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Oligo(U-terpyridines) and Their Ruthenium(II) Complexes: Synthesis and Structural Properties

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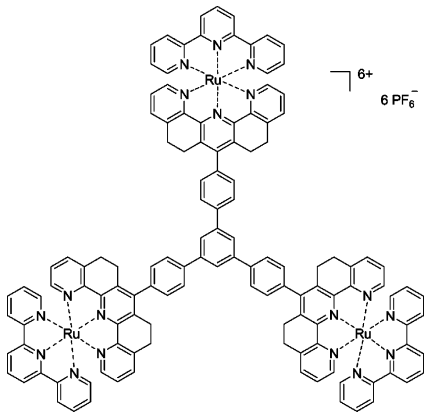

A highly efficient domino reaction starting from tetrahydroquinolinone and a series of bisiminium salts provides the corresponding bis(U-terpyridines). These ligands have been treated with [(tpy)$RuCl_3$] to afford novel dinuclear complexes $[(tpy)Ru(L)Ru(tpy)]^{4+}$. The protocol is also applied for the synthesis of a star-shaped tris(U-terpyridine) and the trinuclear complex $[\{(tpy)Ru\}_3(L)]^{6+}$. In view of potential applications in the fields of metallopolymers and molecular devices, the electronic spectra, as well as the electrochemical potentials of all the complexes have been obtained. According to these data, no significant intermetal interaction has been observed for the ruthenium complexes presented here.

Introduction

Throughout the last few decades, the development of new functional materials, such as inorganic−organic or polymeric structures, has been an increasing field of research.[1] A huge variety of supramolecular systems and synthetic strategies are known to the literature today.[2−4] The basic concepts of supramolecular chemistry are self-recognition and self-assembly, and the interactions involved are mainly of a noncovalent nature (e.g., van der Waals, hydrogen bonding, ionic, or coordinative interactions). Of special interest are the polynuclear transition metal complexes as a result of their potential metal−metal cooperativity. This property is an important aspect in designing molecular devices and controlling the build-up of supramolecular structures, metallopolymers, and molecular devices with new chemical and physical properties.[4] The bridging ligands, typically consisting of two or more chelation sites connected by an appropriate linker, are the key components in such polynuclear ensembles. Among others, 2,2′-bipyridines (bpy),[5] 1,10-phenanthrolines (phe),[6] 2,2′:6′,2″-terpyridines (tpy),[7] or closely related

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(1) (a) Rehahn, M. *Acta Polym.* **1998**, *49*, 201. (b) Manners, I. *Science* **2001**, *294*, 1664.

(2) Lehn, J.-M. *Supramolecular Chemistry—Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.

(3) Schubert, U. S. In *Tailored Polymers & Applications*; Yagci, M. K. M. Y., Nuyken, O., Ito, K., Wnek, G., Eds.; VSP Publishers: Utrecht, The Netherlands, 2000; pp 63−85.

(4) (a) Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553−3590. (b) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2893−2936. (c) Steel, P. J. *Coord. Chem. Rev.* **1990**, *106*, 227−265. (d) Balzani, V.; Barigeletti, F.; Belser, P.; Bernhard, S.; De Cola, L.; Flamigni, L. *J. Phys. Chem.* **1996**, *100*, 16786−16788. (e) De Cola, L.; Belser, P. *Coord. Chem. Rev.* **1998**, *177*, 301−346. (f) Barigeletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1−12. (g) Juris, A.; Prodi, L.; Harriman, A.; Ziessel, R.; Hissler, M.; El-ghayoury, A.; Wu, F.; Riesgo, E.; Thummel, R. P. *Inorg. Chem.* **2000**, *16*, 3590−3598. (h) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391.

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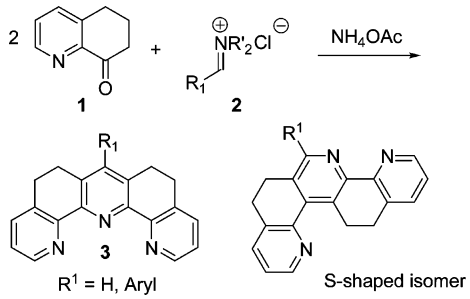
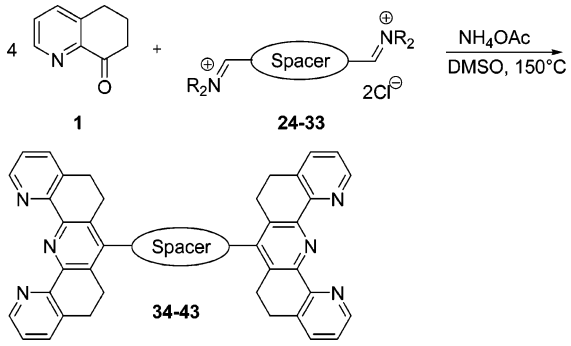
derivatives are the most common chelators. Generally, these binding sites are connected by designed spacers controlling both the distance between the two metal centers and the electronic communication between the terminal sites. The distance can be controlled easily by employing rigid linkers of known dimensions.[8] To attain electronic communication between the incorporated metal centers, research has focused on the conjugating ability of these linkers. Those with one or more π bonds, such as polyenes, polyphenylenes, polyalkynes, or polythiophene, are widely used, whereas the inclusion of tetrahedral centers such as sp^3-carbon atoms may serve as insulators.[9]

Our current interest in polytopic terpyridines and their metal complexes arises from our investigations of the modern applications of the Mannich reaction in the synthesis of various rigid pyridine derivatives, which has resulted in different approaches being developed for these heterocycles.[10] The potential importance of the fields of metallopolymers and novel molecular devices means that the development of novel and more flexible synthetic methods is an active area of research. Our studies in the field of ternary iminium salts have led to the development of highly efficient, one-pot, domino-type reactions yielding a wide range of substituted rigid pyridine derivatives, including bipyridines and terpyridines.[11] Domino reactions offer many advantages compared to traditional syntheses, such as the minimization of waste and the reduced consumption of solvents, reagents, adsorbents, and energy. As shown earlier, the reaction of a ternary iminium salt **2** and two equivalents of 5,6,7,8-tetrahydroquinolinone **1** in the presence of ammonium acetate, as a source of ammonia, under appropriate conditions leads to the formation of rigid U-shaped substituted terpyridines **3**, selectively, whereas the S-shaped isomer is isolated in small amounts in very few cases (Scheme 1).[11l]

SCHEME 1. Synthesis of Substituted U-Shaped Terpyridines 3



SCHEME 2. Synthesis of Bridged Bis(U-terpyridines) 34−43



Results and Discussion

Synthesis of Bis(U-terpyridines): A large variety of bisterpyridines bearing conjugated linkers has been prepared either by the so-called "Kröhnke" condensation[12] or by the cross-coupling reactions of bromo-terpyridines, especially with alkynes.[13] In addition, our previous studies in the field of bridged pyridine derivatives have shown that phenyl-linked bisoligopyridines can be easily synthesized using the Suzuki cross-coupling reaction employing benzene diboronic acid.[14] In a major extension to this, we now establish aromatic bisiminium salts **24**−**33** as versatile building blocks in the highly efficient one-pot synthesis of bis(U-terpyridines) **34**−**43** (Scheme 2).

To the best of our knowledge, these special types of iminium salts have not been described in the literature before. According to Böhme's protocol, bisaminals **14**−**23** have been prepared starting from their corresponding dialdehydes **4**−**13**.[15] Subsequently, bisiminium salts **24**−**33** have been obtained in very good yields (>75%, Scheme 3) by treating the aminals with acetyl chloride.[16] In contrast to other ternary iminium salts, bisiminium salts derived from bulky secondary amines, such as morpholine, have been found to be less hygroscopic and can be stored in a desiccator for months without any sign of decomposition.

Bisiminium salts **24**−**33** have been employed successfully in a highly efficient 2-fold domino sequence with 4 equiv of **1**

(5) Newkome, G. R.; Patri, A. K.; Holder, E.; Schubert, U. S. *Eur. J. Org. Chem.* **2004**, 235−254.

(6) Chouai, L.; Wu, F.; Jang, Y.; Thummel, R. P. *Eur. J. Org. Chem.* **2003**, 2774−2782.

(7) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373−399.

(8) (a) Warrener, R. N.; Ferreira, A. B. B.; Schultz, A. C.; Keene, F. R.; Kelso, L. S.; Butler, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2485−2487. (b) Warrener, R. N.; Houghton, M. A.; Schultz, A. C.; Keene, F. R.; Kelso, L. S.; Dash, R.; Butler, D. N. *Chem. Commun.* **1996**, 1151−1152.

(9) (a) Baba, A. I.; Ensley, H. E.; Schmehl, R. H. *Inorg. Chem.* **1995**, *34*, 1198−1207. (b) Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Malouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786−4795. (c) Schmehl, R. H.; Auerbach, R. A.; Wacholtz, W. F.; Elliott, C. M.; Freitag, R. A.; Merkert, J. W. *Inorg. Chem.* **1986**, *25*, 2440−2445. (d) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1987**, *26*, 2989−2994.

(10) (a) Schubert, U. S.; Eschbaumer, C.; Weidl, C. H. *Synlett* **1999**, 342−344. (b) Cardenas, D. J.; Sauvage, J.-P. *Synlett* **1996**, 916−918. (c) Thummel, R. P. *Synlett* **1992**, 1−12. (d) Thummel, R. P. *Tetrahedron* **1991**, *47*, 6851−6886. (e) Bell, T. W.; Firestone, A. *J. Org. Chem.* **1986**, *51*, 764−765.

(11) (a) Westerwelle, U.; Esser, A.; Risch, N. *Chem. Ber.* **1991**, *124*, 571−576. (b) Westerwelle, U.; Risch, N. *Tetrahedron Lett.* **1993**, *34*, 1775−1778. (c) Keuper, R.; Risch, N. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 1115−1120. (d) Keuper, R.; Risch, N.; Flörke, U.; Haupt, H.-J. *Liebigs Ann. Chem.* **1996**, 705−715. (e) Keuper, R.; Risch, N. *Liebigs Ann. Chem.* **1996**, 717−723. (f) Keuper, R.; Risch, N. *Eur. J. Org. Chem.* **1998**, *2609*, 9−2615. (g) Risch, N.; Keuper, R. *J. Prakt. Chem.* **1998**, 424−429. (h) Sielemann, D.; Keuper, R.; Risch, N. *J. Prakt. Chem.* **1999**, 487−491. (i) Sielemann, D.; Keuper, R.; Risch, N. *Eur. J. Org. Chem.* **2000**, 543−548. (j) Winter, A.; Risch, N. *Synlett* **2003**, 1959−1964. (k) Winter, A.; Risch, N. *Synthesis* **2003**, 2667−2670. (l) Sielemann, D.; Winter, A.; Flörke, U.; Risch, N. *Org. Biomol. Chem.* **2004**, *2*, 863−868. (m) Sielemann, D.; Winter, A.; Risch, N. *Heterocycles* **2004**, *63*, 2615−2621.

