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Di- and Tetranuclear Ruthenium(II) and/or Osmium(II) Complexes of Polypyridyl Ligands Bridged by a Fully Conjugated Aromatic Spacer: Synthesis, Characterization, and Electrochemical and Photophysical Studies

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A series of mono-, di-, and tetranuclear homo/heterometallic complexes of Ru(II) and Os(II) based on the bridging ligand dppz(11–11′)dppz (where dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) (BL) have been synthesized and characterized. This bridging ligand is a long rigid rod with only one rotational degree of freedom and provides complete conjugation between the chromophores. The complexes synthesized are of general formula $[(bpy)_2Ru–BL]^{2+}$, $[(phen)_2/(bpy)_2M–BL–M(bpy)_2/(phen)_2]^{4+}$ (M = Ru(II) and Os(II)), $[(bpy)_2Ru–BL–Os(bpy)_2]^{4+}$, and $[\{(bpy)_2Ru–BL\}_3M]^{8+}$. Detailed ^{1}H NMR studies of these complexes revealed that each chiral center does not influence its neighbor because of the long distance between the metal centers and the superimposed resonances of the diastereoisomers, which allowed the unambiguous assignment of the signals, particularly for homonuclear complexes. Concentration-dependent ^{1}H NMR studies show molecular aggregation of the mono- and dinuclear complexes in solution by π–π stacking. Electrospray mass spectrometry data are consistent with dimerization of mono- and dinuclear complexes in solution. Electrochemical studies show oxidations of Ru(II) and Os(II) in the potential ranges +1.38 to +1.40 and +0.92 to +1.01 V, respectively. The bridging ligand exhibits two one-electron reductions, and it appears that the added electrons are localized on the phenazene moieties of the spacer. All of these complexes show strong metal-to-ligand charge-transfer (MLCT) absorption and ^{3}MLCT luminescence at room temperature. Quantum yields have been calculated, and the emission lifetimes of all complexes have been measured by laser flash photolysis experiments. The luminescence intensity and lifetime data suggest that the emission due to the Ru center of the heteronuclear complexes is strongly quenched (>90%) compared to that of the corresponding model complexes. This quenching is attributed to intramolecular energy transfer from the Ru(II) center to the Os(II) center ($k = (3–5) \times 10^7\ s^{-1}$) across the bridging ligand.

Introduction

Polynuclear Ru(II) and Os(II) complexes of polypyridyl ligands are currently being investigated a lot because of the rich electrochemical and photophysical properties of these systems and potential applications in various supramolecular structures as electronic and photomolecular devices.[1–10] These systems can be developed by covalent linking of prefabricated molecular components with designed spacers (bridging ligands).[2,8,11,12] A judicious choice of building

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(1) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991.
(2) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.
(3) Venturi, M.; Serroni, S.; Juris, A.; Campagna, S.; Balzani, V. *Top. Curr. Chem.* **1998**, *197*, 193.
(4) De Cola, L.; Belser, P. *Coord. Chem. Rev.* **1998**, *177*, 301.

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blocks and spacer and an appropriate design of the structure can, in fact, allow the occurrence of energy/electron transfer along the supramolecular array.[2,4,6,8,13−16] Bis(2,2′-bipyridyl/1,10-phenanthroline)ruthenium(II)/osmium(II) complexes exhibit suitable redox and excited-state properties to play the role of building block and have been widely used for the construction of supramolecular systems.[2−17] However, the key component is the bridging ligands; the size, shape, and electronic nature of the bridge controls the electronic communication between the chromophoric units, and thereby the properties of the molecule as a whole. Generally, polyaromatic bridges provide relatively strong intercomponent electronic coupling and, therefore, are very convenient connectors for the construction of polynuclear metal complexes, especially for the study of long-range energy- and/or electron-transfer processes.[2,6,16] An example of this kind of spacer is tpphz (tetrapyrido[3,2-*a*:2′,3′-*c*:3′′,2′′-*h*:2′′′,3′′′-*j*]phenazine), a fully aromatic rigid system that has been used to prepare mono-,[18,19] di-,[18−24] tri-,[23] tetra-,[21−23,25] hexa-,[23] and decanuclear[23] and polymeric[26] types of complexes. Recently, a mixed metal molecular hexagon with the same bridging ligand has been reported.[27] Details of the stereochemical aspects[20−23] and electrochemical and photophysical properties[19,22,24,25] of these complexes have also been reported. The bridging ligand dppz(11−11′)dppz (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) (BL) is similar to that described above with a longer spacer and one rotational degree of freedom; however, little attention has been given to this ligand. It is an attractive system to study long-range electron/energy-transfer processes with an extended aromatic bridge, which is known to play a crucial role in numerous biological processes.[28] To our knowledge there is only one report of this ligand, which described the binding affinity of its dinuclear Ru(II) complexes with DNA.[29] However, this ligand has not been synthesized separately; the Ru complexes were prepared by the reaction of [RuL$_2$(1,10-phenanthroline-5,6-dione)] and 3,3′,4,4′-tetraaminobiphenyl, and no characterization data or other studies of these complexes have been reported.[29]

We were interested to study long-range metal−metal electronic coupling by using dppz(11−11′)dppz as spacer. We have synthesized this ligand and its homo/heterometallic di- and tetranuclear complexes using [M(bpy/phen)$_2$] (M = Ru(II)/Os(II)) as building block. Herein, we report the synthesis, characterization, and electrochemical and photophysical properties of these complexes.

Experimental Section

Materials. The compounds 2,2′-bipyridine, 1,10-phenanthroline, 3,3′,4,4′-tetraaminobiphenyl, ammonium hexafluorophosphate, tetrabutylammonium tetrafluoroborate, ammonium hexachloroosmate, and tris(2,2′-bipyridine)ruthenium(II) were purchased from Aldrich. Hydrated ruthenium trichloride was purchased from Arora Matthey. Neutral alumina was obtained from the National Chemical Co. The compounds 1,10-phenanthroline-5,6-dione[30] *cis*-[Ru(bpy)$_2$Cl$_2$]·3H$_2$O,[31] *cis*-[Os(bpy)$_2$Cl$_2$]·2H$_2$O,[32] and *cis*-[Ru(phen)$_2$Cl$_2$]·2H$_2$O[31] were prepared according to the literature methods. All organic solvents were of analytical grade and were used as received for synthetic purposes. Solvents for spectral, electrochemical, and photophysical studies were freshly purified by standard procedures before use.

Physical Measurements. Elemental analyses (C, H, and N) were performed on a model 2400 Perkin-Elmer elemental analyzer. The electrospray mass spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. The samples dissolved in acetonitrile were introduced into the ESI source through a syringe pump at the rate of 5 μL/min. The ESI capillary was set at 3.5 kV, and the cone voltage was 40 V. The spectra were collected in 6 s scans, and the printouts are averaged spectra of 6−8 scans. The matrix-assisted laser desorption ionization (MALDI) spectra were recorded by a Voyager-DE STR mass spectrometer (Per Septive Biosystems) using the laser desorption ionization (LDI) method of a solid sample. Infrared spectra were recorded on a Perkin-Elmer spectrum GX FT-IR spectrophotometer as KBr pellets. NMR spectra were recorded on a model DPX 200 Brucker FT-NMR instrument. The UV/vis spectra were recorded on a model 8452A Hewlett-Packard diode array spectrophotometer. Electrochemical measure-

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(5) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.
(6) Sehlicke, B.; Belser, P.; De Cola, L.; Sabbioni, E.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 4207.
(7) Belser, P.; Bernhard, S.; Blum, C.; Beyeler, A.; De Cola, L.; Balzani, V. *Coord. Chem. Rev.* **1999**, *190−192*, 155.
(8) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1.
(9) Juris, A.; Prodi, L.; Harriman, A.; Ziessel, R.; Hissler, M.; El-ghayoury, A.; Wu, F.; Riesgo, E. C.; Thummel, R. P. *Inorg. Chem.* **2000**, *39*, 3590.
(10) El-ghayoury, A.; Harriman, A.; Khatyr, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 185.
(11) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, W. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473.
(12) Macatangay, A.; Zheng, G. Y.; Rillema, D. P.; Jackman, D. C.; Merkert, J. W. *Inorg. Chem.* **1996**, *35*, 6823.
(13) Belser, P.; von Zelewsky, A.; Frank, M.; Seel, C.; Vogtle, F.; De Cola, L.; Barigelletti, F.; Balzani, V. *J. Am. Chem. Soc.* **1993**, *115*, 4076.
(14) Juris, A.; Balzini, V.; Campagna, S.; Denti, G.; Serroni, S.; Frei, G.; Gudel, H. U. *Inorg. Chem.* **1994**, *33*, 1491.
(15) Belser, P.; Dux, R.; Baak, M.; De Cola, L.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 595.
(16) Barigelletti, F.; Flamigni, L.; Collin, J.-P.; Sauvage, J.-P. *Chem. Commun.* **1997**, 333.
(17) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(18) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 1799.
(19) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. *Inorg. Chem.* **1996**, *35*, 2937.
(20) MacDonnell, F. M.; Bodige, S. *Inorg. Chem.* **1996**, *35*, 5758.
(21) Bodige, S.; Torres, A. S.; Maloney, D. J.; Tate, D.; Kinsel, G. R.; Walker, A. K.; MacDonnell, F. M.; *J. Am. Chem. Soc.* **1997**, *119*, 10364.
(22) Campagna, S.; Serroni, S.; Bodige, S.; MacDonnell, F. M. *Inorg. Chem.* **1999**, *38*, 692.
(23) MacDonnell, F. M.; Kim, M.-J.; Bodige, S. *Coord. Chem. Rev.* **1999**, *185−186*, 535.
(24) Chiorboli, C.; Bignozzi, C. A.; Scandola, F.; Ishow, E.; Gourdon, A.; Launay, J.-P. *Inorg. Chem.* **1999**, *38*, 2402.
(25) Ishow, E.; Gourdon, A.; Launay, J.-P.; Lecante, P.; Verelst, M.; Chiorboli, C.; Scandola, F.; Bignozzi, C.-A. *Inorg. Chem.* **1998**, *37*, 3603.
(26) Chen, J.; MacDonnell, F. M. *Chem. Commun.* **1999**, 2529.
(27) Ali, M. M.; MacDonnell, F. M. *J. Am. Chem. Soc.* **2000**, *122*, 11527.
(28) Holmlin, R. E.; Dnadliker, P. J.; Barton, J. K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2714.
(29) Lincoln, P.; Norden, B. *Chem. Commun.* **1996**, 2145.
(30) Hiort, C.; Lincoln, P.; Norden, B. *J. Am. Chem. Soc.* **1993**, *115*, 3448.
(31) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(32) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587.

ments were made using CHI 660A electrochemical workstation equipment. Cyclic and square wave voltammetry studies were carried out in a three-electrode cell consisting of a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and an SCE reference electrode. Solutions of the complexes in purified acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte were deaerated by bubbling nitrogen for 20 min prior to each experiment. Luminescence spectra were recorded on a Perkin-Elmer LS-50B spectrofluorimeter in acetonitrile at room temperature. Luminescence quantum yields were measured in optically diluted solution, using $[Ru(bpy)_3]^{2+}$ in oxygen-free acetonitrile ($\phi = 0.062$) as reference emitter.

