

Photonic Wires of Nanometric Dimensions. Electronic Energy Transfer in Rigid Rodlike $\text{Ru}(\text{bpy})_3^{2+}$ -(ph) $_n$ - $\text{Os}(\text{bpy})_3^{2+}$ Compounds (ph = 1,4-Phenylene; n = 3, 5, 7)

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Abstract: We have synthesized nine rodlike compounds of nanometric dimension with general formula $[\text{M}(\text{bpy})_3(\text{ph})_n\text{M}'(\text{bpy})_3]^{4+}$ ($\text{M} = \text{M}' = \text{Ru}(\text{II})$; $\text{M} = \text{M}' = \text{Os}(\text{II})$; $\text{M} = \text{Ru}(\text{II})$, $\text{M}' = \text{Os}(\text{II})$; $\text{bpy} = 2,2'$ -bipyridine; $\text{ph} = 1,4$ -phenylene; $n = 3, 5, 7$; the central phenylene unit bears two alkyl chains for solubility reasons; the metal-to metal distance is 4.2 nm for the longest spacer). The absorption spectra and the luminescence properties (emission spectra, quantum yields, and excited-state lifetimes) of the nine dinuclear complexes have been investigated in acetonitrile solution at 293 K and in butyronitrile rigid matrix at 77 K. The results obtained have been compared with those found for the separated chromophoric units ($[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Os}(\text{bpy})_3]^{2+}$, and oligophenylene derivatives). The absorption spectrum of each dinuclear complex is essentially equal to the sum of the spectra of the component species, showing that intercomponent electronic interactions are weak. In the homodinuclear compounds, the strong fluorescence of the oligophenylene spacers is completely quenched by energy transfer to the metal-based units, which exhibit their characteristic metal-to-ligand charge-transfer (MLCT) phosphorescence. In the heterodinuclear compounds, besides complete quenching of the fluorescence of the oligophenylene spacers, a quenching of the phosphorescence of the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophoric unit and a parallel sensitization of the phosphorescence of the $[\text{Os}(\text{bpy})_3]^{2+}$ chromophoric unit are observed, indicating the occurrence of electronic energy transfer. The rate of the energy-transfer process from the $[\text{Ru}(\text{bpy})_3]^{2+}$ to the $[\text{Os}(\text{bpy})_3]^{2+}$ unit is practically temperature independent and decreases with increasing length of the oligophenylene spacer (in acetonitrile solution at 293 K, $k_{\text{en}} = 6.7 \times 10^8 \text{ s}^{-1}$ for $n = 3$; $k_{\text{en}} = 1.0 \times 10^7 \text{ s}^{-1}$ for $n = 5$; $k_{\text{en}} = 1.3 \times 10^6 \text{ s}^{-1}$ for $n = 7$). It is shown that such an energy-transfer process takes place via a Dexter-type mechanism (superexchange interaction) with an attenuation coefficient of 0.32 per Å and 1.5 per interposed phenylene unit.

Introduction

Current computers are based on sets of components (wires, switches, transistors, etc.) constructed by the "top down" approach. This approach, however, has nearly reached its intrinsic limitations.¹ A necessary condition for further miniaturization to increase the power of information processing and computation is the "bottom up" construction of molecular-level components capable of performing the functions needed (chemical computer).² Apart from such futuristic applications, the design and construction of a *molecular-level electronic set* (i.e., a set of molecular-level systems capable of performing functions that mimic those of macroscopic components in electronic devices)³ is of great scientific interest since it introduces new

concepts in the field of chemistry and stimulates the ingenuity of research workers engaged in the emerging field of nanotechnology.

Since light is going to play a major role in signal generation, processing, and storage, there is a need to design molecular-level systems capable of elaborating light signals.⁴ Particularly important are molecular-level systems where photoinduced energy- and electron-transfer processes can be obtained over long distances and/or along predetermined directions.⁵ In photoinduced energy- and electron-transfer processes, the spacer linking the starting photoactive unit to the end unit plays a fundamental role. When the spacer is not rigid (i.e., $-(\text{CH}_2)_n-$

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(1) Lewis, T. *Computer* 1996, 29, 78.

(2) (a) *Molecular Electronic Devices*; Carter, F. L., Siatkowsky, R. E., Woltjen, H., Eds.; Elsevier: Amsterdam, 1988. (b) *Molecular Electronics*; Jortner, J., Ratner, M., Eds.; Blackwell: London, 1997. (c) Rouvray, D. *Chem. Br.* 1998, 34 (2), 26.

(3) (a) Balzani, V.; Credi, A.; Venturi, M. In *Supramolecular Science: Where We Are and Where We Are Going*; Ungaro, R., Dalcanale, E., Eds.; Kluwer: Dordrecht, 1999; p 1. (b) Tour, J. M.; Kozaki, M.; Seminario, J. M. *J. Am. Chem. Soc.* 1998, 120, 8486. (c) Seminario, J. M.; Tour, J. M. In *Molecular Electronics—Science and Technology*; Aviran, A., Ratner, M. A., Eds.; New York Academy of Science: New York, 1998; p 69.

(4) (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991. (b) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995. (c) de Silva, A. P.; Gunaratne, H. Q. N.; Gunlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* 1997, 97, 1515. (d) Balzani, V.; Scandola, F. In *Comprehensive Supramolecular Chemistry*; Reinholdt, D. N., Ed.; Pergamon Press: Oxford, 1996; Vol. 10, p 687. (e) Balzani, V.; Gómez-López, M.; Stoddart, J. F. *Acc. Chem. Res.* 1998, 31, 405.

chains),⁶ the geometry of the system is not well defined, and it is difficult to rationalize the results obtained. The role played by a spacer, however, is not only structural, since its chemical nature controls the electronic communication between the selected terminal units. Spacers that are easy to oxidize or to reduce and/or that possess low-energy electronic levels are unsuitable because they can play the role of quenchers on the donor excited state. Another important feature for a spacer is its modular composition, which allows changing distance without changing the electronic nature of the connection. Several kinds of bridges, including a variety of hydrocarbons,^{5a,g,6,7} modified proteins and peptides,^{5d,f} DNA,^{5k,l} phenylenevinyls,^{5o} polyenes,⁸ polyalkynyls,⁹ oligothiophenes,¹⁰ and oligophenylenes,¹¹ have been used. Very interesting results have also been obtained with linear porphyrin arrays¹² as well as with other systems.¹³

(5) (a) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (b) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73. (c) Gust, D.; Moore, T. A. *Top. Curr. Chem.* **1991**, *159*, 103. (d) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369. (e) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (f) McLendon, G.; Hake, R. *Chem. Rev.* **1992**, *92*, 481. (g) Paddon-Row, M. N. *Acc. Chem. Res.* **1994**, *27*, 18. (h) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148. (i) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (j) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707. (k) Dandiker, P. J.; Holmin, R. E.; Barton, J. K. *Science* **1997**, *275*, 1465. (l) Lewis, F. D.; Wu T.; Zhang, Y.; Letsinger, R. L.; Greenfield, S. R.; Wasielewski, M. R. *Science* **1997**, *277*, 673. (m) Bignozzi, C. A.; Schoonover, J. R.; Scandola, F. *Prog. Inorg. Chem.* **1997**, *44*, 1. (n) Collin, J.-P.; Gaviña, P.; Heitz, V.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **1998**, 1. (o) Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature* **1998**, *396*, 60.