(12) (a) Kröhnke, F. *Synthesis* **1976**, 1−24. (b) Potts, K. T.; Cipullo, M. J.; Ralli, P.; Theodoridis, G. *J. Org. Chem.* **1982**, *47*, 3027−3033. (c) Constable, E. C.; Thompson, M. W. C. *New J. Chem.* **1992**, *16*, 855−876. (d) Constable, E. C.; Lewis, J.; Liptrot, M. C.; Raithby, P. R. *Inorg. Chim. Acta* **1990**, *178*, 47−54.

(13) (a) Ziessel, R. *Synthesis* **1999**, 1839−1865. (b) Schubert, U. S.; Eschbaumer, C. *Org. Lett.* **1999**, *1*, 1027. (c) Lehmann, U.; Henze, O.; Schlüter, A. D. *Chem.−Eur. J.* **1999**, *5*, 854. (d) Lehmann, U.; Schlütter, A. D. *Eur. J. Org. Chem.* **2000**, 3483. (e) Fallahpour, R.-A. *Synthesis* **2000**, 1665. (f) Heller, M.; Schubert, U. S. *Synlett* **2002**, 751. (g) Heller, M.; Schubert, U. S. *J. Org. Chem.* **2002**, *67*, 8269.

(14) Sielemann, D.; Winter, A.; Risch, N. *Heterocycles* **2005**, *65*, 1663−1672.

(15) Böhme, H.; Hartke, K. *Chem. Ber.* **1963**, *93*, 1305−1309.

(16) Arend, M.; Westermann, B.; Risch, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 1044−1070.

SCHEME 3. Synthesis of Bisiminium Salts 24−33

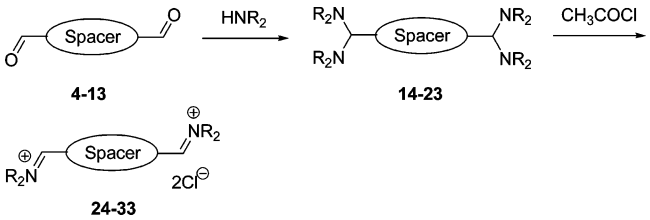
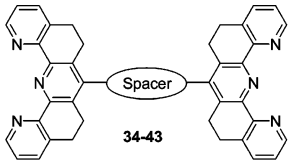
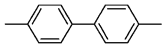
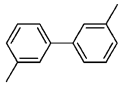
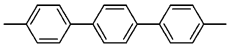
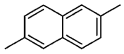
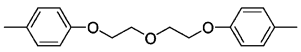
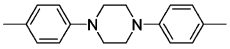


TABLE 1. Synthesis of Bis(U-terpyridines) Using Bisiminium Salts



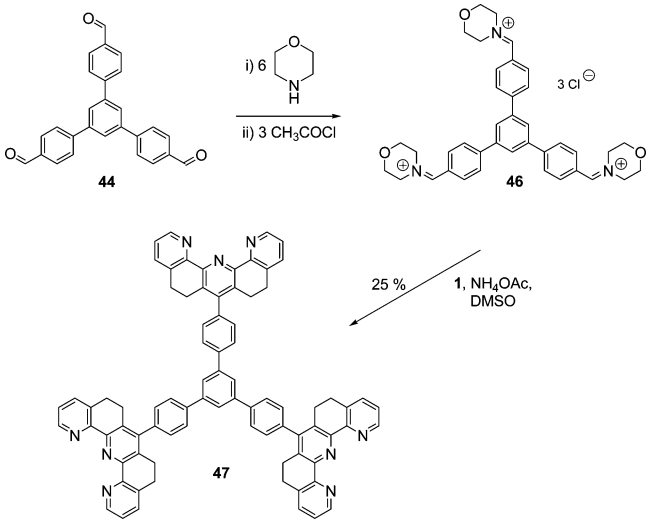
bis(U-terpyridine)	Spacer linkage	yield [%] [a]
34	—	26
35		36
36		31
37		37
38		42
39		42
40		38
41		63
42		22
43		29 [b]

[a] Isolated yield after flash column chromatography on neutral Al_2O_3. [b] In addition, the S-isomer[11l] has also been obtained in 5% yield.

and NH_4OAc, as a source of ammonia, to give bis(U-terpyridines) **34**−**43** in good yields (Scheme 2, Table 1). The proposed mechanism for the selective formation of U-terpyridines has already been discussed elsewhere.[11l] When optimized reaction conditions are used,[11l] the formation of the undesired bis(S-terpyridine) in small amounts has only been observed in a single case (**43**, 5%). Our results show that the length and the substitution pattern of the linker can be tuned easily depending on the structure of the iminium compound. The solubility of the rigid bis(U-terpyridines) can be increased significantly by introducing glycol or amine groups (**42**/**43**), although electronic communication between the terminal sites is hindered in the case of these insulating spacers. A minor drawback of the strategy presented here is that it is limited only to aromatic ternary bisiminium salts so far. Hence, future work will focus on the synthesis of bisiminium salts bearing alkyne or oligothiophene linkers, as these groups are known to attain better electronic communication than polyphenylene linkers.[17]

Our strategy has also been applied for the synthesis of the novel star-shaped tris(U-terpyridine) **47**. This first example of a trisiminium salt published in the literature represents a novel class of iminium derivatives that might serve as key building blocks in the construction of dendritic structures or two-dimensional (2D) networks.[4b] According to our straightforward procedure, trialdehyde **44** has been transferred subsequently to the aminal **45** and iminium salt **46**[15] and converted to star-shaped tris(U-terpyridine) **47** in good overall yield (25%, Scheme 4).

SCHEME 4. Synthesis of Novel Tris(U-terpyridine) 47



Complex Synthesis and Characterization: U-terpyridines are known to form stable octahedral complexes with most of the transition metals.[19] If cations, such as Re(I), Cu(I), Pt(II), Zn(II), Ru(II), Os(II), or Ir(III), are added, metal-containing aggregates are obtained that are photo- and electroactive and may find applications in molecular electronics.[4] Terpyridine−ruthenium complexes are of special interest, because they display interesting photophysical, photochemical, and electrochemical properties, which can be revealed easily by their absorption and emission spectra.[4,13,17] In regard to possible applications in the synthesis of supramolecular assemblies, such as molecular wires, energy transfer along the molecular axis between the metal centers is a fundamental requirement that can be varied by the nature of the spacer unit.[20] It has been our goal to incorporate ligands **34**−**43** into coordination polymers and to investigate the photophysical and electrochemical properties of the metallopolymers obtained. Therefore, the novel bi- and tridental

(17) (a) Harriman, A.; Hissler, M.; Ziessel, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4203−4211. (b) Harriman, A.; Hissler, M.; Khatyr, A.; Ziessel, R. *Chem. Commun.* **1999**, 735−736. (c) Hissler, M.; Harriman, A.; Khatyr, A.; Ziesse, R. *Chem.—Eur. J.* **1999**, *5*, 3366−3381. (d) El-ghayoury, A.; Harriman, A.; Ziessel, R. *Chem. Commun.* **1999**, 2027−2028. (e) Romero, F. M.; Ziessel, R. *Tetrahedron Lett.* **1994**, *35*, 9203−9206. (f) Ziessel, R.; Suffert, J.; Youinou, M.-T. *J. Org. Chem.* **1996**, *61*, 6535−6546.

(18) (a) Constable, C. E.; Cargil Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1992**, 3467−3475. (b) Chow, H.-F.; Chan, I. Y.-K.; Mak, C. C.; Ng, M.-K. *Tetrahedron* **1996**, *52*, 4277−4290. (c) Armspach, C.; Cattalini, M.; Constable, E. C.; Housecroft, C. E. *Chem. Commun.* **1996**, *7*, 1823−1824.

(19) (a) Thummel, R. P.; Jahng, Y. *Inorg. Chem.* **1986**, *25*, 2527−2534. (b) Jahng, Y.; Moon, S. W.; Thummel, R. P. *Bull. Korean Chem. Soc.* **1997**, *18*, 174−179. (c) Benniston, A. C.; Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1884−1885. (d) 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*, 7692−7699. (e) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Chem. Commun.* **1993**, 942−944. (f) Beley, M.; Delabouglise, D.; Houppy, G.; Husson, J.; Petit, J.-P. *Inorg. Chim. Acta* **2005**, *358*, 3075−3083.

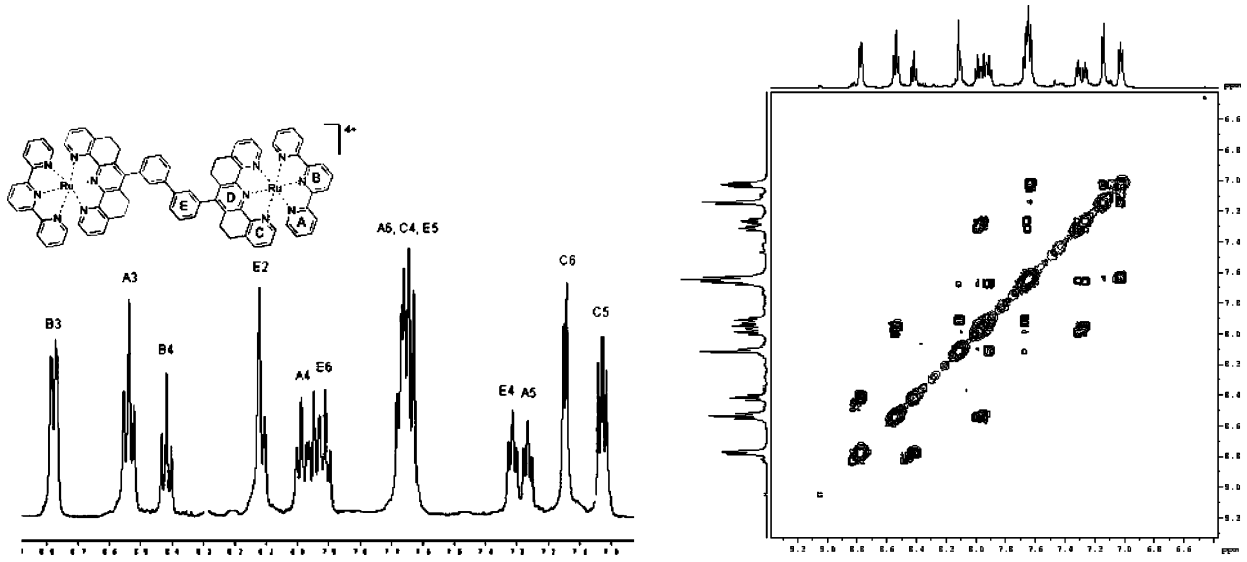
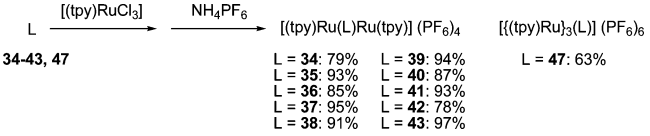


FIGURE 1. One-dimensional (top) and COSY ^{1}H NMR (bottom) of [(tpy)Ru(**38**)Ru(tpy)](PF$_6$)$_4$ (500 MHz, CD_3CN, 298 K).