Flash photolysis experiments were carried out with an Applied Photophysics SP-Quanta Ray GCR-2 (10) Nd:YAG laser using the third harmonic output of 355/532 nm with a pulse width of 8 ns. A DHS2 dichroic harmonic separator was used to separate the third harmonic from the second harmonic and the fundamental of the Nd:YAG laser. The output was directed toward the sample using prisms. The oscilloscope is optically triggered using the photodiode. The monitoring source was a 250 W pulsed xenon lamp which was focused on the sample, at a right angle to the incident laser beam, using lenses and an adjustable iris positioned in front of the sample holder. The beam emerging from the sample was focused onto a Czerny Turner monochromator using a pair of lenses. The monochromator was fitted with a stepper motor control to drive the monochromator to the desired wavelength. The detection was carried out using a Hamamatsu R-928 photomultiplier tube. The signals were captured using a Hewlett-Packard 54201A 100 MHz digital storage oscilloscope. The data were transferred to the computer and analyzed using in-house-developed software. Experiments were performed in acetonitrile solutions under an argon atmosphere.

Synthesis of Ligands. 4-Pyridino[3,2-*h*]quinoxalino[2,3-*f*]quinolin-11-ylbenzene-1,2-diamine (L). A hot methanolic solution (10 mL) of 1,10-phenanthroline-5,6-dione (0.21 g, 1 mmol) was added dropwise to a hot methanolic solution (15 mL) of 3,3′,4,4′-tetraaminobiphenyl (0.214 g, 1 mmol). After complete addition (20 min) the reaction mixture was kept at 60 °C for 0.5 h. During this period a yellow crystalline compound was deposited. The compound was separated by filtration and washed with methanol. The product was dissolved in chloroform (200 mL) under boiling conditions and filtered when hot (to remove a trace amount of BL), and the solvent of the filtrate was evaporated in rotavapor. Yield: 0.31 g (80%). Anal. Calcd for $C_{24}H_{16}N_6$: C, 74.2; H, 4.15; N, 21.6. Found: C, 74.0; H, 4.10; N, 21.4. ^1H NMR [δ (ppm), $CDCl_3$]: 3.67 (br, 4H), 6.88 (d, 1H), 7.28 (d, 1H, partially overlapped with $CHCl_3$), 7.30 (d, 1H), 7.80 (m, 2H), 8.16, 8.20 (d, 1H), 8.34, 8.38 (s, 1H), 8.47 (d, 1H), 9.28 (m, 2H), 9.64 (dd, 1H), 9.69 (dd, 1H). IR (cm^{-1}): 3277, 3350, 3429 (NH_2).

11-Pyridino[3,2-*h*]quinoxalino[2,3-*f*]quinolin-11-ylpyridino-[3,2-*h*]quinoxalino[2,3-*f*]quinoline (BL). A mixture of 1,10-phenanthroline-5,6-dione (0.42 g, 2 mmol) and 3,3′,4,4′-tetraaminobiphenyl (0.214 g, 1 mmol) was refluxed in methanol (30 mL) for 8 h. During this period a yellow microcrystalline compound was separated from the solution. The compound was isolated by filtration, washed with hot methanol and chloroform, and dried in vacuo. Yield: 0.48 g (85%). Anal. Calcd for $C_{36}H_{18}N_8$: C, 76.9; H, 3.22; N, 19.1. Found: C, 76.7; H, 3.09; N, 19.1.

Synthesis of Metal Complexes. $[(bpy)_2Ru-BL](PF_6)_2\cdot 2H_2O$ (1). A mixture of $[(bpy)_2Ru(1,10\text{-phenanthroline-5,6-dione})]Cl_2$ (0.348 g, 0.5 mmol) and L (0.194 g, 0.5 mmol) was refluxed for 12 h in methanol. The solvent of the reaction mixture was then evaporated in rotavapor, the residue was dissolved in water (10 mL) and filtered, and to the filtrate was added an aqueous solution (5 mL) of NH_4PF_6 (0.408 g, 2 mmol). The precipitate thus obtained was purified by column chromatography using a column packed with neutral alumina and acetonitrile−toluene (2:1) as eluent. After the solvent was removed from the desired fraction, the residue was redissolved in acetonitrile (5 mL) and reprecipitated by the vapor diffusion method using diethyl ether. Yield: 0.42 g (65%). Anal. Calcd for $C_{56}H_{38}RuN_{12}O_2P_2F_{12}$: C, 51.7; H, 2.94; N, 12.9. Found: C, 51.5; H, 2.70; N, 12.8. MS [ESMS (CH_3CN), *m*/*z*]: 699.2 ($[\{M\}_{2} - 3PF_6]^{3+}$), 488.1 ($[M - 2PF_6]^{2+}$). ^1H NMR [δ (ppm), CD_3CN]: 7.37−7.80 (m, 8H), 7.92 (dd, 2H), 8.01−8.17 (m, 6H), 8.22 (dd, 2H), 8.28 (dd, 2H), 8.35, 8.39 (s, 2H), 8.41, 8.47 (d, 2H), 8.52 (d, 2H), 8.59 (dd, 4H), 8.93 (dd, 1H), 8.99 (dd, 1H), 9.32 (dd, 1H), 9.39 (dd, 1H). UV/vis [CH_3CN; λ_{max}, nm (ϵ)]: 444 (1.4×10^3), 406 (4.0×10^4), 310sh (6.9×10^4), 290 (9.3×10^4), 254 (5.0×10^4), 240 (4.9×10^4).

$[(bpy)_2Ru-BL-Ru(bpy)_2](PF_6)_4\cdot 2H_2O$ (2). A mixture of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.52 g, 1 mmol) and BL (0.281 g, 0.5 mmol) was refluxed for 12 h under an argon atmosphere in 2-methoxyethanol−water (4:1, 40 mL). Then the volume of the reaction mixture was reduced to dryness by rotary evaporation. The residue was then dissolved in water (10 mL) and filtered, and to the filtrate was added aqueous NH_4PF_6 (0.815 g, 4 mmol). The precipitate thus separated was collected by filtration and washed with water and diethyl ether. The complex was purified by column chromatography using a column packed with deactivated (2% water) alumina and acetonitrile−toluene (1:1) as eluent. The small first fraction was discarded; the large second fraction gave the desired complex. The complex was recrystallized from acetonitrile−diethyl ether by the diffusion method. Yield: 0.7 g (70%). Anal. Calcd for $C_{76}H_{54}Ru_2N_{16}O_2P_4F_{24}$: C, 45.5; H, 2.71; N, 11.2. Found: C, 45.6; H, 2.76; N, 11.0. MS [ESMS (CH_3CN), *m*/*z*]: 1824.5 ($[M - PF_6]^+$), 1168.7 ($[\{M\}_2 - 3PF_6]^{3+}$), 839.0 ($[M - 2PF_6]^{2+}$). ^1H NMR [δ (ppm), CD_3CN]: 7.29 (ddd, 4H), 7.49 (ddd, 4H), 7.77 (d, 4H), 7.88 (d, 4H), 7.94 (ddd, 4H), 8.05 (td, 4H), 8.14 (td, 4H), 8.22 (dd, 4H), 8.54 (d, 4H), 8.58 (d, 4H), 8.68, 8.72 (s, 2H), 8.76, 8.81 (d, 2H) 9.06 (d, 2H), 9.72 (ddd, 4H). UV/vis [CH_3CN; λ_{max}, nm (ϵ)]: 442 (2.4×10^4), 406 (3.9×10^4), 310sh (7.3×10^4), 288 (1.0×10^5), 256 (4.8×10^4), 238 (4.4×10^4).

$[(bpy)_2Os-BL-Os(bpy)_2](PF_6)_4\cdot 2H_2O$ (3). This complex was synthesized following the same procedure as that described for **2**. The only difference is *cis*-$[Os(bpy)_2Cl_2]\cdot 2H_2O$ was taken in place of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$. Yield: 0.74 g (68%). Anal. Calcd for $C_{76}H_{54}Os_2N_{16}O_2P_4F_{24}$: C, 41.8; H, 2.49; N, 10.3. Found: C, 41.4; H, 2.38; N, 10.1. MS [ESMS (CH_3CN), *m*/*z*]: 1287.0 ($[\{M\}_2 - 3PF_6]^{3+}$), 929.0 ($[M - 2PF_6]^{2+}$), 571.0 ($[M - 3PF_6]^{3+}$). ^1H NMR [δ (ppm), CD_3CN]: 7.19 (ddd, 4H), 7.40 (ddd, 4H), 7.66 (d, 4H), 7.78 (d, 4H), 7.81−7.89 (m, 8H), 7.94 (td, 4H), 8.13 (dd, 4H), 8.51 (d, 4H), 8.55 (d, 4H), 8.67, 8.72 (s, 2H), 8.76, 8.80 (d, 2H), 9.05 (d, 2H), 9.49 (ddd, 4H). UV/vis [CH_3CN; λ_{max}, nm (ϵ)]: 660br (5.6×10^3), 474 (2.4×10^4), 406 (3.9×10^4), 314 (6.8×10^4), 292 (1.1×10^5), 256 (5.2×10^4), 238 (5.3×10^4).

$[(bpy)_2Ru-BL-Os(bpy)_2](PF_6)_4\cdot 2H_2O$ (4). A mixture of $[(bpy)_2Ru-BL]Cl_2$ (complex **1** with Cl^- anion) (0.262 g, 0.25 mmol) and *cis*-$[Os(bpy)_2Cl_2]\cdot 2H_2O$ (0.261 g, 0.25 mmol) in ethanol−water (2:1, 40 mL) was refluxed for 20 h. Isolation and purification of this complex was carried out following a procedure similar to that described for **2**. Yield: 0.325 g (62%). Anal. Calcd for $C_{76}H_{54}RuOsN_{16}O_2P_4F_{24}$: C, 43.6; H, 2.60; N, 10.7. Found: C, 43.3; H, 2.74; N, 10.5. MS [ESMS (CH_3CN), *m*/*z*]: 1227.0 ($[\{M\}_2 - 3PF_6]^{3+}$), 884 ($[M - 2PF_6]^{2+}$), 541.0 ($[M - 3PF_6]^{3+}$). ^1H NMR [δ (ppm), CD_3CN]: 7.19 (dd, 2H), 7.29 (dd, 2H), 7.40 (ddd, 2H), 7.66 (ddd, 2H), 7.75−7.93 (m, 14H), 8.04 (td, 2H), 8.09−8.17 (m, 4H), 8.21 (d, 2H), 8.50−8.60 (m, 8H), 8.67, 8.72 (s, 2H), 8.76, 8.80 (d, 2H), 9.06 (d, 2H), 9.45 (ddd, 2H), 9.71 (ddd, 2H). UV/vis [CH_3CN; λ_{max}, nm (ϵ)]: 660br (2.6×10^3), 452 (2.2×10^4), 406 (4.0×10^4), 312 (7.3×10^4), 290 (1.0×10^4), 258 (4.8×10^4), 240 (4.5×10^4).