(6) See, e.g.: Klan, P.; Wagner, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 2198.

(7) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751.

(8) Effenberger, F.; Wolf, H. C. *New J. Chem.* **1991**, *15*, 117.

(9) Harriman, A.; Ziessel, R. *Coord. Chem. Rev.* **1998**, *171*, 331.

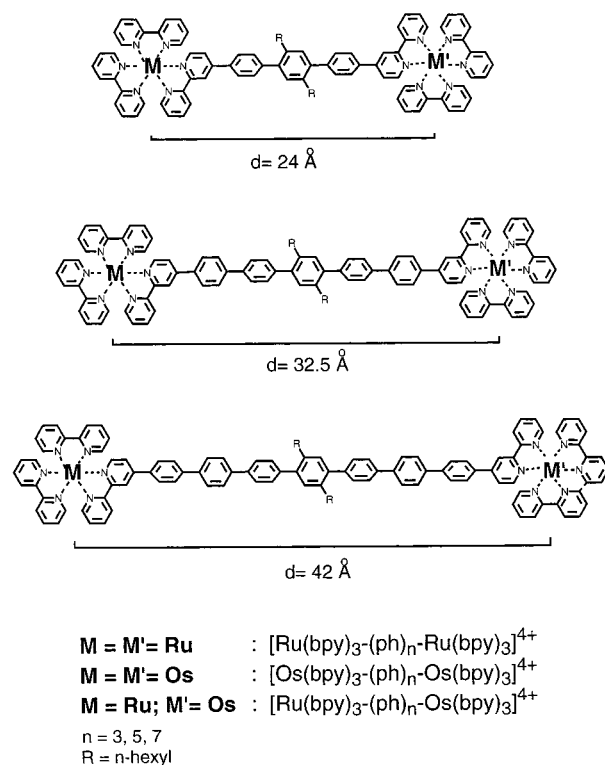
(10) Vollmer, M. S.; Würthner, F.; Effenberger, F.; Emele, P.; Meyer, D. U.; Stümpfig, T.; Port, H.; Wolf, H. C. *Chem. Eur. J.* **1998**, *4*, 260.

(11) (a) Kim, Y.; Lieber, C. M. *Inorg. Chem.* **1989**, *28*, 3990. (b) Osuka, A.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Tamai, N. *Inorg. Chem.* **1990**, *112*, 4958. (c) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1991**, *113*, 4325. (d) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6227. (e) Osuka, A.; Satoshi, N.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y.; Onho, T.; Nozaki, K. *J. Am. Chem. Soc.* **1993**, *115*, 4577. (f) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Cargill Thompson, A. M. W. *J. Am. Chem. Soc.* **1994**, *116*, 7692. (g) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *New J. Chem.* **1995**, *19*, 793. (h) Indelli, M. T.; Scandola, F.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *Inorg. Chem.* **1996**, *35*, 303. (i) Barigelletti, F.; Flamigni, L.; Guardigli, M.; Juris, A.; Beley, M.; Chodorowsky-Kimmes, S.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1996**, *35*, 136.

(12) (a) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759. (b) Hsiao, J.-S.; Krueger, B. P.; Wagner, R. W.; Johnson, T. E.; Delaney, J. K.; Mauzerall, D. C.; Fleming, G. R.; Lindsey, J. S.; Bocian, D. F.; Donohoe, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 111816. (c) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996. (d) Li, F.; Yang, S. Y.; Ciringh, Y.; Seth, J.; Martin, C. H., III; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 10001.

(13) (a) Vögtle, F.; Frank, M.; Nieger, M.; Belsler, P.; von Zelewsky, A.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1643. (b) Berberan-Santos, M. N.; Canceill, J.; Gratton, E.; Jullien, L.; Lehn, J.-M.; So, P.; Sutin, J.; Valeur, B. *J. Phys. Chem.* **1996**, *100*, 15. (c) Balzani, V.; Barigelletti, F.; Belsler, P.; Bernhardt, S.; De Cola, L.; Flamigni, L. *J. Phys. Chem.* **1996**, *100*, 16786. (d) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (e) Frank, M.; Nieger, M.; Vögtle, F.; Belsler, P.; von Zelewsky, A.; De Cola, L.; Barigelletti, F.; Flamigni, L.; Balzani, V. *Inorg. Chim. Acta* **1996**, *242*, 281. (f) Agyin, J. K.; Timberlake, L. D.; Morrison, H. *J. Am. Chem. Soc.* **1997**, *119*, 7945. (g) Tours, J. M. *Chem. Rev.* **1996**, *96*, 537. (h) Balzani V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26. (i) Hong, B.; Ortega, J. V. *Angew. Chem., Int. Ed.* **1998**, *37*, 2131. (j) Ziessel, R.; Hissler, M.; El-ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178–180*, 1251. (k) De Cola, L.; Belsler, P. *Coord. Chem. Rev.* **1998**, *177*, 301.

Chart 1. Formulas of the Compounds and the Abbreviations Used^a



^a Note that, in the abbreviated formulas, the two hexyl chains appended to the central phenylene unit are not shown for the sake of simplicity.

We have prepared¹⁴ nine rodlike compounds of nanometric dimension of general formula $[\text{M}(\text{bpy})_3(\text{ph})_n\text{-M}'(\text{bpy})_3]^{4+}$ ($\text{M} = \text{M}' = \text{Ru}(\text{II})$; $\text{M} = \text{M}' = \text{Os}(\text{II})$; $\text{M} = \text{Ru}(\text{II})$, $\text{M}' = \text{Os}(\text{II})$; $\text{bpy} = 2,2'$ -bipyridine; $\text{ph} = 1,4$ -phenylene; $n = 3, 5, 7$; the central phenylene unit bears two alkyl chains for solubility reasons). The formulas of the compounds and the abbreviations used are shown in Chart 1. Note that, in the abbreviated formulas used throughout the paper, the two alkyl chains appended to the central phenylene unit are not shown for the sake of simplicity. The metal-to-metal distance is 4.2 nm for the longest spacer. In this paper, we report the absorption spectra and the luminescence properties of the nine novel compounds. We have also observed the occurrence of intercomponent electronic energy-transfer processes, measured their rates, and discussed their mechanisms.