SCHEME 5. Synthesis of Di- and Trinuclear Ruthenium Complexes



ligands have been further used to make a set of di- and trinuclear complexes [(tpy)Ru(L)Ru(tpy)]$^{4+}$ and [{tpy)Ru}$_3$(L)]$^{6+}$, as illustrated in Scheme 5.

The dinuclear complexes have been prepared by the direct reaction of the ligand L with an appropriate metal precursor. Therefore, bis(U-terpyridines) **34**−**43** have been treated with 2 equiv of [(tpy)RuCl$_3$][21] in ethanol under reducing conditions,[22] resulting in the formation of dark-red symmetric, dinuclear complexes [(tpy)Ru(L)Ru(tpy)](PF$_6$)$_4$ in very high yields (Scheme 5). The trinuclear complex [{(tpy)Ru}$_3$(L)](PF$_6$)$_6$ has been obtained by the same protocol using 3 equiv of [(tpy)RuCl$_3$].

In general, all complexes exhibit well-resolved ^{1}H NMR spectra, and a number of characteristic features are present. In many cases, all the peaks can be assigned completely by 2D analysis supported by comparison to the spectra of mono- and dinuclear complexes published in the literature.[19a,20] On coordination, a significant shift of the proton resonances is observed. The A6/C6 protons are directed toward the shielding region of the central pyridine ring of the orthogonal neighboring ligand, resulting in some considerable upfield shielding of these protons (approximately 1.4 ppm). The shielding of the more remote A5/C5 protons (about 0.2 ppm) can be explained in a similar fashion.[20,23] As an example, the aromatic region of the ^{1}H NMR and the COSY ^{1}H NMR spectra of [(tpy)Ru(**38**)Ru(tpy)](PF$_6$)$_4$ is presented in Figure 1.

All complexes have been characterized additionally by mass spectrometry. They show the characteristic $[M - PF_6]^+$ peaks in their MALDI-TOF mass spectra, revealing successful coordination. No dissociation of the coordinative bonds has been observed during the laser desorption/ionization process, indicating high stability of these complexes. The representative spectra of complexes [(tpy)Ru(**38**)Ru(tpy)](PF$_6$)$_4$ and [(tpy)Ru(**42**)Ru(tpy)](PF$_6$)$_4$ are shown in Figure 2. The ESI spectra, as shown in the Supporting Information, are also in accordance with the assigned structures.

The IR vibration spectra are dominated by a strong band at around 850 cm^{-1} being characteristic for the hexafluorophosphate counterion.[19a] The other IR bands have been assigned to the vibrations of the respective bis(U-terpyridine) and 2,2′:6′,2″-terpyridine ligands.

Absorption Spectroscopy: In Table 2, the absorption maxima and corresponding intensities for the solutions of [(tpy)Ru(L)-Ru(tpy)](PF$_6$)$_4$ in MeCN are summarized. All complexes show a set of two distinct absorption bands at shorter wavelengths (270−310 nm, log ϵ = 4.3−5.1; Figure 3), which can be assigned to characteristic ligand-centered ^{1}LC transitions ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) in ruthenium−terpyridine complexes. This band is slightly shifted to a longer wavelength compared to those of complex [Ru(tpy)$_2$]$^{2+}$. This effect is due to the greater delocalization of the excited electron on the ligand bearing a conjugated moiety stabilizing the LUMO orbital (π^*).[19f] The less-intense band in the visible region (approximately 480 nm, log ϵ = 3.1−4.6)[19a] is due to the allowed metal to ligand charge-transfer transitions (^{1}MLCT), where an electron is promoted from the metal t_{2g} orbital to a π^* antibonding orbital of the ligand.[24] These transitions appear at lower energy as for the reference substrate [Ru(tpy)$_2$]$^{2+}$. The donor-effect of the substituents in 7-position lowers the energy gap between HOMO and LUMO orbitals of the parent complexes.[19]

Additionally, a band centered around 360 nm is present, which results from mixed ^{1}LC−^{1}MLCT transitions. The data

(20) (a) Encinas, S.; Flamigni, C.; Barigelletti, F.; Constable, E. C.; Housecroft, C. E.; Schofield, E. R.; Figgemeier, E.; Fenske, D.; Neuburger, M.; Vos, J. G.; Zehnder, M. *Chem.*−*Eur. J.* **2002**, *8*, 137−150. (b) Barbieri, A.; Ventura, B.; Barigeletti, F.; De Nicola, A.; Quesada, M.; Ziessel, R. *Inorg. Chem.* **2004**, *43*, 7359−7368. (c) Azhari, E.; Penaud-Berruyer, F.; Azhari, D.; Aït-Haddou, H.; Fontenas, C.; Bejan, E.; Daran, J.-C.; Balavoine, G. G. A. *New J. Chem.* **1998**, 373−380.

(21) (a) Sulliva, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404−1407. (b) Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1994**, 1409−1418.

(22) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chem.* **1995**, *34*, 2759−2767.

(23) Constable, E. C.; Cargill Thompson, A. M. W.; Tocher, D. A.; Daniels, M. A. M. *New J. Chem.* **1992**, *16*, 855.

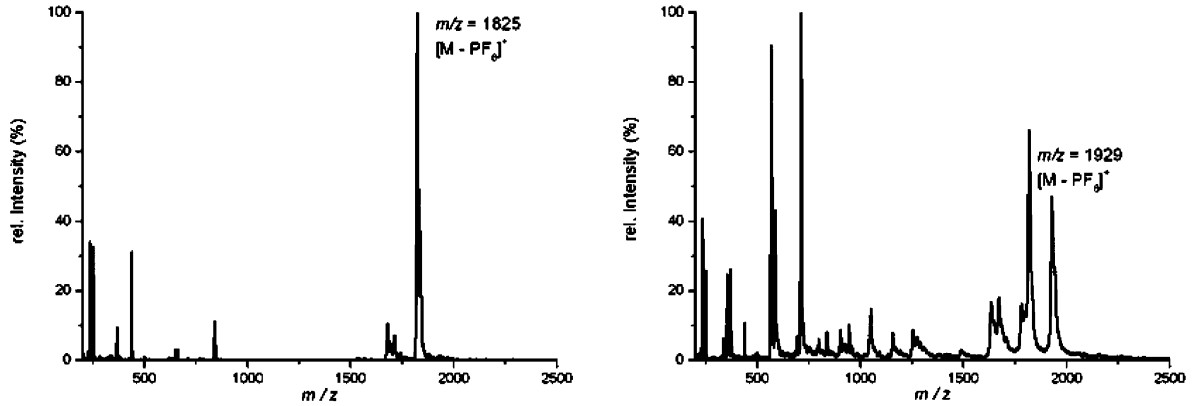


FIGURE 2. MALDI-TOF mass spectra of $[(tpy)Ru(L)Ru(tpy)](PF_6)_4$; L = **38** (left) and L = **42** (right).

TABLE 2. Absorption Data of Complexes in MeCN

complex	λ_{max} [nm] ($\epsilon \times 10^4$ [M^{-1} cm^{-1}])			
	^{1}LC		LC−^{1}MLCT	^{1}MLCT
$[Ru(tpy)]^{2+}$ (ref 2l)	272 (2.8)	307 (5.2)		475 (1.3)
$[(tpy)Ru(\mathbf{3a})]^{2+}$ [a]	269 (2.1)	311 (4.8)		477 (1.2)
$[(tpy)Ru(\mathbf{3b})]^{2+}$ [a]	273 (3.6)	309 (5.1)		481 (1.9)
$[(tpy)Ru(\mathbf{34})Ru(tpy)]^{4+}$	271 (3.5)	308 (4.8)	359 (1.7)	477 (1.7)
$[(tpy)Ru(\mathbf{35})Ru(tpy)]^{4+}$	269 (4.8)	309 (7.4)	358 (2.2)	480 (1.9)
$[(tpy)Ru(\mathbf{36})Ru(tpy)]^{4+}$	268 (3.9)	308 (6.7)	358 (1.9)	481 (1.7)
$[(tpy)Ru(\mathbf{37})Ru(tpy)]^{4+}$	269 (4.5)	310 (7.2)	357 (2.3)	483 (2.1)
$[(tpy)Ru(\mathbf{38})Ru(tpy)]^{4+}$	270 (5.2)	309 (8.9)	359 (2.8)	482 (2.3)
$[(tpy)Ru(\mathbf{39})Ru(tpy)]^{4+}$	269 (5.7)	310 (7.9)	357 (3.0)	479 (2.8)
$[(tpy)Ru(\mathbf{40})Ru(tpy)]^{4+}$	270 (7.5)	308 (12.3)	359 (3.3)	478 (3.1)
$[(tpy)Ru(\mathbf{41})Ru(tpy)]^{4+}$	271 (5.6)	309 (8.4)	357 (2.5)	479 (2.1)
$[(tpy)Ru(\mathbf{42})Ru(tpy)]^{4+}$	271 (6.6)	309 (10.8)	359 (3.7)	478 (2.8)
$[(tpy)Ru(\mathbf{43})Ru(tpy)]^{4+}$	272 (8.1)	310 (13.6)	358 (5.3)	480 (3.9)
$[\{(tpy)Ru\}_3(\mathbf{47})]^{6+}$	269 (6.1)	311 (9.6)	357 (4.2)	483 (2.5)

[a] **3a**: R^1 = Ph;[26] **3b**: R^1 = thiophene-2-yl.[26]