[(phen)$_2$Ru−BL−Ru(phen)$_2$](PF$_6$)$_4$·H$_2$O (5). This complex was synthesized by the reaction of *cis*-[Ru(phen)$_2$Cl$_2$]·2H$_2$O (0.568 g, 1 mmol) and BL (0.281 mg, 0.5 mmol) in 2-methoxyethanol−water (4:1, 40 mL) following a procedure similar to that described for **2**. Yield: 0.73 g (70%). Anal. Calcd for $C_{84}H_{52}Ru_2N_{16}OP_4F_{24}$: C, 48.4; H, 2.47; N, 10.8. Found: C, 48.7; H, 2.69; N, 10.4. MS [ESMS (CH_3CN), *m*/*z*]: 1873.1 ([M − PF$_6$]$^+$), 1200.0 ([{M}$_2$ − 3PF$_6$]$^{3+}$), 864.4 ([M − 2PF$_6$]$^{2+}$) 528.2 (M − 3PF$_6$]$^{3+}$). NMR [δ (ppm), CD_3CN]: 7.62−7.73 (m, 8H), 7.81 (ddd, 4H), 8.04 (dd, 4H), 8.15 (d, 4H), 8.25 (dd, 4H), 8.29 (s, 8H), 8.61−8.66 (m, 6H), 8.67, 8.71 (s, 2H), 8.75, 8.79 (d, 2H), 9.05 (d, 2H), 9.69 (ddd, 4H). UV/vis [CH_3CN; λ_{max}, nm (ϵ)]: 442 (2.0×10^4), 406 (3.6×10^4), 308 (5.3×10^4), 264 (9.8×10^4), 222 (8.1×10^4).

[(bpy)$_2$Ru−BL−Ru(phen)$_2$](PF$_6$)$_4$·2H$_2$O (6). This complex was prepared by the reaction of [(bpy)$_2$Ru−BL]Cl$_2$ (0.262 g, 0.25 mmol) and *cis*-[Ru(phen)$_2$Cl$_2$]·2H$_2$O (0.142 g, 0.25 mmol) in ethanol−water (2:1, 40 mL). The reaction mixture was refluxed for 12 h, and the complex was isolated and purified following a procedure similar to that described for **2**. Yield: 0.38 g (75%). Anal. Calcd for $C_{80}H_{54}Ru_2N_{16}O_2P_4F_{24}$: C, 46.8; H, 2.65; N, 10.9. Found: C, 46.5; H, 2.52; N, 10.8. MS [ESMS (CH_3CN), *m*/*z*]: 1232.3 [{M}$_2$ − 3PF$_6$]$^{3+}$), 887.6 ([M − 2PF$_6$]$^{2+}$), 544.3 ([M − 3PF$_6$]$^{3+}$). NMR [δ (ppm), CD_3CN]: 7.28 (ddd, 2H), 7.48 (ddd, 2H), 7.67 (d, 2H), 7.64−7.72 (m, 2H), 7.75 (d, 2H), 7.77−8.03 (m, 6H), 7.85 (d, 2H), 8.08−8.13 (m, 4H), 8.16−8.25 (m, 6H), 8.28 (s, 4H), 8.55 (dd, 4H), 8.61−8.67 (m, 4H), 8.68, 8.71 (s, 2H), 8.75, 8.79 (d, 2H), 9.04 (d, 2H), 9.67−9.73 (m, 4H). UV/vis [CH_3CN; λ_{max}, nm (ϵ)]: 442 (2.3×10^4), 406 (4.1×10^4), 312 (6.8×10^4), 290 (7.6×10^4), 264 (7.9×10^4).

[{(bpy)$_2$Ru−BL}$_3$Ru](PF$_6$)$_8$·6H$_2$O (7). A mixture of [(bpy)$_2$Ru−BL](PF$_6$)$_2$ (0.38 g, 0.3 mmol) and RuCl$_3$·3H$_2$O (0.026 g, 0.1 mmol) was refluxed in 2-methoxyethanol−water (3:1, 50 mL) under an argon atmosphere for 12 h. Then an aqueous solution (10 mL) of NH_4PF_6 (0.408 g, 2 mmol) was added to this solution. The solvent of the reaction mixture was removed by rotary evaporation, and the residue was washed with water and diethyl ether. The compound was purified by column chromatography using deactivated (3% H_2O) alumina and an acetonitrile−toluene (1:1) mixture as eluent. The desired fraction obtained from the column was purified once more by similar column chromatography. The complex was recrystallized from acetonitrile−diethyl ether by the diffusion method. Yield: 0.18 g (52%). Anal. Calcd for $C_{168}H_{114}Ru_4N_{36}O_6P_8F_{48}$: C, 47.0; H, 2.67; N, 11.7. Found: C, 46.9; H, 2.47; N, 11.6. MAS (MALDI, solid sample, *m*/*z*): 1306.0 ([M − {(bpy)$_2$Ru−BL} − 5PF$_6$ + POF$_4$]$^{2+}$), 1244.0 ([M − 4PF$_6$ + POF$_4$]$^{3+}$), 1223.0 ([M − PF$_6$ + 2POF$_4$ + PO$_2$F$_2$]$^{3+}$), 1200.0 ([M − 7PF$_6$ + POF$_4$ + 3PO$_2$F$_2$]$^{3+}$), 896.0 ([M − 5PF$_6$ + POF$_4$]$^{4+}$), 816.0 ([M − {(bpy)$_2$Ru−BL} − 7PF$_6$ + 2POF$_4$]$^{3+}$), 683.0 ([M − {(bpy)$_2$Ru−BL}$_2$ − 6PF$_6$]$^{2+}$), 661.0 ([M − {(bpy)$_2$Ru−BL}$_2$ − 7PF$_6$ + PO$_2$F$_2$]$^{2+}$). NMR [δ (ppm), CD_3CN]: 7.29 (dd, 6H), 7.48 (dd, 6H), 7.76 (d, 6H), 7.87 (d, 6H), 7.91 (d, 6H), 7.95 (d, 6H), 8.04 (td, 6H), 8.13 (td, 6H), 8.21 (d, 6H), 8.40 (m, 6H), 8.55 (dd, 12H), 8.68, 8.72 (s, 3H), 8.70, 8.74 (s, 3H), 8.78, 8.82 (poorly resolved dd, 6H), 9.07 (poorly resolved dd, 6H), 9.72 (d, 6H), 9.78 (d, 6H). UV/vis [CH_3CN; λ_{max}, nm (ϵ)]: 442 (5.1×10^4), 406 (8×10^4), 314 (1.4×10^5), 290 (2.1×10^5), 258 (1.0×10^5), 234 (9×10^4).

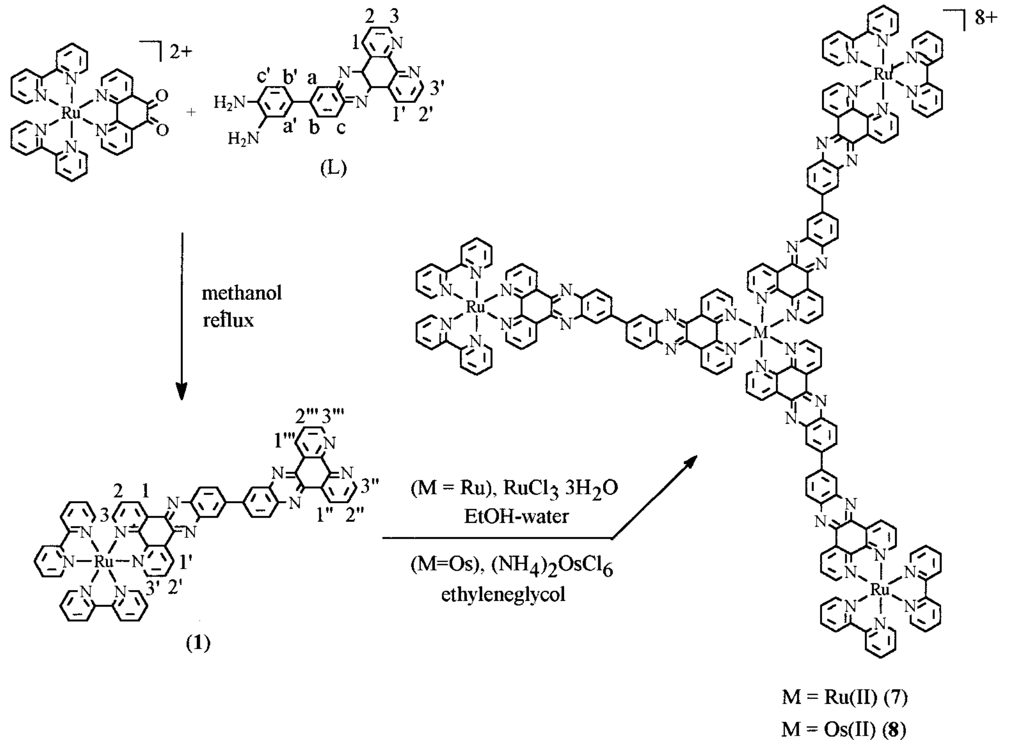
[{(bpy)$_2$Ru−BL}$_3$Os](PF$_6$)$_8$·6H$_2$O (8). (NH$_4$)$_2$OsCl$_6$ (0.044 g, 0.1 mmol) in ethylene glycol (20 mL) was refluxed for 15 min under an argon atmosphere. Then [(bpy)$_2$Ru−BL](PF$_6$)$_2$ (0.38 g, 0.3 mmol) was added to the reaction mixture, and refluxing was continued for 6 h. Then the solvent of the reaction mixture was removed by vacuum distillation. To the semisolid mass was added an aqueous solution of NH_4PF_6 (0.41 g, 2 mmol), and the mixture was stirred for 1 h. The solid complex was then separated by filtration and washed with water and diethyl ether. This complex was then purified following a procedure similar to that described for **7**. Yield: 0.17 g, (40%). Anal. Calcd for $C_{168}H_{114}Ru_3OsN_{36}O_6P_8F_{48}$: C, 46.0; H, 2.62; N, 11.5. Found: C, 45.8; H, 2.78; N, 11.4. MAS (MALDI, *m*/*z*): 1316.0 ([M − {(bpy)$_2$Ru−BL} − 6PF$_6$ + 2PO$_2$F$_2$]$^{2+}$), 1281.0 ([M − 3PF$_6$]$^{3+}$), 1166.0 ([M − {(bpy)$_2$Ru−BL} − 8PF$_6$ + 2HPO$_4$]$^{2+}$), 1152.0 ([M − 7PF$_6$ + 2HPO$_4$]$^{3+}$), 1137.0 ([M − 8PF$_6$ + PO$_2$F$_2$ + HPO$_4$]$^{3+}$), 908.0 ([M − 6PF$_6$ + POF$_4$ + PO$_2$F$_2$]$^{4+}$), 822.0 ([M − {(bpy)$_2$Ru−BL} − 8PF$_6$ + POF$_4$ + 2PO$_2$F$_2$]$^{3+}$). NMR [δ (ppm), CD_3CN]: 7.29 (dd, 6H), 7.49 (dd, 6H), 7.76 (d, 6H), 7.87 (d, 6H), 7.92 (d, 6H), 7.96 (d, 6H), 8.04 (td, 6H), 8.14 (td, 6H), 8.21 (d, 6H), 8.30 (m, 6H), 8.56 (dd, 12H), 8.72, 8.73 (s, 3H), 8.70, 8.75 (s, 3H), 8.78, 8.82 (poorly resolved dd, 6H), 9.08 (poorly resolved dd, 6H), 9.56 (dd, 6H), 9.72 (d, 6H). UV/vis [CH_3CN; λ_{max}, nm (ϵ)]: 660br (2.8×10^3), 448 (4.8×10^4), 406 (8.1×10^4), 312 (1.4×10^5), 292 (2.0×10^5), 258 (9.5×10^4), 234 (9.0×10^4).