Results

Synthesis. Oligophenylene rods¹⁵ have attracted much interest as spacers,^{11,16} but their use has so far been limited to species containing a few phenylene units because of synthetic difficulties related to solubility problems. This difficulty has recently been overcome by appending alkyl chains on the phenylene units.¹⁷ We first prepared symmetric boronic acid derivatives of

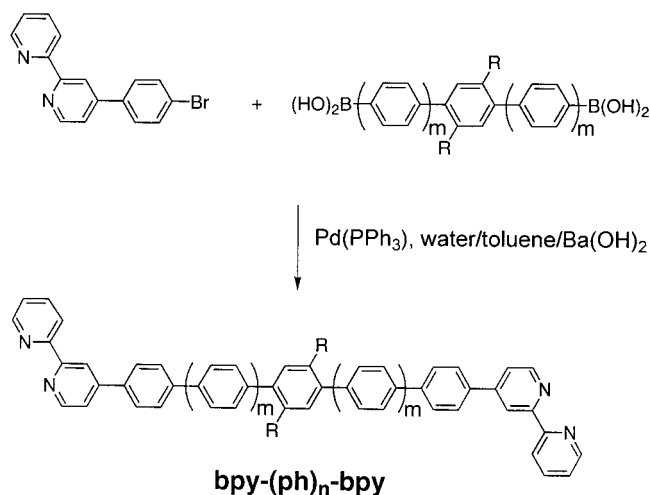
(14) Details on the synthesis will be reported separately: Schlicke, B.; De Cola, L., to be published.

(15) (a) Schlüter, A. D.; Hensel, V.; Liess, P.; Lützwow, K. In *Modular Chemistry*; Michl, J., Ed.; Kluwer: Dordrecht, The Netherlands, 1997; p 241. (b) Yamaji, M.; Tanaka, T.; Suto, K.; Shizuka, H. *Chem. Phys. Lett.* **1996**, *261*, 289. (c) Grimme, J.; Kreyenschmidt, M.; Uckert, F.; Müllen, K.; Scherf, U. *Adv. Mater.* **1995**, *7*, 292.

(16) Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771.

(17) Liess, P.; Hensel, V.; Schlüter, A. D. *Liebigs Ann.* **1996**, 1037. Rehahn, M.; Schlüter, A. D. *Makromol. Chem.* **1990**, *191*, 1991. Hensel, V.; Schlüter, A. D. *Liebigs Ann./Recl.* **1997**, 303.

Scheme 1



R = n-hexyl
m = 0, 1, 2

oligophenylenes, $(\text{HO})_2\text{B}-(\text{ph})_n-\text{B}(\text{OH})_2$ ($n = 1, 3, 5$; the central phenylene unit bears two alkyl chains) and then reacted them with 4'-Br-phenyl-bipyridine to obtain the bis-bipyridine bridging ligands $\text{bpy}-(\text{ph})_n-\text{bpy}$ ($n = 3, 5, 7$), as shown in Scheme 1. The homodinuclear $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Ru}(\text{bpy})_3]^{4+}$ and $[\text{Os}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ complexes were then obtained by reacting the bridging ligands with 2 equiv of the appropriate $\text{M}(\text{bpy})_2\text{Cl}_2$ species, according to a procedure previously used for several other homodinuclear Ru and Os compounds^{13a,c,e} (Scheme 2). The heterodinuclear $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ complexes were prepared again by a previously used procedure,^{13a,c,e} i.e., by reacting the bridging ligands with $\text{Os}(\text{bpy})_2\text{Cl}_2$ to obtain the mononuclear $[\text{bpy}-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{2+}$ species, followed by reactions with $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (Scheme 3). All the compounds have been purified and fully characterized by NMR and mass spectra. Details on the synthesis, purification procedures, and characterization are reported elsewhere.¹⁴

Molecular modeling shows that the metal-to-metal distance is 2.4, 3.3, and 4.2 nm for $n = 3, 5$, and 7, respectively. For $n = 7$, the overall length of the compounds is estimated to be 5 nm.

Spacers and Bridging Ligands. It is well known that oligophenylenes exhibit an intense absorption band and a strong, short-lived fluorescence band in the near-UV spectral region.¹⁸ We have found that the compound $\text{TMS}-(\text{ph})_5-\text{Br}$ (where TMS = trimethylsilyl, and two phenylene units bear alkyl chains) shows an absorption maximum at 270 nm and a fluorescence band with maximum at 340 nm. The $\text{bpy}-(\text{ph})_7-\text{bpy}$ bridging ligand (Scheme 1) shows an absorption band with maximum at 320 nm and a fluorescence band with maximum at 395 nm. Both of the fluorescence bands are very intense (quantum yield around 0.5) and short-lived (lifetime shorter than 1 ns). Even in rigid matrix at 77 K, the fluorescence bands are very strong, while no phosphorescence can be observed.

Metal Complexes. (i) Absorption Spectra. The absorption spectra of the homodinuclear $[\text{Ru}(\text{bpy})_3-(\text{ph})_5-\text{Ru}(\text{bpy})_3]^{4+}$ and $[\text{Os}(\text{bpy})_3-(\text{ph})_5-\text{Os}(\text{bpy})_3]^{4+}$ and the heterodinuclear $[\text{Ru}(\text{bpy})_3-$

$(\text{ph})_5-\text{Os}(\text{bpy})_3]^{4+}$ complexes in acetonitrile solution at 293 K are shown in Figure 1. The spectra of the complexes with $n = 3$ or 7 are identical, within the experimental errors, to those with $n = 5$, with an exception being made for the 300–350-nm region, where the absorptions of the oligophenylene spacers are not negligible compared with the spectra of the two metal-based units. It can also be shown that the absorption spectra of the heterodinuclear $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ complexes are equal to the spectra of the 1:1 mixture of the corresponding homodinuclear $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Ru}(\text{bpy})_3]^{4+}$ and $[\text{Os}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ parent compounds. It is important to notice the presence of isosbestic points in the spectrum of Figure 1. In particular, the isosbestic point at 435 nm is common to all the nine complexes examined. When excitation of the heterodinuclear $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ complexes is performed in correspondence with this isosbestic point, the Ru-based and Os-based units absorb the same fraction of incident light. This is a quite useful feature for the quantitative evaluation of the quenching and sensitization processes, as will be discussed below.

(ii) Luminescence Properties. Regardless of the excitation wavelength, the nine dinuclear complexes exhibit emission bands only in the spectral region above 580 nm (Table 1). In particular, when excitation was performed with UV light, no emission was observed in the spectral region ($\lambda < 450$ nm) where the free oligophenylene spacers and the free oligophenylene bridging ligands exhibit their fluorescence bands. The steady-state luminescence spectra of the $[\text{Ru}(\text{bpy})_3-(\text{ph})_5-\text{Ru}(\text{bpy})_3]^{4+}$ and $[\text{Os}(\text{bpy})_3-(\text{ph})_5-\text{Os}(\text{bpy})_3]^{4+}$ complexes in acetonitrile solution at 293 K are shown in Figure 2a. The spectra of the complexes with $n = 3$ or 7 are identical, within the experiments error, to those with $n = 5$. Figure 2b shows the spectra of the heterodinuclear complexes $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ ($n = 3, 5, 7$). Since the spectra have been obtained with diluted solutions (absorbance around 0.1) and have been corrected for the fraction of absorbed light, their intensities are directly comparable. The maxima of the emission bands, the emission quantum yields, and the excited-state lifetimes are gathered in Table 1, where the luminescence properties of the $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ complexes,¹⁹ taken as models of the metal-based chromophoric units, are also displayed for comparison.