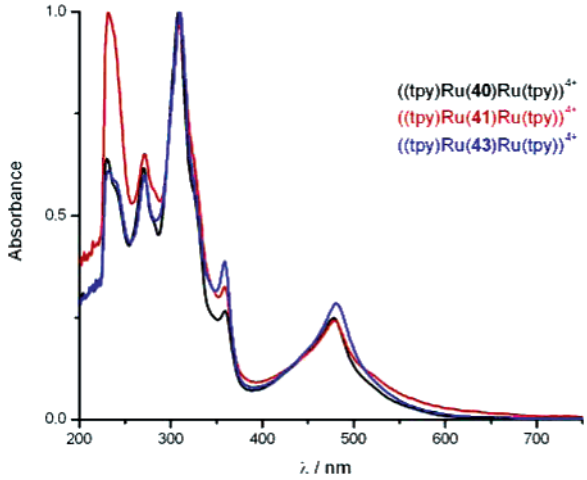


FIGURE 3. Absorption spectra of the dinuclear complexes $[(tpy)Ru(\mathbf{40})Ru(tpy)]^{4+}$, $[(tpy)Ru(\mathbf{41})Ru(tpy)]^{4+}$, and $[(tpy)Ru(\mathbf{43})Ru(tpy)]^{4+}$. All solutions are 10^{-5} M in CH_3CN at 25 °C.

reveal that on passing from the mononuclear to the dinuclear complexes the bands become more intense, on the other hand, no significant shift of the absorption bands can be observed. This indicates that the ^{1}MLCT levels are equal in energy for both types of complexes. Therefore, from a spectroscopic point of view, the coordinated metal centers have to be described as electronically isolated chromophores.[25]

Emission Spectroscopy: It is known from the literature that $[Ru(tpy)2]^{2+}$ only shows weak emission at room temperature.[22]

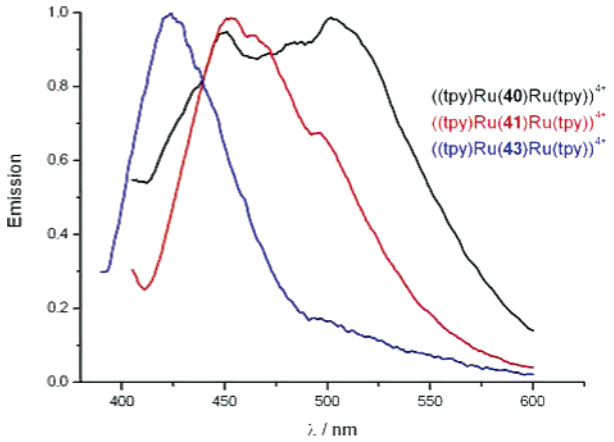


FIGURE 4. Emission spectra of the dinuclear complexes $[(tpy)Ru(\mathbf{40})Ru(tpy)]^{4+}$, $[(tpy)Ru(\mathbf{41})Ru(tpy)]^{4+}$, and $[(tpy)Ru(\mathbf{43})Ru(tpy)]^{4+}$. All solutions are 10^{-5} M in CH_3CN at 25 °C.

Upon functionalization with electron-donating groups at the central pyridine ring, the corresponding Ru(II) complexes become more luminescent at room temperature. In Figure 4 the emission properties of some selected complexes $[(tpy)Ru(L)Ru(tpy)](PF_6)_4$ in dilute MeCN solution are shown. Excitation of the compounds at 340 nm reveals broad emission bands for the solutions that are basically derived from ^{1}MLCT transitions.[20a,c] For all complexes, an unstructured band with a maximum between 400 and 500 nm is revealed upon excitation at 340 nm. These maxima are shifted significantly in comparison to those of the reference complex $[Ru(tpy)_2]^{2+}$ for which the emission maximum is observed at about 360 nm.[19f,20a] The strongest effect is observed for the thienyl-bridged complex (L

(24) (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (b) Juris, A.; Balzani, V.; Barigeletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (c) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (d) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrine Complexes*; Academic Press: London, 1991. (e) Ziessel, R. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer: Dordrecht, The Netherlands, 1993. (f) Schanze, K. S.; MacQeen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63. (g) Didier, P.; Ortmans, I.; Kirsch-De Mesmaeker, A.; Watts, R. *Inorg. Chem.* **1993**, *32*, 5239. (h) Nallas, G. N. A.; Jones, S. W.; Brewer, K. J. *Inorg. Chem.* **1996**, *25*, 6974. (i) Bignozzi, C. A.; Schoonover, J. N.; Scandola, F. *Prog. Inorg. Chem.* **1997**, *44*, 1.

(25) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, 1991.

(26) Winter, A. Oligotope Ligands and Nicotinonitriles—Modern Applications of the Mannich reaction in the Synthesis of Pyridine Derivatives. Ph.D. Thesis, Paderborn University, 2003.

TABLE 3. Emission Data of Complexes in MeCN (Room Temperature)

complex	$\lambda_{max,em}$ [nm]	complex	$\lambda_{max,em}$ [nm]
$[Ru(tpy)]^{2+}$ (ref 20a)	357	$[(tpy)Ru(\mathbf{39})Ru(tpy)]^{4+}$	385
$[(tpy)Ru(\mathbf{34})Ru(tpy)]^{4+}$	368	$[(tpy)Ru(\mathbf{40})Ru(tpy)]^{4+}$	500
$[(tpy)Ru(\mathbf{35})Ru(tpy)]^{4+}$	380	$[(tpy)Ru(\mathbf{41})Ru(tpy)]^{4+}$	451
$[(tpy)Ru(\mathbf{36})Ru(tpy)]^{4+}$	382	$[(tpy)Ru(\mathbf{42})Ru(tpy)]^{4+}$	397
$[(tpy)Ru(\mathbf{37})Ru(tpy)]^{4+}$	379	$[(tpy)Ru(\mathbf{43})Ru(tpy)]^{4+}$	423
$[(tpy)Ru(\mathbf{38})Ru(tpy)]^{4+}$	380	$[\{(tpy)Ru\}_3(\mathbf{47})]^{6+}$	386

TABLE 4. Electrochemical Data for Complexes in MeCN[a]

	$E_{1/2}$ [V]		
complex	oxidation	reduction	
$[Ru(tpy)]^{2+}$ (ref 18b)	+1.20	−0.96	−1.49
$[(tpy)Ru(\mathbf{3a})]^{2+}$ [b]	+1.25	−1.21	−1.46
$[(tpy)Ru(\mathbf{3b})]^{2+}$ [b]	+1.19	−1.33	−1.73
$[(tpy)Ru(\mathbf{34})Ru(tpy)]^{4+}$	+1.22	−1.26	−1.48
$[(tpy)Ru(\mathbf{35})Ru(tpy)]^{4+}$	+1.27	−1.22	−1.46
$[(tpy)Ru(\mathbf{36})Ru(tpy)]^{4+}$	+1.25	−1.23	−1.45
$[(tpy)Ru(\mathbf{37})Ru(tpy)]^{4+}$	+1.21	−1.24	−1.47
$[(tpy)Ru(\mathbf{38})Ru(tpy)]^{4+}$	+1.26	−1.23	−1.46
$[(tpy)Ru(\mathbf{39})Ru(tpy)]^{4+}$	+1.25	−1.25	−1.45
$[(tpy)Ru(\mathbf{40})Ru(tpy)]^{4+}$	+1.18	−1.35	−1.71
$[(tpy)Ru(\mathbf{41})Ru(tpy)]^{4+}$	+1.20	−1.28	−1.51
$[(tpy)Ru(\mathbf{42})Ru(tpy)]^{4+}$	+1.26[c]	−1.32	−1.49
$[(tpy)Ru(\mathbf{43})Ru(tpy)]^{4+}$	+1.24	−1.29	−1.46
$[\{(tpy)Ru\}_3(\mathbf{47})]^{6+}$	+1.25	−1.26	−1.46

[a] [*n*-Bu_4N](BF_4) as the supporting electrolyte; potentials in *V* vs Fc^+/Fc. All solutions are 10^{-5} M in CH_3CN at 25 °C. [b] **3a**: R^1 = Ph;[25] **3b**: R^1 = thiophene-2-yl.[25] [c] Oxidation of the amino group interferes with this process.

= **40**) and the naphthyl-bridged analogue (L = **41**), with the emission maxima occurring at 500 and 451 nm, respectively. As summarized in Table 3, only slight differences for the position of the emission maximum for the oligophenyl-bridged derivatives (L = **35**−**39**) can be observed, indicating the minor influence of the length and substitution pattern of the corresponding spacer units. Our first results indicate that the di- and trinuclear Ru(II) complexes derived from oligo(U-terpyridines) are promising structures with respect to potential photophysical applications.

Electrochemistry: The electrochemical data obtained are reported in Table 4 (potentials vs Fc^+/Fc). The electrochemical behavior is well-documented for both mono- and dinuclear ruthenium complexes and is explained in terms of localized metal- and ligand-centered processes.[24] This general approach has been put to use in the present cases.

All ruthenium complexes exhibit a single one-electron reversible wave for the Ru(II)/Ru(III) oxidation in the range 1.20−1.30 V, which is shifted to a more positive potential than what is observed for $[Ru(tpy)_2]^{2+}$ (1.18 V).[19b] The data comply with those obtained for analogous structures known to the literature.[19c,e,27] The electronic influence of the aromatic substituents results in the metal centers being more resistant to oxidation.[28] The observed potentials for the metal-centered oxidation do not change significantly on passing from mononuclear to dinuclear species. The presence of a single oxidative process within the solvent window at any scan rate supports the conclusion that the metal centers in each complex are identical and, more importantly, noninteracting. If there were significant interactions between the metal centers, then the oxidation of the *first* ruthenium center would affect the potential at which the other centers in the complex are oxidized.[18a,27] In other words, in electronic terms, the bridging ligands L effectively behave as simple aryl-substituted U-terpyridines, and there is no electronic interaction between the U-terpyridyl substituents or the metals coordinated to them.

In all cases, two reduction waves in the region of (−)1.2−(−)1.3 V and (−)1.45−(−)1.6 V, corresponding to the Ru(II)/Ru(I) and Ru(I)/Ru(0) couples, respectively, are also observed.[28,29] Generally, the first reduction is shifted by 0.2 V to a more negative potential compared to that of $[(tpy_2)Ru]^{2+}$, which can be explained by the high electron density caused by the rigid ligands L.[19b] The reductive behavior of the thienyl-bridged complex (L = **40**) is complicated by irreproducible processes between 0.6 and 0.8 V associated with surface binding to the electrodes.[20]

Conclusion

The novel oligo(U-terpyridines) **34**−**43** and **47** presented in this paper have been synthesized by a highly efficient domino reaction sequence, introducing iminium salts **24**−**33** and **46** as key building blocks. This extension of prior work is well suited for the design of bridged terpyridine ligands with highly variable spacer properties. In regard to potential applications in the fields of molecular devices, a set of di- and trinuclear ruthenium(II) complexes have been synthesized, and their electronic and electrochemical behaviors have been investigated. These complexes have been found to be light-emitting upon excitation at 340 nm, with broad emission maxima between 400 and 500 nm. Thus, no metal−metal interaction along the molecular axis could be observed so far. Our strategy promises to be a valuable approach toward the synthesis of ligands capable of transporting energy over large distances on a molecular scale and for use in photophysical applications.