Results and Discussion

Synthesis of the Ligands. The ligand L was synthesized by the reaction of 1,10-phenanthroline-5,6-dione and 3,3′,4,4′-tetraaminobiphenyl (1:1 molar ratio) in methanol under mild conditions. It may be noted that the reaction conditions, viz., temperature, duration of reaction, and slow addition of the dione to a tetramine, are very important. High temperature and a reverse sequence of the addition of reactants resulted in the formation of a significant amount of BL. The ligand L was purified by recrystallization from hot chloroform, in which BL is insoluble. The bridging ligand BL was synthesized by the reaction of 1,10-phenanthroline-5,6-dione and 3,3′,4,4′-tetraaminobiphenyl (2:1 molar ratio) in refluxing methanol. This ligand is insoluble in common organic solvents and was purified by washing with hot methanol, in which reactants are highly soluble, and also with hot chloroform, in which L is soluble.

The ligands L and BL gave satisfactory elemental analysis. The IR spectra of both the ligands show the absence of any band around 1680 cm^{-1} ($\nu_{C=O}$), which eliminates the possibility of partial reaction of the dione with the tetramine. The ligand L shows three bands at 3277, 3350, and 3429 cm^{-1}, which can be assigned to N−H stretching of NH_2. The ^{1}H NMR spectrum of L shows a broad band at 3.67 (4H) ppm due to NH_2. The signals due to the phenanthroline moiety of L appeared at 9.69 (dd, 1H, 1/1′ proton; see Scheme 1 for the numbering scheme), 9.64 (dd, 1H, 1′/1), 9.28 (m, 2H, 3 and 3′), and 7.80 (m, 2H, 2 and 2′). The resonances due to the biphenyl moiety appeared at 8.47 (d, 1H, c′), 7.30 (d, 1H, c), 8.16 and 8.20 (d, 1H, b), 7.28 (d, 1H, b′), 8.34 and 8.38 (s, 1H, a), and 6.88 (d, 1H, a′). The splitting of the signals of “a” and “b” protons is due to second-order coupling, which is discussed in detail in a later section. The ^{1}H NMR spectrum of BL could not be recorded due to its poor solubility in common organic solvents. However, metal complexes of this ligand are highly soluble

Scheme 1



in acetonitrile, and ^{1}H NMR spectra of all complexes were recorded and analyzed.

Synthesis of the Complexes. The mononuclear complex **1** was synthesized by the reaction of $[(bpy)_2Ru(1,10\text{-phenanthroline-5,6-dione})]^{2+}$ and L in refluxing methanol (Scheme 1). This method of preparation eliminated the possibility of the presence of a dinuclear complex as an impurity in the mononuclear complex. The conventional method of synthesis of the mononuclear complex by the reaction of a bridging ligand and a building block in a 1:1 molar ratio always produces some amount of dinuclear complex, complete removal of which is sometimes difficult and requires extensive column chromatography. Complex **1** is the key compound for the synthesis of heterodinuclear (**4**), nonsymmetric homodinuclear (**6**), and polynuclear complexes (**7**, **8**). The homodinuclear complexes **2**, **3**, and **5** were synthesized by the reaction of BL and *cis*-$[Ru(bpy)_2Cl_2]$, *cis*-$[Os(bpy)_2Cl_2]$, and *cis*-$[Ru(phen)_2Cl_2]$, respectively, in a 1:2 molar ratio in 2-methoxyethanol−water. Heterodinuclear (**4**) and nonsymmetric homodinuclear (**6**) complexes were prepared by the reaction of $[(bpy)_2Ru{-}BL]Cl_2$ and *cis*-$[Os(bpy)_2Cl_2]$/*cis*-$[Ru(phen)_2Cl_2]$ (1:1 molar ratio), in refluxing ethanol−water. Tetranuclear complexes **7** and **8** were prepared following a convergent-type synthetic method, shown in Scheme 1. For these reactions the purified PF_6^- salt of the mononuclear complex was used as precursor. The crude Cl^- salt of **1** can be used, but in this case we faced difficulty in the purification of the tetranuclear complexes. All complexes were isolated as their PF_6^- salt and purified by column chromatography using a column packed with deactivated neutral alumina and acetonitrile−toluene as eluent. All of these complexes gave satisfactory C, H, and N analysis.

Mass Spectrometry. Electrospray mass spectrometry (ESMS) of mono- and all dinuclear complexes (**1**−**6**) and MALDI of tetranuclear complexes (**7**, **8**) were investigated. The data with the assignment of the peaks are given in the Experimental Section. It is interesting to note that all of these mono- and dinuclear complexes, apart from the expected peaks due to $[M - nPF_6]^{n+}$ cations, exhibit an unprecedented strong peak at m/z 699.2, 1168.7, 1287.0, 1227.0, 1200.0, and 1232.3 for **1**−**6**, respectively. Partial views of the ESMS spectra of complexes **2** and **4** showing the unexpected peak (m/z 1168.7 in **2** and m/z 1227 in **4**) are displayed in Figure 1. This particular peak corresponds to the dimeric cationic species $[\{M\}_2 - 3PF_6]^{3+}$, formed by supramolecular aggregation (π−π stacking of the bridging ligand). The calculated m/z values for these dimeric species are 698.9, 1167.9, 1286.8, 1227.3, 1200.0, and 1232.0 for **1**−**6**, respectively, which are in excellent agreement with the observed values. The other expected peaks of the dimeric species such as $[\{M\}_2 - 2PF_6]^{2+}$ and $[\{M\}_2 - 4PF_6]^{4+}$ might have overlapped with the peaks of the monomeric species $[M - PF_6]^+$ and $[M - 2PF_6]^{2+}$, respectively. The ESMS technique, in fact, belongs to the class of soft ionization methods and has been used as a powerful tool for characterization of noncovalent architectures.[33−38] Recently, supramolecular π−π dimerization of a dinuclear Ru(II) com-

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(33) Ganem, B.; Li, Y.-T.; Henion, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 6294.

(34) Russel, K. C.; Leize, E.; Van Dorsselaer, A.; Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 209.

(35) Ma, S.; Rudkevich, D. M.; Rebek, J. *J. Am. Chem. Soc.* **1998**, *120*, 4977.

(36) Baca, M.; Kent, S. B. *J. Am. Chem. Soc.* **1992**, *114*, 3992.

(37) Ganem, B.; Li, Y.-T.; Henion, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 7818.

(38) Katta, V.; Chait, B. T. *J. Am. Chem. Soc.* **1991**, *113*, 8534.

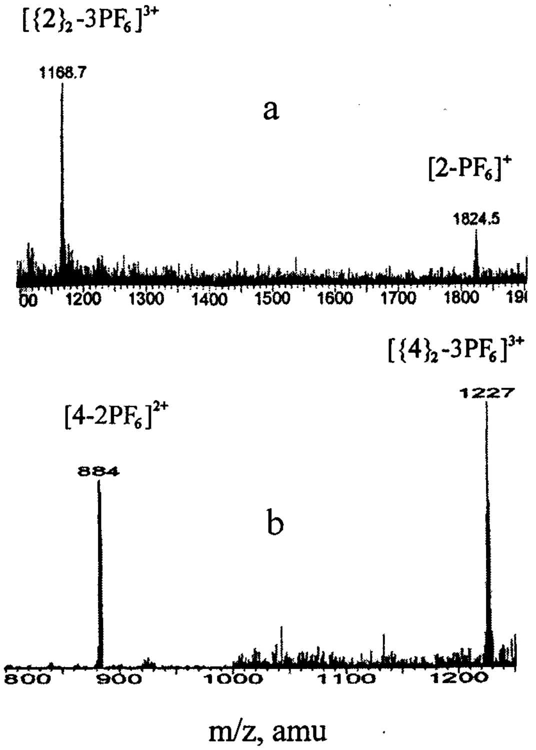

Figure 1. ESMS spectra of $[(bpy)_2Ru-BL-Ru(bpy)_2][PF_6]_4$ (a) and $[(bpy)_2Ru-BL-Os(bpy)_2][PF_6]_4$ (b).

plex containing an extended aromatic moiety as spacer (Ru−Ru distance 20 Å) has been characterized on the basis of ESMS data.[39,40] An extended aromatic character of the bridge and a long distance between the metal centers, which reduces steric and/or Coulombic repulsions, favor $\pi-\pi$ stacking.

The MALDI mass spectra of the tetranuclear complexes **7** and **8** are interpreted taking into consideration the partial hydrolysis of PF_6^- to POF_4^-, $PO_2F_2^-$, and HPO_4^{2-}. Partial hydrolysis of PF_6^- is well documented in the cases where PF_6^- ions act as counterions.[41−46] Recently, a heptanuclear ruthenium(II) polypyridyl complex has been characterized on the basis of ESMS data taking into consideration partial hydrolysis of PF_6^- to POF_4^-, $PO_2F_2^-$, and HPO_4^{2-}.[46] The tetranuclear complexes also exhibit some peaks corresponding to the species which originate from fragmentation of the complex; these species are not impurities as evident from ^1H NMR spectra. Similar fragmentation of polynuclear ruthenium(II) polypyridyl complexes was also observed by others in ESMS, even at a low accelerating voltage.[24,39,40] It has been reported that hydrolysis of PF_6^- could take place during the isolation procedure.[46] However, we have not observed any evidence of hydrolysis of PF_6^- in the ESMS of our mono- and dinuclear complexes, in which PF_6^- was added during the isolation process. The observed difference could be due to the fact that for the synthesis of tetranuclear complexes we used the PF_6^- salt of the mononuclear precursor $[(bpy)_2Ru-BL](PF_6)_2$, and the synthetic method involves long-time refluxing in the presence of water, which could have hydrolyzed PF_6^-.