Experiments have also been performed in butyronitrile rigid matrix at 77 K, and the results obtained are again shown in Table 1. The luminescence intensity was found to exhibit a monoexponential decay in all cases, except for the emission at 740 nm of the $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ compounds, where a rise time was observed (see, e.g., Figure 3).

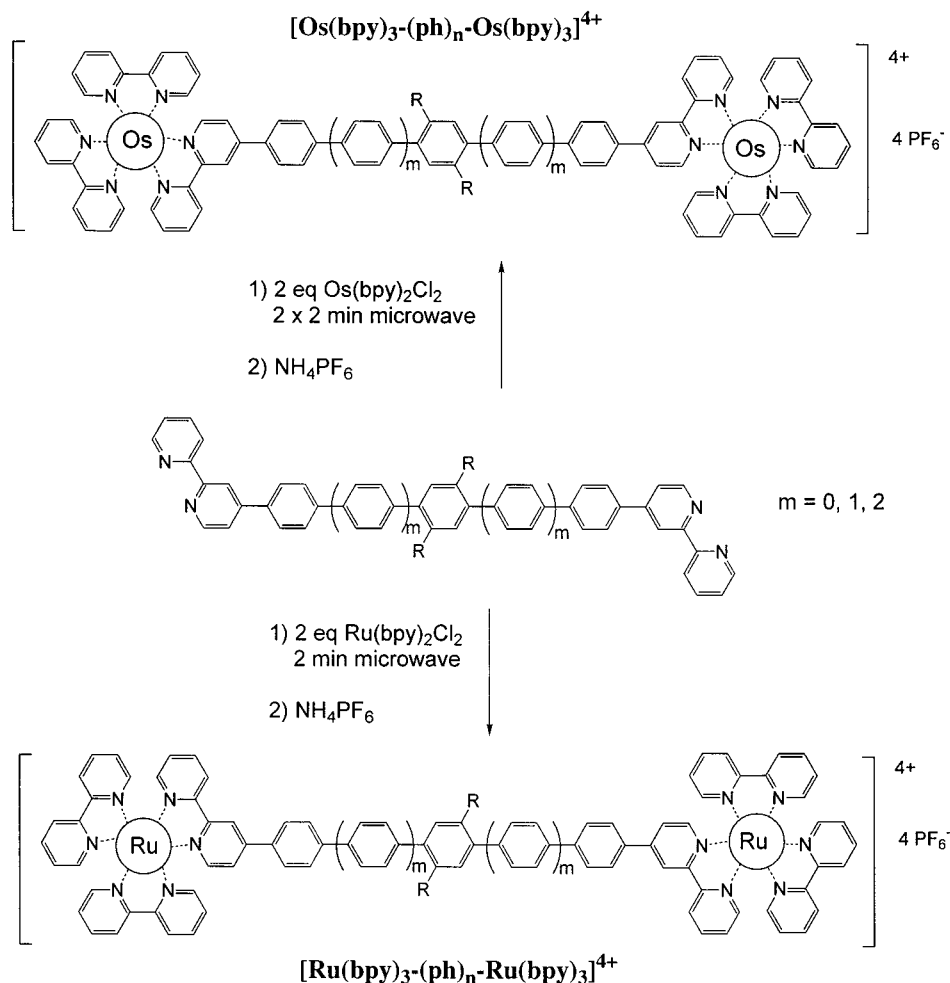
Discussion

Absorption Spectra and Luminescence Properties. To a first approximation, the $[\text{M}(\text{bpy})_3-(\text{ph})_n-\text{M}'(\text{bpy})_3]^{4+}$ compounds (Chart 1) can be viewed as made of $[\text{M}(\text{bpy})_3]^{2+}$ and $[\text{M}'(\text{bpy})_3]^{2+}$ chromophoric groups ($\text{M} = \text{M}' = \text{Ru}(\text{II})$; $\text{M} = \text{M}' = \text{Os}(\text{II})$; $\text{M} = \text{Ru}(\text{II})$, $\text{M}' = \text{Os}(\text{II})$), separated by oligophenylene-type spacers ($n = 3, 5, 7$). Each one of the three separated component units exhibits characteristic absorption and emission bands (Figures 1–3, Table 1). Extensive investigations performed on $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ and related complexes¹⁹ have shown that (i) their high-intensity absorption

(18) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Compounds*; Academic Press: London, 1965. (b) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Dekker: New York, 1993.

(19) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (b) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, 1991.

Scheme 2. Synthesis of the Homodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Ru}(\text{bpy})_3]^{4+}$ and $[\text{Os}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ Complexes ($n = 3, 5, 7$)^a



^a Note that, for the sake of simplicity, the two alkyl chains appended to the central phenylene unit are not shown in the abbreviations used.

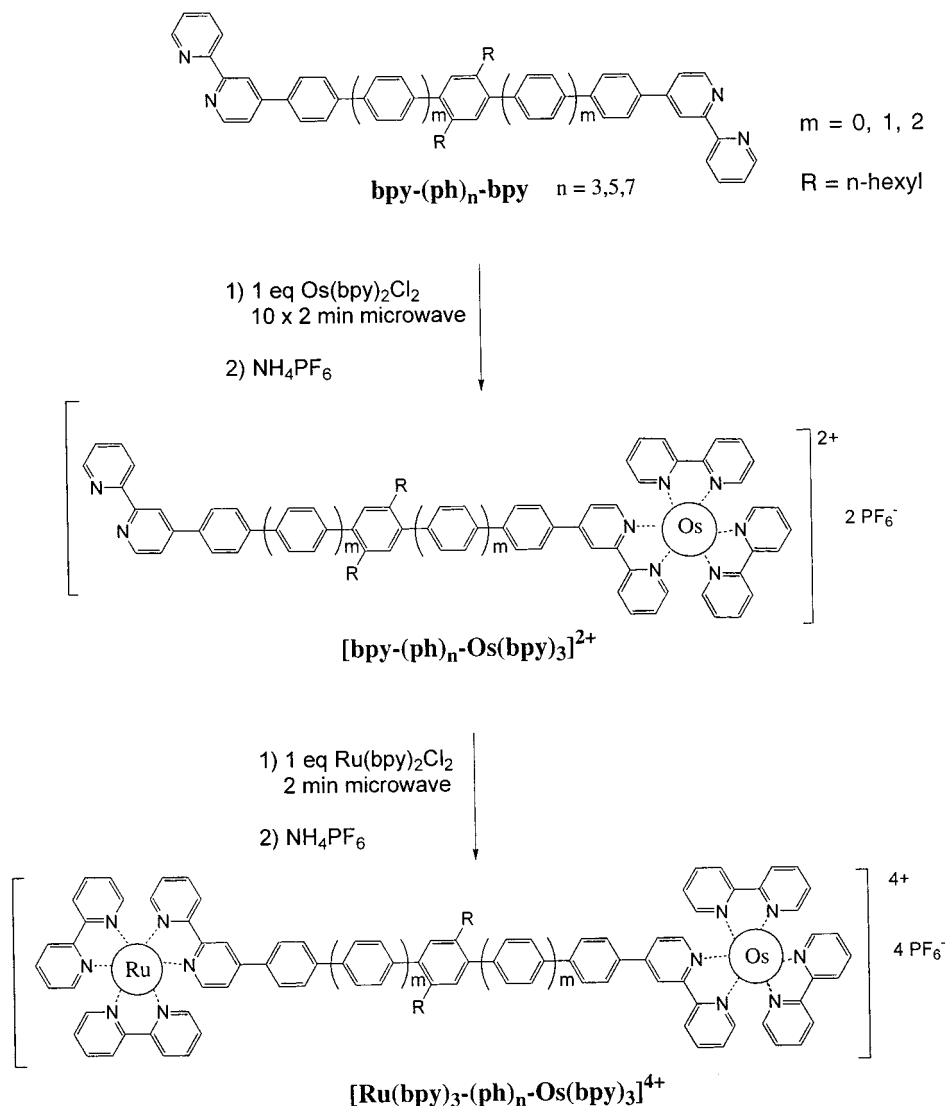
bands in the 250–300-nm spectral region are due to spin-allowed ligand-centered (LC) transition; (ii) their absorption bands in the 400–550-nm region are due to spin-allowed metal-to-ligand charge-transfer (MLCT) transitions; (iii) for the compounds of the heavier (Os) metal, spin-forbidden MLCT bands can also be seen in the 550–700-nm region; (iv) luminescence takes place from the lowest-energy triplet MLCT excited state; and (v) the luminescent excited state is very rapidly populated with unitary efficiency regardless of the excitation wavelength. As to the oligophenylene units, their absorption and emission bands in the near-UV spectral region are due to spin-allowed $\pi\text{-}\pi^*$ transitions.¹⁸