Experimental Section

General. All reagents were purchased from commercial sources and used without prior purification unless specified. All solvents were dried and distilled according to standard procedures and stored under argon. All reactions were conducted under argon. 5,6,7,8-Tetrahydroquinolinone **1**[30] and aldehydes **7**−**13**[31] and **44**[32] were prepared by procedures described in the literature. Chromatographic separation was performed on neutral aluminum oxide. ^1H and ^{13}C NMR (500 and 125 MHz, respectively) were obtained in $CDCl_3$

(27) Collin, J.-P.; Laine, P.; Sauvage, J.-P., Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434−435.

(28) Elliot, C. M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519.

(29) (a) Balzani, V.; De Cola, L.; Barigeletti, F. *Top. Curr. Chem.* **1990**, *158*, 31−71. (b) Grosshenny, V.; Ziessel, R. *Tetrahedron Lett.* **1992**, *33*, 8075−8078. (c) Arana, C.; Yan, S.; Keshavarz-K., M.; Potts, K. T.; Abruña, H. D. *Inorg. Chem.* **1992**, *31*, 3680−3682. (d) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248−4253.

(30) (a) Crabb, T. A.; Turner, C. H. *J. Chem. Soc, Perkin Trans. 1* **1980**, 1778−1782. (b) Thummel, R. P.; Lefoulon, F.; Cantu, D.; Mahadevan, R. *J. Org. Chem.* **1984**, *49*, 2208−2212.

(31) (a) Helm, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6227−6238. (b) Lourak, M.; Vanderesse, R.; Fort, Y.; Caubere, P. *J. Org. Chem.* **1989**, *54*, 4840−4844. (c) Feringa, B. L.; Hulst, R.; Rikers, R.; Brandsma, L. *Synthesis* **1988**, 316−318. (d) Hagiya, K.; Mitsui, S.; Taguchi, H. *Synthesis* **2003**, 823−828. (e) Katritzky, A. R.; Belyakov, S. A.; Denisko, O. V.; Maran, U.; Dalal, N. S. *J. Chem. Soc., Perkin Trans. 2* **1998**, 611−616. (f) Mayence, A.; Eynde, J. J. V.; Krogstad, F. M.; Krogstad, D. J.; Cushion, M. T.; Huang, T. L. *J. Med. Chem.* **2004**, *47*, 2700−2705.

(32) Weber, E.; Hecker, M.; Koepp, E.; Orlia, W.; Czugler, M.; Csoeregh, I. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1251−1258.

(unless otherwise stated) with TMS as internal standard. Mass spectroscopy was carried out by electron impact (EI, 70 eV), matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF, matrix substance DCTB), and electrospray ionization (ESI) techniques. UV/vis and emission spectra were measured at 298 K in outgassed CH_3CN.

General Procedure for the Synthesis of Aminals 14−23 and 45. A mixture of an aromatic dialdehyde (0.1 mol) and morpholine (35.7 mL, 0.41 mol) was stirred for 12 h at room temperature. The solid so obtained was recrystallized from Et_2O.[15]

1,1,2,2-Tetramorpholinoethane (14). Reaction of glyoxal **4** (23 mL, 40% aq solution, 0.2 mol) and morpholine (70 mL, 0.8 mol) afforded 56.3 g (76%) as a yellow powder: mp 109 °C (lit.[33] mp 112 °C) after recrystallization from Et_2O; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.26 (s, 2H), 3.51−3.64 (m, 16H), 2.37−2.41 (m, 16H).

1,4-Bis(dimorpholinomethyl)benzene (15). Reaction of terephthaldehyde **5** (26.8 g, 0.2 mol) and morpholine (70 mL, 0.8 mol) afforded 74.1 g (83%) as a pale yellow powder: mp 214 °C (lit.[34] mp 216 °C) after recrystallization from Et_2O; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 4H), 3.52−3.66 (m, 18H), 2.35−2.46 (m, 16H).

1,3-Bis(dimorpholinomethyl)benzene (16). Reaction of isophthaldehyde **6** (6.7 g, 0.05 mol) and morpholine (10.5 mL, 0.12 mol) afforded 19.4 g (87%) as a yellow powder: mp 198 °C after recrystallization from Et_2O; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91−7.13 (m, 4H), 3.57−3.65 (m, 16H), 3.55 (s, 2H), 2.38−2.46 (m, 16H).

4,4′-Bis(dimorpholinomethyl)biphenyl (17). Reaction of 4,4′-diformylbiphenyl **7** (8.4 g, 0.04 mol) and morpholine (10.5 mL, 0.12 mol) afforded 20.1 g (96%) of a pale yellow powder: mp > 250 °C after recrystallization from Et_2O; IR (KBr) ν 2959, 2805, 1492, 1452, 1394, 1301, 1290, 1207, 1138, 1016, 1001, 876; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, ^3J = 8.3 Hz, 4H), 7.14 (d, ^3J = 8.3 Hz, 4H), 3.54−3.72 (m, 18H), 2.37−2.48 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 134.9, 129.2, 127.1, 89.3, 67.7, 50.4; EI-MS (70 eV) *m*/*z* 522 (3, M^+), 435 (100), 349 (49), 292 (26), 277 (22), 175 (71). Anal. Calcd for $C_{30}H_{42}N_4O_4$ (522.7): C, 68.94; H, 8.10; N, 10.72. Found: C, 69.01; H, 8.07; N, 10.75.

3,3′-Bis(dimorpholinomethyl)biphenyl (18). Reaction of 3,3′-diformylbiphenyl **8** (3.0 g, 14 mmol) and morpholine (4.9 mL, 56 mmol) afforded 6.9 g (95%) of a colorless powder: mp 231 °C after recrystallization from Et_2O; IR (KBr) ν 2976, 2856, 2821, 1475, 1348, 1270, 1205, 1141, 1114, 1018, 869, 756; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.51 (m, 6H), 7.16−7.22 (m, 2H), 3.62−3.75 (m, 18H), 2.37−2.45 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 135.0, 128.6, 127.9, 127.2, 89.5, 67.6, 50.0; EI-MS (70 eV) *m*/*z* 436 (9), 211 (15), 88 (100), 57 (98). Anal. Calcd for $C_{30}H_{42}N_4O_4$ (522.7): C, 68.94; H, 8.10; N, 10.72. Found: C, 68.89; H, 8.15; N, 10.68.

4,4″-Bis(dimorpholinomethyl)-*p*-terphenyl (19). Reaction of 4,4″-diformyl-*p*-terphenyl **9** (14.3 g, 50 mmol) and morpholine (17.5 mL, 0.2 mol) afforded 26.3 g (88%) of a pale yellow powder: mp > 250 °C after recrystallization from EtOH; IR (KBr) ν 2954, 2854, 2813, 1701, 1602, 1484, 1398, 1274, 1105, 1016, 877, 821, 765; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 4H), 7.36 (d, ^3J = 8.4 Hz, 4H), 7.22 (d, ^3J = 8.4 Hz, 4H), 3.83 (s, 2H), 3.59−3.72 (m, 16H), 2.35−2.46 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 140.1, 133.6, 129.7, 127.8, 127.4, 89.2, 67.6, 50.0; EI-MS (70 eV) *m*/*z* 327 (68), 267 (55), 242 (100), 87 (36). Anal. Calcd for $C_{36}H_{46}N_4O_4$ (598.8): C, 72.21; H, 7.74; N, 9.36. Found: C, 72.25; H, 7.70; N, 9.41.

2,5-Bis(dimorpholinomethyl)thiophene (20). Reaction of 2,5-thiophenedicarbaldehyde **10** (0.5 g, 3.57 mmol) and morpholine (0.62 mL, 7.14 mmol) afforded 1.58 g (98%) of a yellow powder: mp 203 °C after recrystallization from Et_2O; IR (KBr) ν 2951, 2915, 2881, 2855, 2800, 1735, 1466, 1442, 1397, 1278, 1143, 1023, 914; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (s, 2H), 3.92 (s, 2H), 3.67−3.75 (m, 16H), 2.46−2.56 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 125.9, 88.2, 66.9, 50.2. Anal. Calcd for $C_{22}H_{36}N_4O_4S$ (452.6): C, 58.38; H, 8.02; N, 12.38. Found: C, 58.32; H, 7.97; N, 12.36.

2,6-Bis(dimorpholinomethyl)naphthalene (21). Reaction of 2,6-diformylnaphthalene **11** (4.2 g, 22.6 mmol) and morpholine (8 mL, 91 mmol) afforded 7.73 g (69%) of a yellow powder: mp > 250 °C after recrystallization from EtOH; IR (KBr) ν 2956, 2910, 2884, 2848, 2821, 2796, 1724, 1450, 1392, 1303, 1290, 1272, 1137, 1110, 1016, 867; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80−8.17 (m, 4H), 7.38−7.60 (m, 2H), 4.02 (s, 2H), 3.71−3.84 (m, 16H), 2.40−2.65 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.3, 133.1, 132.7, 129.5, 125.9, 123.5, 89.6, 67.9, 52.7. Anal. Calcd for $C_{28}H_{40}N_4O_4$ (496.6): C, 67.71; H, 8.12; N, 11.28. Found: C, 67.67; H, 8.01; N, 11.20.

1,5-Bis-(4-dimorpholinomethylphenoxy)-3-oxopentane (22). Reaction of 1,5-(di-(4-formyl-phenoxy)-3-oxopentane **12** (31.44 g, 0.1 mol) and morpholine (35 mL, 0.4 mol) afforded 47.02 g (75%) of a yellow powder: mp 223 °C after recrystallization from Et_2O; IR (KBr) ν 2944, 2835, 2815, 1526, 1412, 1272, 1251, 1155, 1106, 1023; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, ^3J = 8.2 Hz, 4H), 6.91 (d, ^3J = 8.2 Hz, 4H), 4.11−4.24 (m, 4H), 3.90−4.02 (m, 4H), 3.64−3.76 (m, 16H), 3.61 (s, 2H), 2.33−2.55 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 130.3, 126.9, 114.2, 88.9, 70.3, 68.3, 67.6, 49.9. Anal. Calcd for $C_{34}H_{50}N_4O_7$ (626.8): C, 65.51; H, 8.04; N, 8.94. Found: C, 65.44; H, 8.08; N, 8.89.