^{1}H NMR Studies. The ^1H NMR spectra of complexes **1**−**8** were recorded in CD_3CN. Octahedral metal centers with bidentate ligands generally show stereoisomerism.[47,48] In the dinuclear complexes with a symmetric bridging ligand and the same terminal ligands, the coordination environment of the metal centers is equivalent. In all such cases two diastereoismeric forms, $\Delta\Lambda$ (*meso*) and $\Delta\Delta/\Lambda\Lambda$ (*rac*), may exist.[47−53] The number of stereoisomeric possibilities in polynuclear complexes increases exponentially with the number of metal centers.[47] Therefore, it is expected that all of our di- and tetranuclear complexes exist in a number of stereoisomeric forms, and full characterization of ^1H NMR spectra requires isomeric resolutions. However, the spectra of our complexes, especially symmetric di- and tetranuclear complexes (**2**, **3**, **5**, **7**, and **8**), are not as complicated as expected, and in spite of the presence of a large number of aromatic protons, the signals can be assigned unambiguously. This relatively simple magnetic pattern actually originates from the large separation between the metal centers. At such distances, each chiral center does not influence its neighbors, so that the ^1H NMR spectra of all stereoisomers superimpose.[40] The mononuclear and heterodinuclear complexes, however, show overlapping of several resonances. The ^1H NMR spectra of complexes **2**, **4**, and **7** with the assignment of the signals are illustrated in Figure 2. The assignment has been made with the aid of COSY spectra recorded in the same solvent. The COSY spectrum of complex **2** is submitted as Supporting Information (Figure S1).

It may be noted that in all dinuclear complexes the signals due to *ortho* protons of the biphenyl moiety of BL, marked as a (singlet) and b (doublet), exhibit unequal splitting (Figure 2A,B). Tetranuclear complexes, however, exhibit two sets of signals for a and b protons. The ^1H NMR spectrum of BL could not be recorded due to poor solubility in common solvents; therefore, to find the source of splitting of the signals due to a and b protons, the ^1H NMR spectrum of 3,3′,4,4′-tetraaminobiphenyl (precursor of BL) is recorded in the same solvent. The spectrum of this compound shows a splitting pattern for the aromatic protons (Figure S2, Supporting Information) similar to that observed for a, b, and c protons in the dinuclear complexes. This splitting is

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(39) Ishow, E.; Gourdon, A.; Launay, J.-P. *Chem. Commun.* **1998**, 1909.

(40) Ishow, E.; Gourdon, A.; Launay, J.-P.; Chiorboli, C.; Scandola. *Inorg. Chem.* **1999**, *38*, 1504.

(41) Thompson, S. J.; Bailey, P. M.; White, C.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 490.

(42) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *134*, 319.

(43) Wimmer, F. L.; Snow, M. R. *Aust. J. Chem.* **1978**, *31*, 267.

(44) Horn, E.; Snow, R. *Aust. J. Chem.* **1980**, *33*, 2369.

(45) Fernandez-Galan, R.; Manzano, B. R.; Otero, A.; Lanfranchi, M.; Pellinghelli, M. A. *Inorg. Chem.* **1994**, *33*, 2309.

(46) Moucheron, C.; Mesmaeker, K.-De; Dupont-Gervais, A.; Leize, E.; Dorsselaer, V. A. *J. Am. Chem. Soc.* **1996**, *118*, 12834.

(47) Keene, F. R. *Coord. Chem. Rev.* **1997**, *166*, 121.

(48) Paul, P.; Tyagi, B.; Bilakhiya, A. K.; Dastidar, P.; Suresh, E. *Inorg. Chem.* **2000**, *39*, 14.

(49) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146.

(50) Hage, R.; Dijkhius, A. H. J.; Haasnoot, J. G.; Prins, R.; Reedijk, J.; Buchanan, B. E.; Vos, J. G. *Inorg. Chem.* **1988**, *27*, 2185.

(51) Hua, X.; von Zelewsky, A. *Inorg. Chem.* **1995**, *34*, 5791.

(52) Rutherford, T. J.; Quagliotto, M. G.; Keene, F. R. *Inorg. Chem.* **1995**, *34*, 3857.

(53) Kelso, L. S.; Reitsma, D. A.; Keene, F. R. *Inorg. Chem.* **1996**, *35*, 5144.

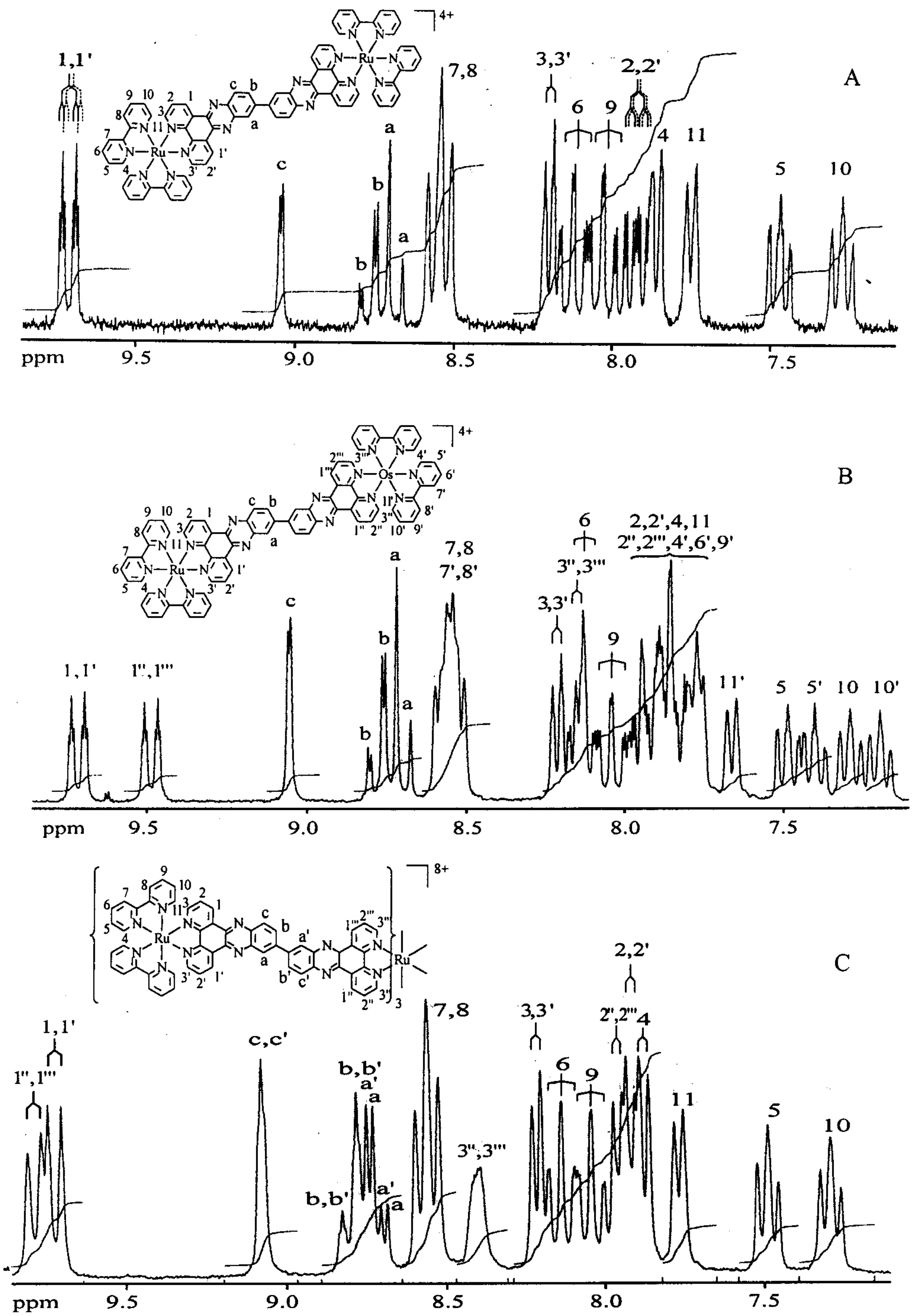

Figure 2. ^{1}H NMR spectra of $[(bpy)_2Ru-BL-Ru(bpy)_2]^{4+}$ (A), $[(bpy)_2Ru-BL-Os(bpy)_2]^{4+}$ (B), and $[\{(bpy)_2Ru-BL\}_3-Ru]^{8+}$ (C) in CD_3CN.

attributed to the second-order coupling, which results in unequal splitting of the signal and changes in chemical shifts. This type of splitting is often observed in trisubstituted benzenes and disubstituted pyridines (ABC-type system) where the $\Delta\delta$ to J ratio is small ($\Delta\delta$ is the chemical shift difference between the interacting nuclei).[54,55] The other possible reason for splitting could be the torsional isomerism, which arises due to rotation of the molecule around the pivotal bond. However, it can be ruled out because of the fact that the molecule is free to rotate and the torsional isomers are unlikely to exist independently in solution long enough for the NMR time scale to distinguish between the two. In the tetranuclear complexes, the *ortho* and *meta* protons of the two benzene rings of the biphenyl moiety of BL are not magnetically equivalent because of the different chemical environments around the central and peripheral metal ions. For this reason these protons show two sets of signals, marked as a, b, and c for one ring and a′, b′, and c′

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(54) Rahman, A. U. *Nuclear Magnetic Resonance: Basic Principles*; Springer-Verlag: New York, 1986; pp 50−61.

(55) Paudler, W. W. *Nuclear Magnetic Resonance: General Concepts and Application*; John-Wiley and Sons Inc.: New York, 1987; pp 169−187.

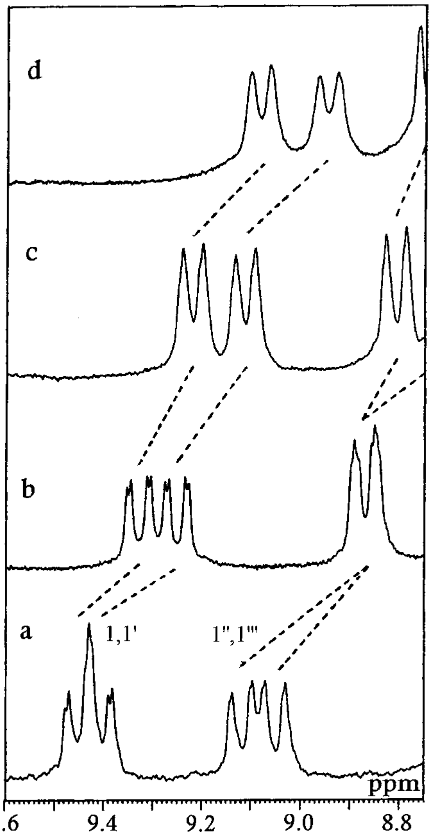

Figure 3. Partial view of the ^{1}H NMR spectra of [(bpy)$_2$RuBL]$^{2+}$ at various concentrations in CD$_3$CN: (a) 0.8, (b) 3.0, (c) 6.0, and (d) 12.0 mM solution.

for the other ring (Figure 2C). The signals due to b, b′ and c, c′ are, however, not well resolved.