In dinuclear metal complexes, electronic interaction between the mononuclear components may range from very strong (with profound changes in the absorption spectrum on passing from mononuclear to dinuclear species) to very weak (with almost equal properties for separated and bridged units), depending on the type of bridge.^{5i,j,m,n} The interaction between the two metal-based units of the compounds examined in this paper is certainly weak, as shown by the following results: (i) the absorption spectra in the visible region of the homodinuclear $[\text{M}(\text{bpy})_3\text{-(ph)}_n\text{-M}(\text{bpy})_3]^{4+}$ species are practically identical to those of the corresponding $[\text{M}(\text{bpy})_3]^{2+}$ model compound; (ii) the absorption spectra in the visible region of the heteronuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ complexes are practically identical to those of 1:1 mixtures of their corresponding homodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Ru}(\text{bpy})_3]^{4+}$ and $[\text{Os}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$

parent compounds; (iii) the emission maximum, lifetime, and (in the homodinuclear complexes) quantum yield of the phosphorescence band of each $[\text{M}(\text{bpy})_3]^{2+}$ unit are unaffected by the length of the oligophenylene spacer and by the nature of the metal contained in the $[\text{M}'(\text{bpy})_3]^{2+}$ unit (Table 1). It should be recalled, however, that even an interaction of a few cm^{-1} (which cannot be noticed in spectroscopic experiments) may be sufficient to cause intercomponent energy-transfer processes. This is, indeed, the case for the heterodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ complexes, as discussed in the next section.

Intercomponent Energy Transfer. A schematic energy-level diagram for the heterodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ compounds is shown in Figure 4. For the metal-based components, an approximate value of the energy of the lowest spin-allowed MLCT excited state is given by the energy of the maximum of the corresponding absorption band, whereas the energy of the lowest spin-forbidden MLCT excited state can be obtained from the maximum of the emission band at 77 K. The position of the lowest triplet excited state of the $\text{bpy}(\text{ph})_7\text{-bpy}$ bridging ligand is not known because of the lack of phosphorescence. The energy of the lowest triplet excited state is 22 900 cm^{-1} for biphenyl and 20 400 cm^{-1} for *p*-terphenyl.¹⁸ If the energy of the lowest excited triplet decreases as $1/n$, as it is known to happen for the maximum of the lowest energy absorption band,^{15c,20} and the singlet–triplet separation remains

(20) (a) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962.

Scheme 3. Synthesis of the Heterodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ Complexes ($n = 3, 5, 7$)^a

^a Note that, for the sake of simplicity, the two alkyl chains appended to the central phenylene unit are not shown in the abbreviations used.

constant, it can be estimated that the energy of the lowest excited triplet is around $19\,000\text{ cm}^{-1}$ for pentaphenyl and $17\,000\text{ cm}^{-1}$ for heptaphenyl. Since the hexyl substituent in the central phenylene unit should slightly decrease conjugation, it can be expected that the lowest triplet of the spacer, even for $n = 7$, is higher than the energy of the ³MLCT excited state of the Ru-based moiety ($16\,800\text{ cm}^{-1}$). That the lowest excited state of any of the oligophenylene spacers lies above the ³MLCT state of the Ru-based moiety is also confirmed by the fact that the emission intensity and lifetime of the Ru-based units of the $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Ru}(\text{bpy})_3]^{4+}$ compounds are not quenched by any spacer (Table 1). As far as the metal-based units are concerned, the diagram shown in Figure 4 can be used for each one of the three heteronuclear complexes since, as we have seen above, the energy levels of the metal-based units are unaffected by the length of the oligophenylene spacer and by the nature of the metal present on the other end of the compound.

None of the nine dinuclear complexes shows any evidence of oligophenylene fluorescence. This clearly means that the potentially fluorescent oligophenylene excited state is very efficiently quenched by the connected metal-based units.

As shown in Figure 2 and Table 1, in the heterodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ compounds, the phosphorescence intensity and lifetime of the Ru-based unit are quenched. Under

the experimental conditions used (complex concentration $3.0 \times 10^{-5}\text{ M}$; excited-state lifetime $< 250\text{ ns}$), *intermolecular* quenching processes can be excluded, so that the observed quenching has to be due to *intercomponent* interaction. The exact amount of intensity quenching can be obtained by comparing the behaviors of the various complexes on excitation at 435 nm (isosbestic point, Figure 1), i.e., under conditions in which each metal-based unit absorbs the same fraction of incident light. As shown in Figure 2 and Table 1, the emission quantum yield and lifetime of the Ru-based unit are quenched in the heterodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ compounds, and the quenching effect increases on decreasing the number of phenylene units contained in the spacer. From Figure 2, it can also be noticed that the quenching of the phosphorescence intensity of the Ru-based unit is accompanied by a corresponding sensitization of the Os-based unit. Therefore, the quenching process occurs via an energy-transfer mechanism. This is also confirmed by the fact that a rise time for the Os-based phosphorescence can be observed which is in good agreement with the lifetime of the decay of the Ru-based phosphorescence (see, e.g., Figure 3).