***N*,*N*′-Bis(4-dimorpholinophenyl)piperazine (23).** Reaction of *N*,*N*′-di(4-formylphenyl)piperazine **13** (29.43 g, 0.1 mol) and morpholine (35 mL, 0.4 mol) afforded 50.97 g (84%) of an orange powder: mp 209 °C after recrystallization from Et_2O; IR (KBr) ν 2933, 2811, 2795, 1510, 1460, 1233, 1150, 1090, 1023, 876; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (d, ^3J = 7.9 Hz, 4H), 6.89 (d, ^3J = 7.9 Hz, 4H), 3.52−3.73 (m, 26H), 2.31−2.49 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 130.1, 128.8, 116.9, 88.6, 68.4, 50.1, 49.3. Anal. Calcd for $C_{34}H_{50}N_6O_4$ (606.8): C, 67.30; H, 8.31; N, 13.85. Found: C, 67.25; H, 8.22; N, 13.94.

1,3,5-Tris(4′,4″,4‴-bismorpholinomethylphenyl)benzene (45). Reaction of 1,3,5-tris(4′,4″,4‴-formylphenyl)benzene **44** (1.42 g, 3.6 mmol) and morpholine (1.9 mL, 21.6 mmol) afforded 3.01 g (97%) of a yellow powder: mp 250 °C after recrystallization from Et_2O; IR (KBr) ν 2952, 2848, 2807, 1504, 1452, 1394, 1270, 1139, 1114, 1016, 875; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 3H), 7.72 (d, ^3J = 8.0 Hz, 6H), 7.34 (d, ^3J = 8 Hz, 6H), 3.59−3.73 (m, 27H), 2.39−2.52 (m, 24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 141.0, 133.9, 129.7, 127.2, 125.4, 89.2, 67.6, 50.0. Anal. Calcd for $C_{51}H_{66}N_6O_6$ (859.1): C, 71.30; H, 7.74; N, 9.78. Found: C, 71.26; H, 7.78; N, 9.83.

General Procedure for the Synthesis of Iminium Salts 24−33 and 46. A solution of acetyl chloride (1 equiv per aminal group) in absolute Et_2O (25 mL) was added slowly to a suspension of an aminal (0.05 mol) in absolute Et_2O (150 mL) at 0 °C. The reaction mixture was then kept at room temperature for 12 h. The bisiminium salt was filtered off, washed rapidly with absolute Et_2O (50 mL), and dried in vacuo. Due to their hygroscopic nature and low solubility in organic solvents, bisiminium salts were used in the synthesis of U-terpyridines **34−43** and **47** without any further purification and characterization.[16]

General Procedure for the Synthesis of Bis(U-terpyridines) 34−43. A solution of 5,6,7,8-tetrahydroquinolinone **1** (6 mmol) and ammonium acetate (6.1 mmol) in dry DMSO (15 mL) was heated for 5 min at 85 °C. In a second flask, a suspension of **1** (6 mmol) and a bisiminium salt (3.05 mmol) in dry DMSO (10 mL) was heated until a clear solution was formed. The solution of the bisiminium salt and the ketone was then added to the first flask and heated at 150 °C for 16 h. The reaction mixture was cooled, and water (40 mL) was added. The solution was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with water (3 × 20 mL) and dried over $MgSO_4$. After removal of

(33) Duhamel, L.; Duhamel, P.; Plé, G. *C. R. Hebd. Seances Acad. Sci. Ser. C* **1970**, *271*, 751−753.

(34) Kerfanto, M. *Bull. Soc. Chim. Fr.* **1975**, 196−200.

the solvent, the residue was purified by chromatography on Al_2O_3 (elution with CH_2Cl_2/methanol, 50:1).[11l]

5,5′,6,6′,8,8′,9,9′-Octahydro-7,7′-biquino[8,7-*b*]-1,10-phenanthroline (34). Reaction of **1** (1.76 g, 12 mmol), ammonium acetate (0.5 g, 6.5 mmol), and **24** (0.82 g, 3.05 mmol) according to the predescribed protocol resulted in the isolation of 0.44 g (26%) as a brownish powder: mp > 270 °C after recrystallization from EtOAc; IR (KBr) ν 3028, 2935, 2883, 2829, 1563, 1442, 1400, 1225, 1176, 845, 778, 759; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (m, 4H), 7.18−7.39 (m, 8H), 2.88−3.09 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 152.1, 148.8, 147.5, 136.4, 136.3, 133.9, 123.9, 27.8, 27.6. Anal. Calcd for $C_{38}H_{28}N_6$ (568.67): C, 80.26; H, 4.96; N, 14.78. Found: C, 80.31; H, 5.02; N, 14.89.

1,4-Di-(5,6,8,9-tetrahydrochino[8,7-*b*][1,10]phenanthrolin-7-yl)benzene (35). Reaction of **1** (1.76 g, 12 mmol), ammonium acetate (0.5 g, 6.5 mmol), and **25** (1.05 g, 3.05 mmol) according to the predescribed protocol resulted in the isolation of 0.70 g (36%) as a brownish powder: mp > 270 °C (lit.[35] mp > 300 °C) after recrystallization from EtOH; IR (KBr) ν 3035, 2927, 2825, 1555, 1437, 1388, 1236, 1174, 853, 752; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76−8.85 (m, 4H), 7.51−7.58 (m, 4H), 7.33 (s, 4H), 7.16−7.24 (m, 4H), 2.93−3.09 (m, 8H), 2.74−2.89 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 150.9, 149.2, 147.5, 137.3, 136.0, 133.9, 132.6, 129.5, 124.0, 27.9, 25.9. Anal. Calcd for $C_{44}H_{32}N_6$ (644.77): C, 81.96; H, 5.00; N, 13.03. Found: C, 81.91; H, 5.07; N, 13.01.

1,3-Di-(5,6,8,9-tetrahydrochino[8,7-*b*][1,10]phenanthrolin-7-yl)benzene (36). Reaction of **1** (1.76 g, 12 mmol), ammonium acetate (0.5 g, 6.5 mmol), and **26** (1.05 g, 3.05) according to the predescribed protocol resulted in the isolation of 0.60 g (31%) as a brown powder: mp > 270 °C (lit.[35] mp > 300 °C) after recrystallization from EtOH; IR (KBr) ν 3031, 2931, 2846, 1549, 1432, 1377, 1234, 1167, 861, 759; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79−8.92 (m, 4H), 7.55−7.62 (m, 4H), 7.08−7.29 (m, 8H), 2.77−3.12 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 150.8, 149.1, 147.5, 138.8, 136.2, 133.7, 132.5, 129.1, 127.5, 125.3, 124.0, 27.8, 25.8. Anal. Calcd for $C_{44}H_{32}N_6$ (644.77): C, 81.96; H, 5.00; N, 13.03. Found: C, 82.03; H, 5.05; N, 13.10.

4,4′-Di-(5,6,8,9-tetrahydrochino[8,7-*b*][1,10]phenanthrolin-7-yl)biphenyl (37). Reaction of **1** (1.76 g, 12 mmol), ammonium acetate (0.5 g, 6.5 mmol), and **27** (1.29 g, 3.05 mmol) according to the predescribed protocol resulted in the isolation of 0.81 g (37%) as a brownish powder: mp > 270 °C after recrystallization from EtOH; IR (KBr) ν 2950, 2829, 1637, 1557, 1550, 1438, 1390, 1214, 1112, 815, 782, 615; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72−8.78 (m, 4H), 7.55−7. 62 (m, 4H), 7.03−7.28 (m, 12H), 2.97−3.06 (m, 8H), 2.81−2.92 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 153.1, 150.7, 140.5, 136.8, 136.3, 134.6, 132.9, 129.7, 124.0, 27.8, 25.8. Anal. Calcd for $C_{50}H_{36}N_6$ (720.9): C, 83.31; H, 5.03; N, 11.66. Found: C, 83.37; H, 5.08; N, 11.77.

3,3′-Di-(5,6,8,9-tetrahydrochino[8,7-*b*][1,10]phenanthrolin-7-yl)biphenyl (38). Reaction of **1** (1.76 g, 12 mmol), ammonium acetate (0.5 g, 6.5 mmol), and **28** (1.29 g, 3.05 mmol) according to the predescribed protocol resulted in the isolation of 0.91 g (42%) as a brownish powder: mp > 270 °C after recrystallization from EtOH; IR (KBr) ν 2933, 2817, 1625, 1555, 1431, 1375, 1222, 1116, 819, 781, 615; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75−8.81 (m, 4H), 7.47−7.58 (m, 6H), 7.28−7.37 (m, 6H), 7.05−7.09 (m, 4H), 2.79−2.93 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 153.8, 150.2, 148.7, 138.1, 137.4, 136.5, 136.1, 133.0, 129.6, 127.5, 125.8, 124.9, 123.7, 27.6, 25.8. Anal. Calcd for $C_{50}H_{36}N_6$ (720.9): C, 83.31; H, 5.03; N, 11.66. Found: C, 83.27; H, 4.99; N, 11.58.

4,4″-Di-(5,6,8,9-tetrahydrochino[8,7-*b*][1,10]phenanthrolin-7-yl)-[1,1′;4′,1″]terphenyl (39). Reaction of **1** (1.76 g, 12 mmol), ammonium acetate (0.5 g, 6.5 mmol), and **29** (1.52 g, 3.05 mmol) according to the predescribed protocol resulted in the isolation of 0.98 g (41%) as a brownish powder: mp > 270 °C (lit.[11m] mp > 250 °C) after recrystallization from EtOH; IR (KBr) ν 2935, 2812, 1631, 1549, 1441, 1370, 1199, 1108, 777; ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD, 20:1) δ 8.52 (d, ^3J = 4.7 Hz, 4H), 7.79−7.84 (m, 4H), 7.57−7.63 (m, 4H), 7.21−7.35 (m, 12H), 2.89−2.92 (m, 8H), 2.75−2.83 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD, 20:1) δ 152.1, 150.3, 148.5, 140.7, 136.6, 136.3, 129.5, 128.0, 127.9, 124.3, 27.6, 25.6. Anal. Calcd for $C_{50}H_{36}N_6$ (767.0): C, 84.40; H, 5.06; N, 10.55. Found: C, 84.36; H, 5.01; N, 10.44.