It is interesting to note that the chemical shifts and multiplicity of the protons which are attached to the 1,10-phenanthroline unit of BL are strongly concentration dependent. The ^{1}H NMR spectra of the mononuclear complex **1** and the dinuclear complex **2** were recorded at various concentrations. With increasing concentration the resonances of all protons attached to the phenanthroline units of BL show a significant upfield shift while the chemical shifts of other protons remain almost unchanged. Portions of the spectra of complex **1** showing 1, 1′, 1″, and 1‴ protons[56] (see complex **1** in Scheme 1 for numbering), recorded at various concentrations (0.8−12 mM), are displayed in Figure 3. This displacement of chemical shifts with a change in concentration is attributed to an aggregation of the complex in solution by $\pi-\pi$ stacking of the bridging ligand.[18,19,25,39,40,57,58]

The ^{1}H NMR spectra of the dinuclear complex **2** were also recorded at various concentrations (4, 8, and 16 mM) and an observation similar to that found for the mononuclear complex is noted. Portions of the spectra showing the changes in the chemical shifts of 1 and 1′ protons[59] with increasing concentration are illustrated in Figure 4. It may be noted that in both mono- and dinuclear complexes one set of signals move toward the upfield region faster than the other set, and in the dinuclear complex the more shielded set of signals are significantly broaden and at the highest concentration (16 mM) exhibit a multiplet instead of a doublet (Figure 4). These changes in chemical shifts and multiplicity are due to a modification of the local electronic density and/or the ring current effects in the vicinity of the protons concerned. An effective aggregation brings protons closer and generates a cyclic current effect, which results in changes of the chemical shifts,[19,40,60,61] which may be affected further by the surrounding aromatic rings. If the protons concerned are pointed toward the shielding face of an approaching aromatic ring of the neighboring ligand, the shielding effect is enhanced, whereas if the protons are pointed toward the deshielding zone of an aromatic ring, the shielding effect partially compensates.[48,62−64] Therefore, the changes in chemical shifts, specially at high concentration,

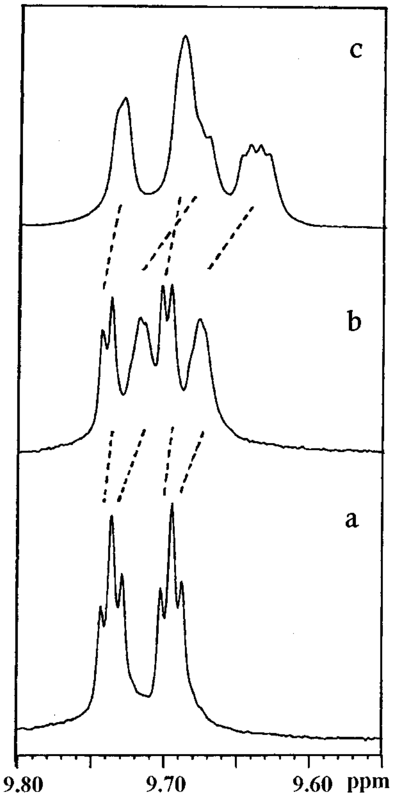

Figure 4. Partial view of the ^{1}H NMR spectra of [(bpy)$_2$Ru−BL−Ru(bpy)$_2$]$^{4+}$ at various concentrations in CD$_3$CN: (a) 4.0, (b) 8.0, and (c) 16.0 mM solution.

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[56] The 8.75−9.6 ppm portion of the ^{1}H NMR spectrum is shown. With increasing concentration these signals move toward the upfield region, and at concentrations of 6 and 12 mM the signals due to the 1″ and 1‴ protons are partially overlapped with the strong signal at 8.59 ppm. For this reason the spectrum is shown up to 8.75 ppm.

[57] Rudi, A.; Kashman, Y.; Gut, D.; Lellouche, F.; Kol, M. *J. Chem. Soc., Chem. Commun.* **1997**, 17.

[58] Gourdon, A.; Launay, J.-P. *Inorg. Chem.* **1998**, *37*, 5336.

[59] At high concentration the signals due to the protons marked as 2, 2′ and 3, 3′ are moved significantly and overlapped with other signals of the upfield region, but the resonances due to the 1 and 1′ protons are well separated from the other signals. For this reason only this portion of the spectrum is chosen to show the changes with increasing concentration.

[60] Philp, P.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154.

[61] Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Menzer, S.; Perez Garcia, I.; Prodi, I.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *117*, 11171.

[62] Thummel, R. P.; Lefoulon, F.; Korp, J. D. *Inorg. Chem.* **1987**, *26*, 2370.

[63] Hanan, G. S.; Arana, C. R.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.—Eur. J.* **1996**, *2*, 1292.

are probably not the true measure of the extent of aggregation for a big molecule with a large number of aromatic rings in different orientations. The ring current effect of various degrees could be one of the reasons for the unequal upfield shift of the two sets of protons. The other possible reason could be the orientation of the molecules in dimeric form. Since BL is not planar, therefore, depending on the dihedral angle between the benzene rings of the biphenyl moiety, the dimerization may take place in such a way that one side of the BL (along the M−M axis) aggregates more effectively compared to the other side. The ^{1}H NMR data, therefore, suggest that both mono- and dinuclear complexes exhibit molecular aggregation in solution, which is consistent with the ESMS data. The bridging ligand BL is insoluble in common organic solvents, indicating extensive intermolecular $\pi-\pi$ interaction between the molecules.[40]

In the tetranuclear complexes the appearance of separate signals for each half of BL (Figure 2C) made the spectrum quite different from that of complex **2**. The most significant difference observed is the substantial downfield shift of the 3″ and 3‴ protons compared to the chemical shifts of 3 and 3′, which appeared almost at the same position as found in the dinuclear complexes. In general, the protons adjacent to nitrogen in free (uncomplexed) polypyridyl ligands show the highest deshielding effect, but after complexation with the $[M(bpy)_2]^{2+}$ unit, they show a substantial upfield shift due to the ring current effect of the neighboring bpy ligand.[63,64] In the tetranuclear complexes the central metal is coordinated by three phenanthroline units of BL, and probably the ring current effect on the 3″ and 3‴ protons imposed by neighboring phenanthroline units is less compared to that on the 3 and 3′ protons imposed by bpy ligands coordinated to the peripheral metal ion. Because of this, the 3″ and 3‴ protons are less shielded compared to the 3 and 3′ protons. It may be noted that the signals due to the 3″ and 3‴ protons are poorly resolved and look like a multiplet, which could be due to the fact that the six 3″ and 3‴ protons are not magnetically equivalent because of strain imposed on the central metal ion by the three giant $[(bpy)_2Ru-BL]^{2+}$ units. The other possible reason could be the formation of *mer* and *fac* isomers, the 3″ and 3‴ protons of which are not expected to be magnetically equivalent. If these protons appear at a closely spaced magnetic field, then the signals may look like a multiplet. However, with the present ^{1}H NMR data it is difficult to detect the *mer* and *fac* isomers of the tetranuclear complexes.

Absorption Spectra. The UV−vis spectra of all the complexes were recorded in acetonitrile, and the data are presented in the Experimental Section. The spectra of complexes **2**−**4** are illustrated in Figure 5. All of these complexes exhibit a strong band in the range 442−448 nm for Ru(II), and at 474 nm for Os(II), which can be attributed to the metal-to-ligand charge-transfer (MLCT) transition ($d\pi-\pi^*$).[19,21,40,65] Each metal ion, however, is coordinated to two terminal ligands (bpy/phen) and a phenanthroline unit of BL; therefore, two types of MLCTs, $d\pi-\pi^*$ (BL) and $d\pi-\pi^*$ (bpy/phen), are possible. The electrochemical studies (discussed later) revealed that the first two ligand-based reductions are due to the bridging unit, which suggests that the lowest unoccupied molecular orbital (LUMO) is associated with BL. The lowest energy band (442−448 nm), therefore, can be assigned to the $d\pi-\pi^*$ (BL) MLCT transition. The free (uncomplexed) ligand BL shows strong absorption at 410 and 300 nm in DMSO. Therefore, the absorption observed at 406 nm in all complexes is the charge-transfer (CT) band associated with BL due to the $\pi-\pi^*$ transition. For Os(II) complexes a broad band centered around 660 nm is observed, which can be assigned to the spin-forbidden MLCT transitions.[48,65,66] The high-energy bands at 290 and 264 nm are ligand-centered (LC) due to $\pi \rightarrow \pi^*$ transitions of bpy and phen ligands, respectively.[6,11,65] There is no significant difference in the λ_{max} value of the MLCT (BL) bands of mono-, di-, and tetranuclear complexes, indicating weak or no electronic interaction between the metal centers.[9,24,65]

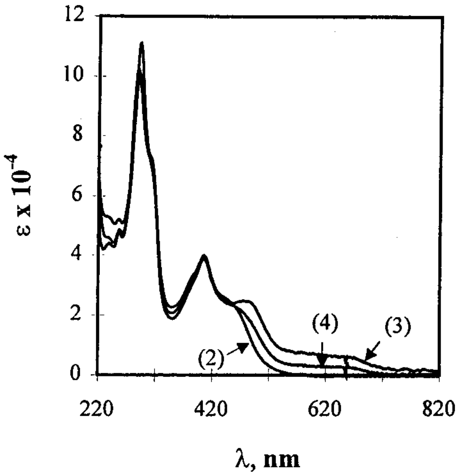

Figure 5. UV−vis spectra of complexes **2**−**4** recorded in acetonitrile.

Electrochemistry. Cyclic and square wave voltammograms of complexes **1**−**8** were recorded in acetonitrile, and the data are summarized in Table 1. The cyclic voltammograms of **2** and **4** are illustrated in Figure 6. The mono- and all dinuclear complexes containing ruthenium exhibit metal-based oxidations (Ru(II) → Ru(III)) in the potential range +1.38 to +1.40 V. The osmium centers of complexes **3**, **4**, and **8** show Os(II) → Os(III) oxidation at +0.92, +0.94, and +1.01 V, respectively. In the homodinuclear complexes the oxidations of two metal centers occur at closely spaced potentials and are indistinguishable. However, in the heterodinuclear complex two one-electron oxidations take place at well-separated potentials (Figure 6b). In the tetranuclear complex **7**, the three peripheral metal centers have the same coordination environment, but it is different from that of the central metal ion (Scheme 1). Cyclic and square wave voltammograms of **7** show that the oxidation of three noninteracting peripheral metal ions and that of the central metal ion occur at closely spaced (indistinguishable) poten-

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(64) Paul, P.; Tyagi, B.; Bilakhiya, A. K.; Bhadbhade, M. M.; Suresh, E.; Ramachandraiah, G. *Inorg. Chem.* **1998**, *37*, 5733.