The rate constant of the energy-transfer process can be obtained from the equation

$$k = (1/\tau) - (1/\tau^0) \quad (1)$$

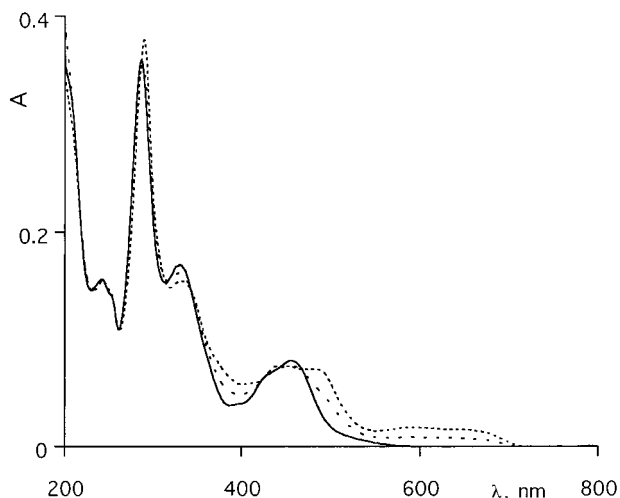


Figure 1. Absorption spectra of the $[\text{Ru}(\text{bpy})_3-(\text{ph})_5-\text{Ru}(\text{bpy})_3]^{4+}$ (full line), $[\text{Os}(\text{bpy})_3-(\text{ph})_5-\text{Os}(\text{bpy})_3]^{4+}$ (dotted line), and $[\text{Ru}(\text{bpy})_3-(\text{ph})_5-\text{Os}(\text{bpy})_3]^{4+}$ (dashed line) complexes in acetonitrile solution at 293 K. The concentration of the solution was 3.0×10^{-6} M in all cases. The spectra of the complexes with $n = 3$ or 7 are identical to those with $n = 5$, except in the 250–350-nm region, where the absorption of the oligophenylene spacers is not negligible compared with the spectra of the two metal-based units.

where τ° and τ are the phosphorescence lifetimes of the Ru(II)-based component in the $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Ru}(\text{bpy})_3]^{4+}$ and $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ compounds, respectively. The values obtained in acetonitrile solution at 293 K and in butyronitrile rigid matrix at 77 K are shown in Table 2. As one can see, there is no appreciable temperature effect. For the acetonitrile solutions, where the relative emission intensities have been measured, the energy-transfer rate constant can also be calculated from the equation

$$k_{\text{en}} = (I^\circ/I)(I^\circ/I - 1) \quad (2)$$

where I° and I are the relative emission intensities, after appropriate normalization for absorption, of the Ru-based emission of $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Ru}(\text{bpy})_3]^{4+}$ and $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ compounds, respectively. The values obtained in this way are equal, within the experimental error, to those obtained from eq 1.

Energy-Transfer Mechanism. Energy transfer can take place by Coulombic (Förster)²¹ and exchange (Dexter)²² mechanisms. In the former one, the main contribution to the rate constant comes from the dipole–dipole interaction between donor and acceptor. The rate constant according to this mechanism can be calculated from spectroscopic and structural parameters by using eqs 3 and 4:²²

$$k_{\text{en}} = 1/\tau^\circ (R_0/r)^6 \quad (3)$$

$$R_0^6 = 5.87 \times 10^{-25} \phi^\circ/n^4 \int F(\tilde{\nu})\epsilon(\tilde{\nu})\tilde{\nu}^{-4} d\tilde{\nu} \quad (4)$$

where R_0 is the so-called critical radius, i.e., the distance at which the energy-transfer rate and the intrinsic deactivation rate of the donor are equal (50% transfer efficiency), $\tilde{\nu}$ is the frequency (cm^{-1}), and n , ϕ° , and r are the refractive index of the solvent, the luminescence quantum yield of the donor, and the donor–acceptor distance, respectively. From eq 6, R_0 is about 10 Å, which is a value considerably smaller than the

metal–metal distance (24 Å) in the $[\text{Ru}(\text{bpy})_3-(\text{ph})_n-\text{Os}(\text{bpy})_3]^{4+}$ compound with the shortest spacer ($n = 3$). In other words, the calculated Förster rate constant over the 24-Å distances of the $[\text{Ru}(\text{bpy})_3-(\text{ph})_3-\text{Os}(\text{bpy})_3]^{4+}$ compound is 2–3 orders of magnitude smaller than the experimental rate constant. One may object that the metal–metal distance is likely a structural parameter not fully appropriate for this type of calculations, since the MLCT states involved in the energy-transfer process are not localized on the metals but involve, to some extent, the bpy ligands and, perhaps, also the oligophenylene bridge. It seems reasonable to admit, however, that the Coulombic contribution cannot account for the relatively fast energy-transfer processes experimentally observed.

The Dexter-type energy-transfer mechanism is described as a double electron exchange between donor and acceptor.^{7,23} When the electronic coupling is weak, energy transfer can be considered to occur nonadiabatically, and the rate constant of energy transfer can be expressed as in eq 5;²⁴ ν_{en} and ΔG^\ddagger can be obtained from eqs 6 and 7, respectively:

$$k_{\text{en}} = \nu_{\text{en}} \exp(-\Delta G^\ddagger/RT) \quad (5)$$

$$\nu_{\text{en}} = [2(H_{\text{en}})^2/h](\pi^3/\lambda RT)^{1/2} \quad (6)$$

$$\Delta G^\ddagger = (\lambda/4)(1 + \Delta G^\circ/\lambda)^2 \quad (7)$$

Following the usual assumptions,²⁵ the free energy change ΔG° can be expressed as the difference between the spectroscopic energies of the donor and acceptor (ca. 3000 cm^{-1} , as estimated from the energy of the Ru-based and Os-based emission maxima at 77 K), and the reorganization energy λ can be estimated to be ca. 1500 cm^{-1} . This yields a value of about 0.1 for the exponential term of eq 5. This means that, for the compound with the shortest spacer ($n = 3$), ν_{en} is less than 10^8 s^{-1} , and, as a consequence (eq 6), the electronic interaction energy H_{en} is less than 1 cm^{-1} . This fully justifies the nonadiabatic treatment.

In energy- and electron-transfer processes, an important issue is the distance dependence of the rate constant. While this issue has been extensively investigated for electron-transfer processes, much less data are available in the case of energy transfer.

In the frame of the superexchange mechanism,²⁶ H_{en} follows an approximate exponential decay with increasing distance r , viz.,

$$H_{\text{en}} \propto \exp(-0.5\beta r) \quad (8)$$

Since the other terms in eqs 5–7 are not expected to be distance dependent, also the energy-transfer rate constant should fall off exponentially as

$$k_{\text{en}} \propto \exp(-\beta r) \quad (9)$$

As can be seen from the formulas shown in Chart 1, each compound contains a central phenylene unit which bears the hexyl chains, while the number of unsubstituted phenylene units

(23) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, CA, 1978.

(24) (a) Jortner, J. *J. Phys. Chem.* **1979**, *64*, 4860. (b) Orlandi, G.; Monti, S.; Barigelletti, F.; Balzani, V. *Chem. Phys.* **1980**, *52*, 313. (c) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2552. (d) Scandola, F.; Balzani, V. *J. Chem. Educ.* **1983**, *60*, 814. (e) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (f) Closs, G.; Miller, J. R. *Science* **1989**, *244*, 35.