2,5-Di-(5,6,8,9-tetrahydrochino[8,7-*b*][1,10]phenanthrolin-7-yl)thiophene (40). Reaction of **1** (1.17 g, 8 mmol), ammonium acetate (0.63 g, 8.2 mmol), and **30** (1.30 g, 3.7 mmol) according to the predescribed protocol resulted in the isolation of 0.92 g (38%) as a brownish powder: mp > 270 °C after recrystallization from EtOH; IR (KBr) ν 2959, 2802, 1633, 1512, 1444, 1120, 1023, 765, 649; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65−8.69 (m, 2H), 7.10−7.75 (m, 10H), 2.89−3.00 (m, 2H), 2.70−2.88 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 150.6, 147.1, 142.8, 135.6, 132.4, 131.9, 126.9, 121.6, 28.1, 25.9. Anal. Calcd for $C_{42}H_{30}N_6S$ (650.8): C, 77.51; H, 4.56; N, 12.91. Found: C, 77.49; H, 4.61; N, 12.88.

2,6-Di-(5,6,8,9-tetrahydrochino[8,7-*b*][1,10]phenanthrolin-7-yl)naphthalene (41). Reaction of **1** (1.17 g, 8 mmol), ammonium acetate (0.63 g, 8.2 mmol), and **31** (1.62 g, 3.7 mmol) according to the predescribed protocol resulted in the isolation of 1.81 g (63%) as a brown solid: mp > 270 °C after recrystallization from EtOH; IR (KBr) ν 3052, 2940, 2836, 1721, 1575, 1550, 1438, 1390, 1280, 1249, 1214, 815, 779, 757, 715, 657, 480; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76−8.87 (m, 4H), 8.07−8.12 (m, 2H), 7.57−7.69 (m, 4H), 7.35−7.51 (m, 8H), 2.90−3.08 (m, 8H), 2.68−2.90 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 149.7. 149.4, 147.6, 137.3, 136.5, 135.2, 132.7, 131.0, 130.0, 128.8. 128.4, 128.2, 123.9, 27.2, 25.1. Anal. Calcd for $C_{48}H_{34}N_6$ (694.8): C, 82.97; H, 4.93; N, 12.10. Found: C, 82.91; H, 4.88; N, 12.21.

[4,4′-Di-(5,6,8,9-tetrahydrochino[8,7-b][1,10]phenanthrolin-7-yl)-1,7-diphenyl]-1,4,7-trioxaheptan (42). Reaction of **1** (1.17 g, 8 mmol), ammonium acetate (0.63 g, 8.2 mmol), and **32** (1.87 g, 4.1 mmol) according to the predescribed protocol resulted in the isolation of 0.92 g (29%) as a brown powder: mp > 270 °C after recrystallization from EtOH; IR (KBr) ν 3288, 3052, 2929, 2877, 2836, 1662, 1606, 1509, 1438, 1388, 1243, 1220, 1110, 842, 815, 777, 613, 530; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69−8.70 (m, 4H), 7.49−7.65 (m, 4H), 7.19−7.31 (m, 4H), 6.90−7.12 (m, 8H), 4.19−4.38 (m, 4H), 3.97−4.10 (m, 4H), 2.62−2.90 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 152.8, 151.1, 149.3, 147.7, 135.5, 133.5, 133.0, 130.3, 129.8, 123.5, 115.2, 70.3, 67.7, 27.8, 25.9. Anal. Calcd for $C_{54}H_{44}N_6O_3$ (825.1): C, 78.62; H, 5.38; N, 10.19. Found: C, 78.59; H, 5.32; N, 10.18.

4,4′-Di-(5,6,8,9-tetrahydrochino[8,7-*b*][1,10]phenanthrolin-7-yl)-*N*,*N*′-diphenylpiperazine (43). Reaction of **1** (1.17 g, 8 mmol), ammonium acetate (0.63 g, 8.2 mmol), and **33** (2.07 g, 4.1 mmol) according to the predescribed protocol resulted in the isolation of 0.73 g (22%) as a brown solid: mp > 270 °C after recrystallization from EtOH; IR (KBr) ν 3290, 3052, 3002, 2937, 2834, 1662, 1643, 1608, 1575, 1515, 1440, 1388, 1222, 1186, 1110, 1000, 815, 781, 707, 661, 615; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61−8.77 (m, 4H), 7.58−7.66 (m, 8H), 7.37−7.48 (m, 8H), 7.21−7.28 (m, 4H), 3.63−3.73 (m, 8H), 2.88−2.97 (m, 8H), 2.74−2.85 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 152.8, 152.2, 150.8, 148.6, 147.4, 147.1, 135.1, 129.6, 128.1, 123.6, 123.2, 46.7, 40.0, 27.8, 25.9. Anal. Calcd for $C_{54}H_{44}N_8$ (805.0): C, 80.57; H, 5.51; N, 13.92. Found: C, 80.55; H, 5.49; N, 13.96.

1,3,5-Tris-[(5,6,8,9-tetrahydroquino[8,7-b][1,10]phenantrolin-7-yl]phenyl]benzene (47). Reaction of **1** (1.76 g, 12 mmol), ammonium acetate (0.94 g, 12.2 mmol), and **46** (1.41 g, 2 mmol) according to the predescribed protocol resulted in the isolation of 0.58 g (25%) as a brown solid: mp > 270 °C after recrystallization from EtOH; IR (KBr) ν 2935, 2883, 2806, 1564, 1440, 1222, 1176, 820, 789, 705 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71−8.85

(35) Hegde, V.; Jahng, Y.; Thummel, R. P. *Tetrahedron Lett.* **1987**, *28*, 4023−4026.

(m, 6H), 7.48−7.62 (m, 21H), 7.05−7.11 (m, 4H), 2.76−2.95 (m, 24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 152.6, 150.7, 147.3, 136.2, 135.8, 134.2, 133.3, 133.0, 132.2, 131.6, 128.4, 127.9, 125.2, 122.5, 35.3, 26.4. Anal. Calcd for $C_{81}H_{57}N_9$ (1156.4): C, 84.13; H, 4.97; N, 10.90. Found: C, 84.05; H, 5.03; N, 10.92.

Synthesis of [(tpy)RuCl$_3$]. A mixture of $RuCl_3 \cdot H_2O$ (262 mg, 1 mmol) and 2,2′:6′,2″-terpyridine (234 mg, 1 mmol) in absolute ethanol (125 mL) was heated at reflux for 3 h. After this time, the reaction was cooled to room temperature and the fine brown powder was filtered off. The product was washed with ethanol (3 × 25 mL) and Et_2O (3 × 25 mL) and dried in vacuo to give 440 mg (88%) of [(tpy)$RuCl_3$].[21]

General Procedure for the Synthesis of Complexes [(tpy)Ru(L)Ru(tpy)](PF$_6$)$_4$. A mixture of the bis(U-terpyridine) (0.1 mmol), [(tpy)$RuCl_3$] (0.2 mmol), and *N*-ethylmorpholine in ethanol (7 mL) was heated at reflux for 24 h. After cooling to room temperature, the mixture was filtered to remove the remainder of the unreacted ligand. The filtrate was then treated with an excess of NH_4PF_6 (150 mg). The red-orange solid was isolated and purified by recrystallization from toluene/acetonitrile (1:1) and/or flash column chromatography on Al_2O_3 using the same solvents.[22]

[(tpy)Ru(34)Ru(tpy)](PF$_6$)$_4$. Reaction of **34** (114 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 287 mg (79%) as a red solid. IR (KBr) ν 3653, 3586, 3098, 2992, 2835, 1607, 1453, 1418, 1234, 850, 762 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.75 (d, ^3J = 7.9 Hz, 4H, B3/5), 8.51−8.55 (m, 4H, A3), 8.42−8.47 (m, 2H, B4), 8.01−8.06 (m, 4H, A4), 7.63−7.77 (m, 8H, A6/C4), 7.19−7.25 (m, 4H, A5), 7.01−7.14 (m, 4H, C6), 6.79−6.98 (m, 4H, C5), 3.11−3.41 (m, 16H); UV/vis λ_{max} (ϵ) 477 (17 320), 359 (16 980), 308 (48 250), 271 (35 130); MALDI-TOF MS *m*/*z* 1673 [M − PF$_6$]$^+$. Anal. Calcd for $C_{68}H_{50}F_{24}N_{12}P_4Ru_2$ (1817.2): C, 44.94; H, 2.77; N, 9.25. Found: C, 45.07; H, 2.81; N, 9.33.

[(tpy)Ru(35)Ru(tpy)](PF$_6$)$_4$. Reaction of **35** (129 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 352 mg (93%) as a red solid. IR (KBr) ν 3644, 3591, 3081, 2955, 1621, 1432, 1408, 1214, 851, 766 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.76 (d, ^3J = 8.1 Hz, 4H, B3/5), 8.49−8.53 (m, 4H, A3), 8.33−8.41 (m, 2H, B4), 7.95−8.04 (m, 4H, A4), 7.52 (s, 4H), 7.51−7.66 (m, 8H, A6/C4), 7.17−7.21 (m, 4H, A5), 6.99−7.15 (m, 4H, C6), 6.81−6.95 (m, 4H, C5), 3.09−3.39 (m, 16H); UV/vis λ_{max} (ϵ) 480 (19 050), 358 (22 300), 309 (74 020), 269 (48 210); MALDI-TOF MS *m*/*z* 1749 [M − PF$_6$]$^+$, 802 [M − 2 PF$_6$]$^{2+}$. Anal. Calcd for $C_{74}H_{54}F_{24}N_{12}P_4Ru_2$ (1893.3): C, 46.94; H, 2.87; N, 8.88. Found: C, 46.87; H, 2.81; N, 8.95.

[(tpy)Ru(36)Ru(tpy)](PF$_6$)$_4$. Reaction of **36** (129 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 322 mg (85%) as a red solid. IR (KBr) ν 3438, 3111, 3052, 2946, 1616, 1541, 1429, 1401, 1345, 1298, 1012, 855, 714, 543 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.81 (d, ^3J = 7.8 Hz, 4H, B3/5), 8.55−8.61 (m, 4H, A3), 8.41−8.47 (m, 2H, B4), 7.92−8.05 (m, 4H, A4), 7.73 (s, 1H), 7.37−7.68 (m, 11H), 7.19−7.26 (m, 4H, A5), 7.02−7.17 (m, 4H, C6), 6.84−6.99 (m, 4H, C5), 3.16−3.41 (m, 16H); UV/vis λ_{max} (ϵ) 481 (17 270), 358 (19 050), 308 (67 240), 268 (39150); MALDI-TOF MS *m*/*z* 1749 [M − PF$_6$]$^+$. Anal. Calcd for $C_{74}H_{54}F_{24}N_{12}P_4Ru_2$ (1893.3): C, 46.94; H, 2.87; N, 8.88. Found: C, 46.99; H, 2.95; N, 8.81.