(65) Bilakhiya, A. K.; Tyagi, B.; Paul, P. *Polyhedron* **2000**, *19*, 1233.

(66) Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 4750.

Table 1. Electrochemical Data for All Complexes in Acetonitrile

	$E_{1/2}$, V (ΔE_p, mV)^a					
	oxidations		reductions			
complex	Ru	Os	BL		bpy/phen	
1	1.40 (150)		−1.04 (190)		−1.30 (140)	−1.51 (170)
2	1.38 (96)		−0.79 (70)	−0.95 (72)	−1.29 (130)	−1.52 (130)
3		0.92 (84)	−0.78 (60)	−0.92 (60)	−1.23 (84)	−1.50 (150)
4	1.38 (86)	0.94 (86)	−0.78 (72)	−0.95 (79)	−1.25 (140)	−1.50 (140)
5	1.39 (76)		−0.79 (59)	−0.95 (92)	−1.26 (110)	−1.58 (230)
6	1.39 (78)		−0.75 (95)	−0.94 (104)	−1.26 (115)	−1.63 (113)
7	1.38 (110)		−0.74 (120)	−0.95 (125)	−1.29^b	−1.68^b
8	1.38 (40)	1.00 (92)	−0.73 (65)	−0.94 (130)	−1.30^b	−1.62^b

[a] Potential values vs SCE. [b] Potentials from square wave voltammograms.

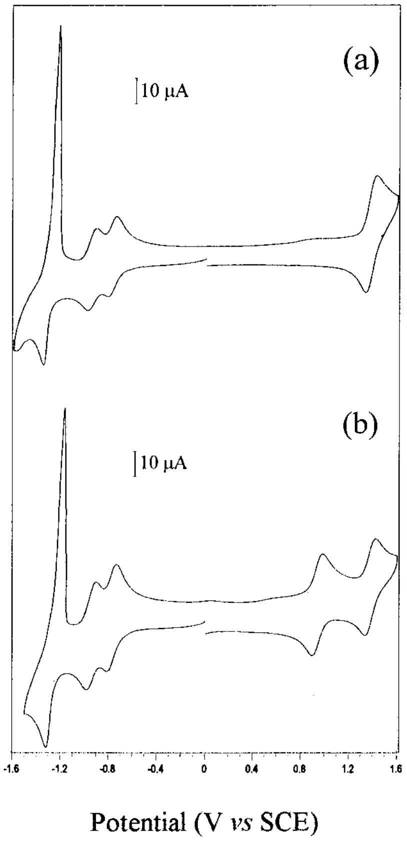

Figure 6. Cyclic voltammograms of complexes **2** (a) and **4** (b) recorded in acetonitrile.

tials. It has been reported that the central metal ion of tetranuclear complexes of similar type with a tpphz bridging ligand oxidized at 0.10−0.15 V higher potential compared to that of peripheral subunits.[22,25] The oxidations of peripheral and central metals at different potentials mainly depend on the metal−metal interactions and chemical environments. In a dendritic tetranuclear Ru system based on the 2,3-bis(2′-pyridyl)pyrazine (dpp) bridging ligand, the oxidation of the central Ru(II) was not observed because the interaction between the peripheral and the central metal ions was very strong and the oxidation of the inner metal was displaced out of the potential window available in acetonitrile.[66] Recently, the oxidations of the inner metal of a series of tri- and hexanuclear complexes with the same bridging ligand have been reported. They were recorded in liquid SO_2, and the oxidation of the central metal ion(s) occurred at 0.48 and 0.71 V higher potential compared to that of their respective peripheral metal ions in tri- and hexanuclear complexes, respectively.[67] This anodic shift of the oxidation of the central metal ion is significantly high compared to that found in the tetranuclear complexes based on a tpphz bridge. This difference is due to the different degrees of intercomponent electronic interaction. Our bridging ligand BL is significantly longer than tpphz, and there is no spectroscopic evidence of intercomponent electronic interaction; therefore, oxidation of the peripheral metals virtually has no effect on the central metal ion. The chemical environments of the peripheral and central metal ions are also similar. Therefore, the oxidation of the central metal of complex **7** is expected to be very close to that of the peripheral metal ions. Even the oxidation of the central metal ion occurs at a potential a few millivolts positive of that of the peripheral metal ions, so they are also difficult to differentiate, especially when two waves of 3:1 current ratio are very close. Therefore, the observed indistinguishable oxidation potentials of the peripheral and central metal ions in **7** are not unexpected. In the tetranuclear complex **8**, three peripheral Ru(II) atoms exhibit oxidations at the same potential as found in **7**, and the central Os(II) shows oxidation at +1.00 V (Figure 7), which is very close to the observed oxidation potential of Os(II) (+0.94 V) in the heterodinuclear complex **4**.

All of these complexes exhibit a number of ligand-based redox couples. However, the analysis of the reduction patterns was often complicated by the presence of a sharp spike. An anodic spike with a large current was observed around −1.2 V when the cathodic scan was reversed from −1.6/−1.5 V (Figure 6); however, no spike was observed when the scan was reversed from −1.2 V. When the scan was continued up to −2.0 V, a cathodic spike around −1.7 V was observed. This observation is similar to one noted in the complex $[Ru(O{-}phen)_3]^{2+}$.[68] This spike is probably due to adsorption of the reduced species on the working electrode. Similar adsorption problems have also been reported by many others with ruthenium(II) and osmium(II) polypyridyl complexes,[19,22,25] especially when phenanthroline-based ligands were used. In our complexes, a comparison of the current height of the first two ligand-based reductions with that of

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(67) Ceroni, P.; Paolucci, F.; Paradisi, C.; Juris, A.; Roffia, S.; Serroni, S.; Campagna, S.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 5480.

(68) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.

Table 2. Luminescence Data[a]

complex	Ru					Os				
	λ_{max} (nm)	τ (ns)	$10^3\phi$	I_{rel}	I_{rel}^b	λ_{max} (nm)	τ (ns)	$10^3\phi$	I_{rel}^b	10^7k
1	623	428	12.27	100						
2	632	297	8.52	76	100					
3						724	71	0.043	100	
2 + **3**	632	286		38	50					
4[c]	627	21	0.54	1.5	1.5	726			75	4.42
5	630	290	6.34	52						
6	632	240	6.05	50						
7	630	245	6.53	58						
8[c]	~630	24	0.58	5						3.76

[a] In deareated acetonitrile solution at room temperature. [b] In dichloromethane. [c] The lifetime and quantum yield of the Os(II) center were not measured due to poor resolution of the emission band in acetonitrile.

metal oxidations of homo- and heterodinuclear complexes (Figure 6) clearly indicates that the first two reductions are one-electron processes. These two redox waves are attributed to successive one-electron reductions of the bridging ligand BL. These reductions occur at a potential 0.35 and 0.5 V positive of the first reduction potential found in $[Ru(bpy)_3]^{2+}$ due to bpy, indicating that BL is a better π-electron acceptor compared to bpy/phen. The added two electrons might have occupied each of the low-energy LUMO and LUMO + 1, which mainly localized on the phenazine moiety of the BL. This is consistent with the observation of only one one-electron reduction wave for tpphz[19,22,25] and two one-electron reductions due to bqpy in their dinuclear complexes, as they contain one and two phenazine moieties, respectively. Both the reduction potentials of BL are slightly anodically shifted compared to that of bqpy. All of our dinuclear complexes exhibit reductions due to the terminal ligands (bpy/phen) at a more negative potential (Table 1). The tetranuclear complexes show stepwise reductions of the bridging ligands. The terminal ligands exhibit reductions at more negative potentials; however, full interpretation is difficult due to adsorption of reduced species on the working electrode.

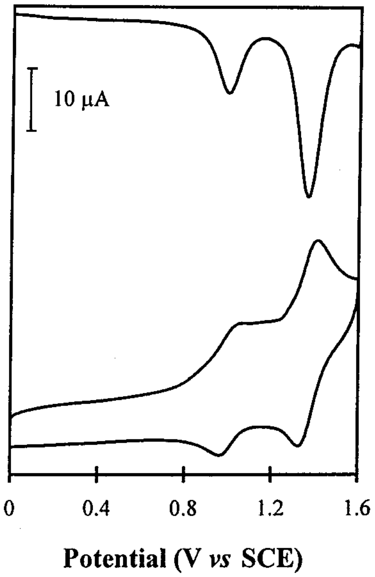

Figure 7. Osteryoung square wave and cyclic voltammograms of **8** showing oxidations of the metal ions.

Luminescence. The steady-state emission spectra of all complexes were recorded in acetonitrile and dichloromethane at room temperature. The observed band around 630 nm is due to the ^{3}MLCT excited state of the Ru(II)-based unit.[2,6,9,13] The emission maxima, relative intensities of the bands, quantum yields, and excited-state lifetimes of the complexes are given in Table 2. The emission spectra of the isoabsorptic solutions (460 nm) of $[(bpy)_2Ru-BL-Ru(bpy)_2]^{4+}$, $[(bpy)_2Os-BL-Os(bpy)_2]^{4+}$, $[(bpy)_2Ru-BL-Os(bpy)_2]^{4+}$, and a 1:1 mixture of $[(bpy)_2Ru-BL-Ru(bpy)_2]^{4+}$ and $[(bpy)_2Os-BL-Os(bpy)_2]^{4+}$ are illustrated in Figure 8. In acetonitrile solution the intensity of the emission band due to the Os(II) center is very weak, and in heterodinuclear complexes it appears as a poorly resolved shoulder. However, in dichloromethane the intensity of the emission band increases significantly, and the emission due to the Os(II) center of the heterodinuclear complexes is well resolved (Figure 8b). The emission due to the Os(II) center in the 1:1 mixture of $[(bpy)_2Ru-BL-Ru(bpy)_2]^{4+}$ and $[(bpy)_2Os-BL-Os(bpy)_2]^{4+}$ could not be observed; it is covered by the tail of the very strong emission band of the Ru(II) center. It may be noted that the Ru-based luminescence intensity of the above-mentioned mixture is 50% compared to that of an isoabsorptic solution of a dinuclear Ru(II) complex, indicating that intermolecular quenching between Ru(II) and Os(II) complexes does not occur under the experimental conditions used.[13,69] However, the Ru-based emission intensity of $[(bpy)_2Ru-BL-Os(bpy)_2]^{4+}$ is quenched by 95% in acetonitrile and 97% in dichloromethane relative to that of an isoabsorptic equimolar 1:1 mixture of dinuclear Ru(II) (**2**) and dinuclear Os(II) (**3**) complexes (Figure 8a). This observation suggests that in the heterodinuclear complex the luminescence of the Ru-based unit is intramolecularly quenched.[6,24,69,70]

The luminescence spectra of the isoabsorptic solution of the tetranuclear complexes **7** (Ru_4) and **8** (Ru_3Os) were recorded in acetonitrile (Figure S3, Supporting Information) but not in dichloromethane because of poor solubility. The emission intensity due to the Ru-based unit of Ru_3Os (**8**) is drastically reduced compared to that of Ru_4 (**7**), indicating intramolecular quenching of the Ru(II) luminescence by the Os(II) center. The Ru-based emission intensity in Ru_3Os (**8**) is 8% relative to the 75% emission intensity of the isoab-

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(69) De Cola, L.; Balzini, V.; Barigelletti, F.; Flamigni, L.; Belser, P.; von Zelewsky, A.; Frank, M.; Vogtle, F. *Inorg. Chem.* **1993**, *32*, 5228.

