^3	<i>c</i>
7	403(23.9), 426 sh	460 620	14.5×10^3 1.59×10^3	<i>c</i>
8	352 (4.80)	465		0.46
9	321 (7.42), 363 (7.62)	444		0.79
10	321 (4.54), 366 (4.05)	440		0.09
11	272 (3.25), 327 (5.69), 358 (4.89)	437		0.09
12	383 (12.0)	520	2.1	0.028
13	370 (14.5)	502	2.5	0.022
14	367 (sh), 405 (8.34)	486	4.2	0.060
15	350 (sh), 390 (18.2)	506	0.39	0.044

^a $\lambda_{\text{ex}} = 350$ nm. ^b CH_2Cl_2 solution at room temperature except for **6** and **7**, which were measured in $\text{DMF}/\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:1:1 by volume) at 77 K, and **15**, which was measured in DMSO at room temperature. ^c No reliable Φ_{em} was obtained for **6** and **7** because the lack of reliable absorbance at 77 K and refractive index for DMSO at 77 K.

In conclusion, we have synthesized strongly emissive conjugated dipyrindines containing a fluorene or carbazole moiety as the central core. These compounds are demonstrated to be useful building blocks for the construction of macrocyclic supramolecules with different geometries. Because of the luminescent nature of some of the complexes, sensor applications may be pos-

sible. Extension and further exploration of this study is in progress.

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