[(tpy)Ru(37)Ru(tpy)](PF$_6$)$_4$. Reaction of **37** (144 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 374 mg (95%) as a red solid. IR (KBr) ν 3435, 3117, 2955, 1610, 1466, 1441, 857, 763, 563 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.72 (d, ^3J = 8.2 Hz, 4H, B3/5), 8.54−8.59 (m, 4H, A3), 8.35−8.42 (m, 2H, B4), 8.02−8.09 (m, 4H, A4), 7.52−7.82 (m, 12H), 7.21−7.37 (m, 8H), 7.11−7.17 (m, 4H, C6), 6.87−6.98 (m, 4H, C5), 3.02−3.35 (m, 16H); UV/vis λ_{max} (ϵ) 483 (21 160), 357 (23 040), 310 (72 160), 269 (45 250); MALDI-TOF MS *m*/*z* 1825 [M − PF$_6$]$^+$. Anal. Calcd for $C_{80}H_{58}F_{24}N_{12}P_4Ru_2$ (1969.4): C, 48.79; H, 2.97; N, 8.53. Found: C, 48.71; H, 2.92; N, 8.60.

[(tpy)Ru(38)Ru(tpy)](PF$_6$)$_4$. Reaction of **38** (144 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 358 mg (91%) as a red solid. IR (KBr) ν 3441, 3111, 2942, 1617, 1452, 1421, 1013, 851, 761, 559 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.77 (d, ^3J = 8.0 Hz, 4H, B3/5), 8.51−8.57 (m, 4H, A3), 8.37−8.46 (m, 2H, B4), 8.12 (s, 2H, E2), 7.95−8.05 (m, 4H, A4), 7.57−7.81 (m, 10H, A6/C4/E5), 7.20−7.31 (m, 6H, A5), 7.02−7.22 (m, 4H, C6), 6.81−7.00 (m, 4H, C5), 3.10−3.39 (m, 16H); UV/vis λ_{max} (ϵ) 482 (23 160), 359 (28 410), 309 (89 120), 270 (51 980); MALDI-TOF MS *m*/*z* 1825 [M − PF$_6$]$^+$, 840 [M − 2 PF$_6$]$^{2+}$. Anal. Calcd for $C_{80}H_{58}F_{24}N_{12}P_4Ru_2$ (1969.4): C, 48.79; H, 2.97; N, 8.53. Found: C, 48.84; H, 3.02; N, 8.47.

[(tpy)Ru(39)Ru(tpy)](PF$_6$)$_4$. Reaction of **39** (159 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 384 mg (94%) as a red solid. IR (KBr) ν 3437, 3108, 2951, 1612, 1441, 1411, 1025, 876, 751, 549 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.73 (d, ^3J = 7.7 Hz, 4H, B3/5), 8.49−8.56 (m, 4H, A3), 8.32−8.45 (m, 2H, B4), 8.02−8.09 (m, 4H, A4), 7.54 (s, 4H), 7.39−7.81 (m, 12H), 7.21−7.33 (m, 8H), 7.02−7.16 (m, 4H, C6), 6.79−6.97 (m, 4H, C5), 3.14−3.38 (m, 16H); UV/vis λ_{max} (ϵ) 479 (27 880), 357 (29 780), 310 (79 230), 269 (57 120); MALDI-TOF MS *m*/*z* 1901 [M − PF$_6$]$^+$, 878 [M − 2 PF$_6$]$^{2+}$. Anal. Calcd for $C_{86}H_{62}F_{24}N_{12}P_4Ru_2$ (2045.5): C, 50.50; H, 3.06; N, 8.22. Found: C, 50.54; H, 3.11; N, 8.29.

[(tpy)Ru(40)Ru(tpy)][PF$_6$]$_4$. Reaction of **40** (130 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 330 mg (87%) as a dark red solid. IR (KBr) ν 3106, 3072, 2852, 1600, 1448, 1405, 1388, 853, 765, 557 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.78 (d, ^3J = 8.0 Hz, 4H, B3/5), 8.52−8.55 (m, 4H, A3), 8.47 (s, 2H), 8.39−8.44 (m, 2H, B4), 7.97−8.03 (m, 4H, A4), 7.53−7.75 (m, 8H, A6/C4), 7.23−7.27 (m, 4H, A5), 7.06−7.21 (m, 4H, C6), 6.84−7.01 (m, 4H, C5), 3.08−3.44 (m, 16H); UV/vis λ_{max} (ϵ) 478 (30 910), 359 (33 130), 308 (122 500), 270 (75 450); MALDI-TOF MS *m*/*z* 1755 [M − PF$_6$]$^+$. Anal. Calcd for $C_{72}H_{52}F_{24}N_{12}P_4Ru_2S$ (1899.3): C, 45.53; H, 2.76; N, 8.85. Found: C, 45.48; H, 2.72; N, 8.89.

[(tpy)Ru(41)Ru(tpy)][PF$_6$]$_4$. Reaction of **41** (139 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 354 mg (91%) as a dark red solid; IR (KBr) ν 3110, 3077, 2948, 1627, 1600, 1448, 1409, 1388, 1284, 855, 765, 557; ^{1}H NMR (500 MHz, CD_3CN) δ 8.83 (d, ^3J = 7.9 Hz, 4H, B3/5), 8.54−8.61 (m, 4H, A3), 8.35−8.45 (m, 2H, B4), 7.95 (s, 2H), 7.92−8.01 (m, 4H, A4), 7.39−7.72 (m, 12H), 7.21−7.31 (m, 4H, A5), 7.03−7.17 (m, 4H, C6), 6.79−6.97 (m, 4H, C5), 3.15−3.39 (m, 16H); UV/vis λ_{max} (ϵ) 479 (21 310), 359 (25 200), 309 (83 870), 271 (56 400); MALDI-TOF MS *m*/*z* 1799 [M − PF$_6$]$^+$, 972 [M − 2 PF$_6$]$^{2+}$. Anal. Calcd for $C_{78}H_{56}F_{24}N_{12}P_4Ru_2$ (1943.4): C, 48.21; H, 2.90; N, 8.65. Found: C, 48.16; H, 2.93; N, 8.71.

[(tpy)Ru(42)Ru(tpy)][PF$_6$]$_4$. Reaction of **42** (165 mg, 0.2 mmol), Ru(tpy)Cl_3 (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 323 mg (78%) as a dark red solid; IR (KBr) ν 3075, 2921, 2834, 1639, 1517, 1448, 1405, 1386, 1346, 1228, 1195, 851, 765, 557 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.82 (d, ^3J = 8.2 Hz, 4H, B3/5), 8.49−8.57 (m, 4H, A3), 8.33−8.46 (m, 2H, B4), 8.06−8.11 (m, 4H, A4), 7.59−7.75 (m, 8H, A6/C4), 7.21−7.38 (m, 8H), 7.01−7.17 (m, 4H, C6), 6.85−6.97 (m, 4H, C5), 6.82 (d, ^3J = 7.9 Hz, 4H), 4.12−4.23 (m, 4H), 3.69−3.74 (m, 4H), 3.14−3.32 (m, 16H); UV/vis λ_{max} (ϵ) 480 (39 420), 359 (52 640), 310 (13 620), 271 (81 490); MALDI-TOF MS *m*/*z* 1929 [M − PF$_6$]$^+$; 1784 [M + H − 2 PF$_6$]$^+$. Anal. Calcd for $C_{84}H_{66}F_{24}N_{12}O_3P_4Ru_2$ (2073.5): C, 48.66; H, 3.21; N, 8.11. Found: C, 48.61; H, 3.25; N, 8.17.

[(tpy)Ru(43)Ru(tpy)][PF_6]$_4$. Reaction of **43** (161 mg, 0.2 mmol), [(tpy)$RuCl_3$] (185 mg, 0.42 mmol), and NH_4PF_6 (150 mg, 0.92 mmol) according to the predescribed protocol resulted in the isolation of 398 mg (97%) as a dark red solid; IR (KBr) ν 2956, 2925, 2856, 1724, 1604, 1513, 1448, 1388, 1286, 1245, 1124, 849, 765, 557; ^{1}H NMR (500 MHz, CD_3CN) δ 8.79 (d, ^3J = 8.0 Hz, 4H, B3/5), 8.51−8.62 (m, 4H, A3), 8.35−8.42 (m, 2H, B4), 8.12−8.23 (m, 4H, A4), 7.55−7.82 (m, 8H, A6/C4), 7.16−7.36 (m, 8H), 7.06−7.13 (m, 4H, C6), 6.88−7.03 (m, 8H), 3.51−3.69 (m, 8H), 3.09−3.29 (m, 16H); UV/vis λ_{max} (ϵ) 478 (28 500), 359 (37 220), 309 (108 330), 271 (66 200); MALDI-TOF MS *m*/*z* 1909 [M − PF_6]$^+$. Anal. Calcd for $C_{84}H_{66}F_{24}N_{14}P_4Ru_2$ (2053.5): C, 49.13; H, 3.24; N, 9.55. Found: C, 49.19; H, 3.30; N, 9.48.

[{(tpy)Ru}$_3$(47)][PF_6]$_6$. Reaction of **47** (231 mg, 0.2 mmol), [(tpy)$RuCl_3$] (278 mg, 0.63 mmol), and NH_4PF_6 (225 mg, 1.38 mmol) according to the predescribed protocol resulted in the isolation of 382 mg (63%) as a dark red-purple solid; IR (KBr) ν 3430, 3092, 2961, 1630, 1574, 1429, 1395, 1308, 1175, 1071, 847, 721, 704, 635 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 8.75−8.81 (m, 6H, B3/5), 8.49−8.57 (m, 6H, A3), 8.31−8.43 (m, 4H, B4), 8.01−8.13 (m, 6H, A4), 7.66 (s, 3H), 7.51−7.82 (m, 24H), 7.33−7.41 (m, 6H, A5), 7.16−7.27 (m, 6H, C6), 6.89−7.08 (m, 6H, C5), 3.01−3.52 (m, 24H); UV/vis λ_{max} (ϵ) 483 (25 120), 357 (41 870), 311 (96 040), 269 (60 800); MALDI-TOF MS *m*/*z* 2885 [M − PF_6]$^+$, 865 [M − 3 PF_6]$^{3+}$. Anal. Calcd for $C_{126}H_{90}F_{36}N_{18}P_6Ru_3$ (3029.2): C, 49.96; H, 2.99; N, 8.32. Found: C, 50.07; H, 3.04; N, 8.22.

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Supporting Information Available: Selected electrospray ionization mass spectra (ESI MS) of dinuclear complexes [(tpy)-Ru(L)Ru(tpy)](PF_6)$_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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