(70) Barigelletti, F.; Flamigni, L.; Guardigli, M.; Juris, A.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1996**, *35*, 136.

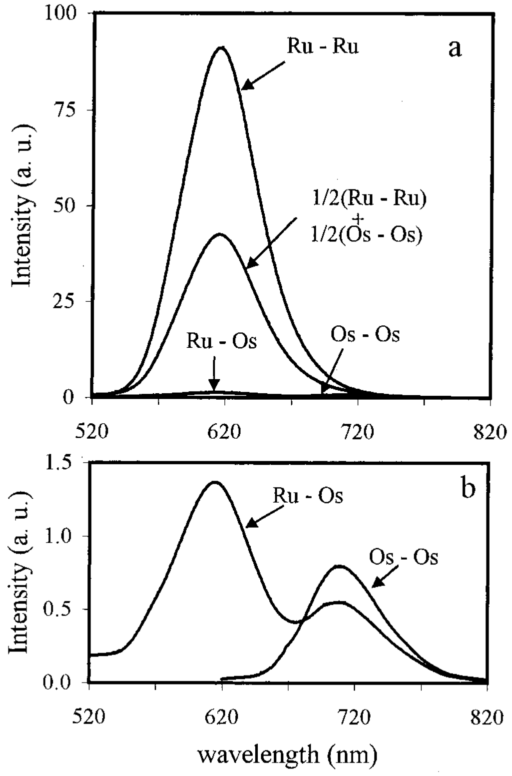

Figure 8. Relative luminescence spectra of (a) **2**−**4** and a 1:1 mixture of **2** and **3** in dichloromethane at room temperature. (b) Spectra of **3** and a 1:1 mixture of **2** and **3** shown with an expanded *y*-scale (the scale of (a) is multiplied by 60).

sorptic (460 nm) solution of Ru_4 (**7**). In principle, comparison of the emission intensity due to Ru(II) of Ru_3Os (**8**) should be made with an equimolar 3:1 mixture of Ru_4 and Os_4 complexes. As we have not prepared a tetranuclear Os(II) complex (Os_4) and also we have observed that there is no intermolecular quenching between Ru(II) and Os(II) complexes, the above-mentioned approximation seems reasonable. Moreover, in acetonitrile the emission due to the Os(II) center appears as a weak shoulder of low intensity (difficult to detect in the Ru_3Os complex) and has little effect on the intensity of the emission band due to the Ru(II) unit. The data, therefore, suggest that in the heterotetranuclear complex the emission due to Ru(II) is quenched to 8%.

Emission lifetimes of all complexes were measured at room temperature in deaerated acetonitrile (Table 2). The emission decay profile of complex **2** is submitted as Supporting Information (Figure S4). In the luminescence data two things may be noted: (i) the lifetime of the mononuclear Ru(II) complex (**1**) is significantly longer compared to that of the dinuclear complexes and (ii) the lifetimes of the heterodinuclear and heterotetranuclear complexes are too short relative to those of their corresponding homonuclear complexes. The shorter lifetime of the homodinuclear complex relative to the corresponding mononuclear complex could be due to the electron-withdrawing effect of the second metal center. This effect results in an increase of the charge separation distance and a consequent decrease in electronic coupling in the MLCT state.[24] In this context it may be noted that the emission maximum of the dinuclear complex exhibits a red shift compared to that of the mononuclear complex and the lifetime generally decreases with decreasing emission energy, according to the energy-gap law.[71] The short lifetimes of the Ru-based unit of the heterodinuclear and heterotetranuclear complexes is due to strong quenching of the emission of the Ru(II) center. The Ru-based MLCT states are higher than the Os-based MLCT states; therefore, as in many other Ru(II)−Os(II) di/polynuclear systems, intramolecular energy transfer from the Ru-based MLCT state to that of the Os-based unit is thermodynamically favorable. This quenching process, therefore, is attributed to energy transfer from the Ru(II) center to the Os(II) center.[24,69,70,72] In this case the possibility of through-space energy transfer seems unlikely. The bridging ligand BL is a long rigid rod with only one rotational degree of freedom, and also the metal−metal distance is quite high; therefore, it is extremely difficult for the metal centers to be close enough to allow through-space energy transfer. The experimental conditions (1×10^5 M solution) and the luminescence intensity of the pure and 1:1 mixture of the dinuclear Ru(II) and Os(II) complexes clearly ruled out the possibility of the intermolecular energy transfer. It is, therefore, suggested that energy transfer takes place through the bridging ligand. It may be noted that even an interaction of a few reciprocal centimeters, which cannot be noticed in spectroscopic and electrochemical experiments, is sufficient to cause fast intercomponent energy- and electron-transfer processes.[1,69,72] The rate constant for energy transfer can be calculated from eq 1,[4,6,69]

$$k = 1/\tau - 1/\tau_0 \tag{1}$$

where τ and τ_0 are the lifetimes of the Ru-based component of the heteronuclear complexes (**4** and **8**) and homonuclear model complexes (**2** and **7**), respectively. The rate constant can also be obtained from eq 2,[73,74]

$$k = (\phi^0_{em} - \phi_{em})/\phi_{em}\tau_0 \tag{2}$$

where ϕ^0_{em} and τ_0 are the emission quantum yield and lifetime of the Ru(II) chromophore of the model complex, respectively, and ϕ_{em} is the quantum yield of the Ru(II) unit of the heteronuclear complexes. The rate constants obtained by eq 2 (4.97×10^7 s^{-1} for **4** and 4.19×10^7 s^{-1} for **8**) compare well with those calculated by eq 1 (4.42×10^7 s^{-1} for **4** and 3.76×10^7 s^{-1} for **8**). These rate constants (10^7 s^{-1}) are comparable to many other literature values measured for relevant systems with rigid spacers.[6,69,70] However, these values are smaller by an order of 10^2 compared to that found in $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$.[24] These relatively low rate constants in our complexes compared to the complex with a tpphz bridging ligand are due to weak intercomponent electronic communication because of the large separation between the metal centers and nonplanarity of the bridging

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(71) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

(72) Frank, M.; Nieger, M.; Vogtle, F.; Belser, P.; von Zelewsky, A.; De-Cola, L.; Balzini, V.; Barigelletti, F.; Flamigni, L. *Inorg. Chim. Acta* **1996**, 281.

(73) Gulyas, P. T.; Smith, T. A.; Paddon-Row: M. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1325.

(74) Schanze K. S.; Sauer, K. *J. Am. Chem. Soc.* **1988**, *110*, 1180.

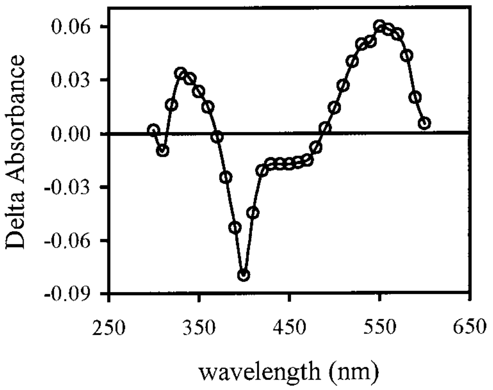

Figure 9. Transient absorption spectrum of **2** recorded in deoxygenated acetonitrile solution following excitation at 532 nm and 100 ns after the flash.

ligand, which reduces π-conjugation across the bridge. In principle, the possibility of electron transfer cannot be completely ruled out considering the fact that the excited electron remains in a common BL-localized LUMO. However, an energy-transfer process seems to be more likely in this case (for electron transfer generally $k \geq 10^9$ s^{-1})[2].

Transient differential absorption spectra of complexes **2**, **3**, **5**, and **7** were recorded in deaerated acetonitrile solution following excitation at 532 nm and after 100 ns of the flash. The spectrum of complex **2** is shown in Figure 9. This spectrum exhibits two bleached bands near 405 and 450 nm, which are attributed to the bleaching of the BL-centered $\pi-\pi^*$ transition and MLCT bands, respectively.[75,76] The bleaching of the BL-centered CT bands indicates the excited electron is localized on the bridging moiety. The absorption band observed around 560 nm is most likely associated with the π-radical anion of the bridging ligand, as produced by charge transfer from the metal center.[75−78]

Conclusion. A series of mono-, di-, and tetranuclear complexes of Ru(II) and Os(II) with a long fully aromatic spacer have been synthesized and characterized. The ^{1}H NMR studies show that due to a large separation between the metal centers the resonances of the diastereoisomers are superimposed. Because of this, the signals of the ^{1}H NMR spectra are assigned unambiguously, for homonuclear complexes in particular. The mono- and dinuclear complexes show dimerization in solution by $\pi-\pi$ stacking of the bridging ligand as evident from ^{1}H NMR and ESMS data. Electrochemical studies show that the first two ligand-based reductions are due to successive one-electron reductions of the bridging ligand, indicating that BL is a better π-electron acceptor compared to bpy/phen. The added electrons are mainly localized on the phenazine part of the BL. All of these complexes exhibit emission at room temperature originating from the lowest energy MLCT (M → BL) excited state. The luminescence data suggest that in the heterodinuclear and heterotetranuclear complexes energy transfer takes place from the Ru(II) center to the Os(II) center through the bridging ligand. There is no spectroscopic and electrochemical evidence for intercomponent electronic communication; however, luminescence data show the existence of a weak intercomponent interaction. The long length of the bridging ligand and the rotation about the pivotal bond (nonplanarity reduces π-conjugation) are probably responsible this spacer being a weak electronic communicator.

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Supporting Information Available: 1D and COSY ^{1}H NMR spectra of $[(bpy)_2Ru\text{-}BL\text{-}Ru(bpy)_2]^{4+}$, ^{1}H NMR spectrum of the aromatic proton of 3,3′,4,4′-tetraaminobiphenyl, relative luminescence spectra of **7** and **8**, and emission decay of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(75) Baba, A. I.; Shaw, J. R.; Simon, J. A.; Thummel, R. P.; Schmehl, R. H. *Coord. Chem. Rev.* **1998**, *171*, 43.

(76) Grosshenny, V.; Harriman, A.; Romero, F. M.; Ziessel, R. *J. Phys. Chem.* **1996**, *100*, 17472.

(77) Baba, A. I.; Ensley, E. H.; Schmehl, R. H. *Inorg. Chem.* **1995**, *34*, 1198.

(78) Ruthkosky, M.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 6406.