(25) (a) Ryu, C. K.; Schmehl, R. H. *J. Phys. Chem.* **1989**, *93*, 7961. (b) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.

(26) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.

(21) Förster, Th. H. *Discuss. Faraday Soc.* **1959**, *27*, 7.

(22) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

Table 1. Luminescence Data

	298 K ^a						77 K ^b			
	Ru			Os			Ru		Os	
	λ_{\max} (nm)	τ (ns)	Φ	λ_{\max} (nm)	τ (ns)	Φ	λ (nm)	τ (μ s)	λ (nm)	τ (μ s)
[Ru(bpy) ₃ -(ph) ₃ -Ru(bpy) ₃] ⁴⁺	624	210	1.6×10^{-2}				594	5.4		
[Os(bpy) ₃ -(ph) ₃ -Os(bpy) ₃] ⁴⁺				740	42	3.3×10^{-3}			722	1.1
[Ru(bpy) ₃ -(ph) ₅ -Os(bpy) ₃] ⁴⁺	622	1.5		740	42		596	2.2×10^{-3}	715	1.1
[Ru(bpy) ₃ -(ph) ₅ -Ru(bpy) ₃] ⁴⁺	622	201	1.4×10^{-2}				594	5.7		
[Os(bpy) ₃ -(ph) ₅ -Os(bpy) ₃] ⁴⁺				740	44	2.4×10^{-3}			718	1.1
[Ru(bpy) ₃ -(ph) ₅ -Os(bpy) ₃] ⁴⁺	622	68		740	41		596	0.093	718	1.1
[Ru(bpy) ₃ -(ph) ₇ -Ru(bpy) ₃] ⁴⁺	621	200	1.5×10^{-2}				593	5.6		
[Os(bpy) ₃ -(ph) ₇ -Os(bpy) ₃] ⁴⁺				740	41	2.6×10^{-3}			720	1.2
[Ru(bpy) ₃ -(ph) ₇ -Os(bpy) ₃] ⁴⁺	624	163		740	41		594	0.612	717	1.2
Ru(bpy) ₃ ²⁺ ^c	615	170	1.6×10^{-2}				582	5.0		
Os(bpy) ₃ ²⁺ ^c				743	49	3.5×10^{-3}			710	0.83

^a Air-equilibrated acetonitrile solution. ^b Butyronitrile rigid matrix. ^c Reference 13e.

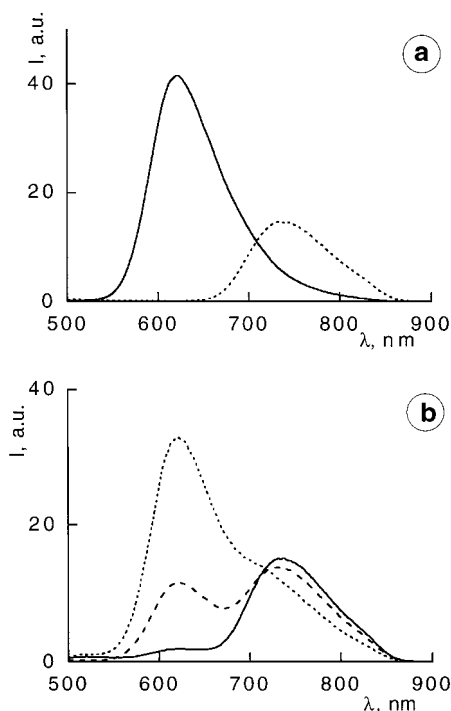


Figure 2. (a) Luminescence spectra of the complexes [Ru(bpy)₃-(ph)₅-Ru(bpy)₃]⁴⁺ (full line) and [Os(bpy)₃-(ph)₅-Os(bpy)₃]⁴⁺ (dotted line). (b) Luminescence spectra of the complexes [Ru(bpy)₃-(ph)_n-Os(bpy)₃]⁴⁺ ($n = 3$, full line; $n = 5$, dashed line; $n = 7$, dotted line). The spectra were recorded in acetonitrile solution at 293 K. In all cases, excitation was performed in the isosbestic point at 435 nm.

increases by two units on passing from [Ru(bpy)₃-(ph)₃-Os(bpy)₃]⁴⁺ to [Ru(bpy)₃-(ph)₅-Os(bpy)₃]⁴⁺, and by two more units on passing to [Ru(bpy)₃-(ph)₇-Os(bpy)₃]⁴⁺. Therefore, one can expect that the rate constant is also related to the number of phenylene units by the equation

$$k_{\text{en}} \propto \exp(-\gamma n) \quad (9)$$

where n is the number of phenylene units. A plot of k_{en} vs the metal-to-metal distance or number of interposed phenylene units for the energy-transfer process in the [Ru(bpy)₃-(ph)_n-Os(bpy)₃]⁴⁺ compounds is shown in Figure 5. As one can see, the plot is roughly linear, with an attenuation coefficient of 0.32 per Å and 1.5 per phenylene unit. For comparison, the attenuation coefficient is 2.6 per σ bond for triplet-triplet energy transfer from a benzophenonyl to a naphthyl unit connected by steroid-type bridges,²⁷ and 1.33 per Å and 1.59 per σ bond for

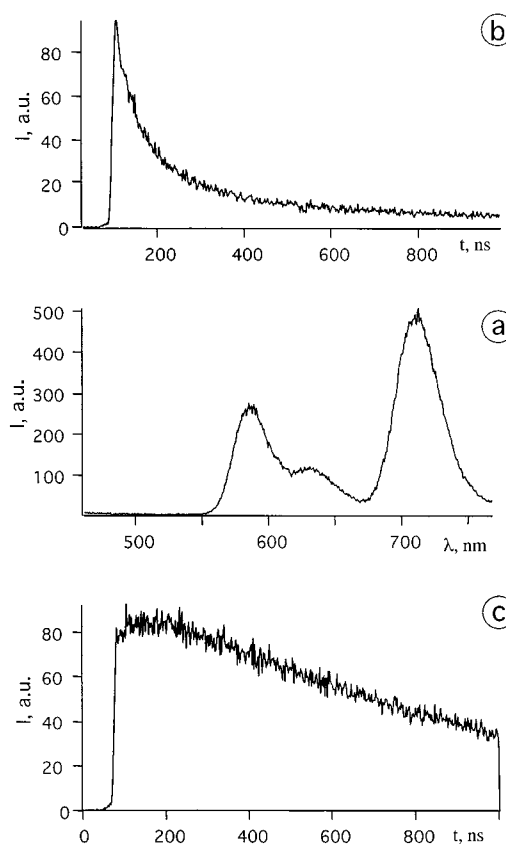


Figure 3. Luminescence spectrum (a) and intensity decay (b and c) for the [Ru(bpy)₃-(ph)₅-Os(bpy)₃]⁴⁺ compound in rigid matrix at 77 K. The emission of the Ru-based moiety occurs between 550 and 650 nm (b), and that of the Os-based moiety occurs between 680 and 750 nm (c). The decay of the Ru-based emission (93 ns) is the same as the rise time of the Os-based emission (95 ns).

singlet-singlet energy transfer from 1,4-dimethoxynaphthalene to a cyclic ketone connected by rigid, elongated hydrocarbon bridges.²⁸

The results obtained are consistent with literature reports indicating that phenylene spacers have a small effect in decreasing electronic coupling, e.g., for photoinduced electron transfer in electron donor/electron acceptor bis-porphyrin compounds^{11c,d} and singlet-singlet energy transfer between porphyrins.^{11b,e} Efficient electronic communication through

(27) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M. *Am. Chem. Soc.* **1988**, *110*, 2652.

(28) Oevering, H.; Verhoeven, J.; Paddon-Row, N.; Cotsaris, E.; Hush, N. S. *Chem. Phys. Lett.* **1988**, *143*, 488.

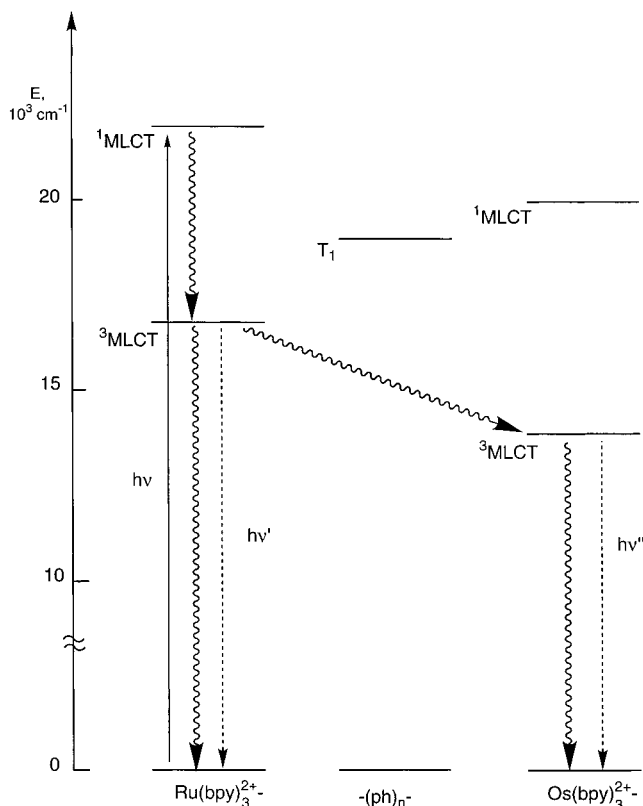


Figure 4. Schematic energy-level diagram for the heterodinuclear $\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ compounds. The energy of the T_1 level of the oligophenylene linker is that estimated for pentaphenylene (see text).

Table 2. Energy-Transfer Rate Constants (k_{en} , s^{-1})^a

	at 298 K ^a	at 77 K ^b
$[\text{Ru}(\text{bpy})_3\text{-(ph)}_3\text{-Os}(\text{bpy})_3]^{4+}$	6.7×10^8	4.5×10^8
$[\text{Ru}(\text{bpy})_3\text{-(ph)}_5\text{-Os}(\text{bpy})_3]^{4+}$	1.0×10^7	1.1×10^7
$[\text{Ru}(\text{bpy})_3\text{-(ph)}_7\text{-Os}(\text{bpy})_3]^{4+}$	1.3×10^6	1.4×10^6

^a From the $\text{Ru}(\text{bpy})_3^{2+}$ to the $\text{Os}(\text{bpy})_3^{2+}$ unit, calculated by eq 1.
^b Acetonitrile solution. ^c Butyronitrile rigid matrix.

phenylene bridges is also shown by the presence of intervalence bands in $(\text{Meph-tpy})\text{Ru}^{\text{II}}[\text{tpy}(\text{ph})_2\text{-tpy}]\text{Ru}^{\text{III}}(\text{tpy-phMe})^{5+}$ (tpy = 2,2':6',2''-terpyridine; interaction energy ca. 170 cm^{-1})²⁹ and $(\text{NH}_3)_5\text{Ru}^{\text{II}}[\text{py}(\text{ph})_2\text{-py}]\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$ (py = pyridine).^{11a}

Conclusions

In the homodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Ru}(\text{bpy})_3]^{4+}$ and $[\text{Os}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ complexes, the fluorescence of the oligophenylene spacer is quenched by energy transfer to the metal-based units, which exhibit the absorption spectra and excited-state properties of the corresponding $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ model compounds. In the heterodinuclear $[\text{Ru}(\text{bpy})_3\text{-(ph)}_n\text{-Os}(\text{bpy})_3]^{4+}$ complexes, the fluorescence of the

(29) Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434.

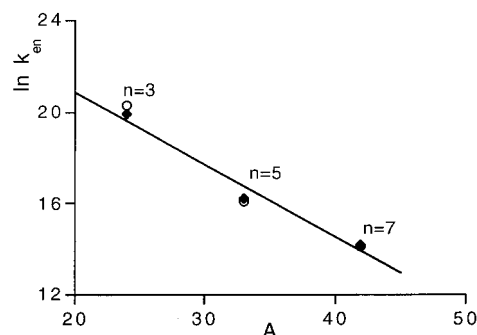


Figure 5. Plot of $\ln k_{\text{en}}$ vs metal-to-metal distance: (○) acetonitrile solution, 293 K; (◆) butyronitrile rigid matrix, 77 K; n is the number of phenylene units of the spacer.

oligophenylene spacer is completely quenched, and the phosphorescence of the Ru-based unit is quenched (to a degree which depends on the length of the spacer) by energy transfer to the Os-based unit. The results obtained show that the energy-transfer process from the Ru-based to the Os-based unit does not depend on temperature and occurs via a superexchange (Dexter) mechanism. The rate constant of the energy-transfer process has been found to decrease exponentially, with an attenuation coefficient 1.5 per interposed phenylene unit and 0.32 per Å. Interestingly, a further decrease in the energy of the triplet excited state of the oligophenylene spacer (Figure 4) could switch the energy-transfer mechanism from superexchange mediated to exoergic hopping, with a dramatic increase in the rate of the process, similar to what described for photo-induced electron transfer in ref 5o.

Experimental Section

Absorption and emission spectra were obtained on air-equilibrated solutions using previously described equipment.^{13c} When necessary, the luminescence intensity values were corrected to take into account the different absorbance values of the solutions. Luminescence decay measurements were performed with an Edinburgh single-photon-counting instrument. Time-resolved emission spectra were obtained using a Hamamatsu C-5680 streak camera equipped with a M 5677 sweep unit. Excitation at 337 nm was achieved by a pulsed (fwhm 600 ps) nitrogen laser (LTB, MGS 405 TD) operating at a repetition rate of 20 Hz. The time resolution of this set is ca. 200 ps, as limited by the laser pulse width. Estimated errors are as follows: band maxima, $\pm 2 \text{ nm}$; relative luminescence intensity, $\pm 20\%$; lifetimes, $\pm 10\%$.

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