HETEROCYCLES, Vol. 65, No. 7, 2005, pp. 1663 - 1672
Received, 23rd February, 2005, Accepted, 28th April, 2004, Published online, 28th April, 2005

SYNTHESIS OF DITOPIC OLIGOPYRIDINES USING THE SUZUKI COUPLING REACTION

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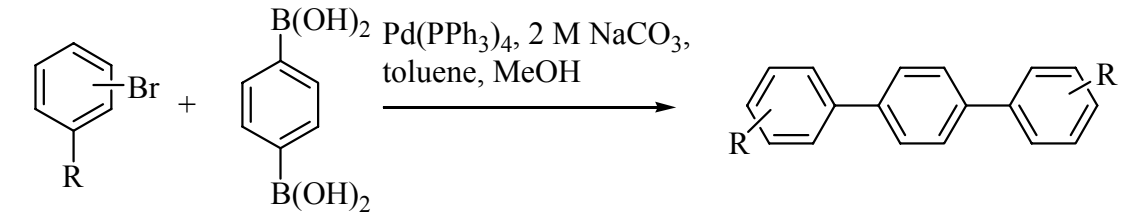
Abstract – The synthesis of various bridged oligopyridines using the Suzuki cross-coupling reaction is reported. It is shown that these ditopic derivatives are versatile ligands for complexation reactions with diverse metal ions, such as Ru(II) and Pt(II).

The assembly of metal centers covalently linked in supramolecular structures has been the object of several investigations in the past few years. Especially oligopyridine derivatives, which can be used for the preparation of luminescent and redoxactive polynuclear metal complexes, have received broad attention.[1-6] Energy- and/or electron transfer processes can be induced by light in these systems. A variety of potential applications such as artificial photosynthesis,[7] photocatalysis,[8] photovoltaic cells[9] are beginning to emerge from this new field of research.

In view of these attractive applications we are interested in simple synthetic methods for the synthesis of bridged oligopyridines bearing 2,2'-bipyridine or 2,2':6'2''-terpyridine subunits. Our studies in the field of ternary iminium salts have led to the development of highly efficient one pot procedures yielding a wide range of functionalized rigid biypridines and terpyridines which are well suited for Pd(0)-catalyzed coupling reactions.[10-14]

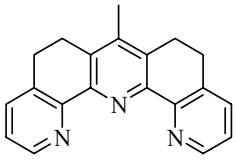
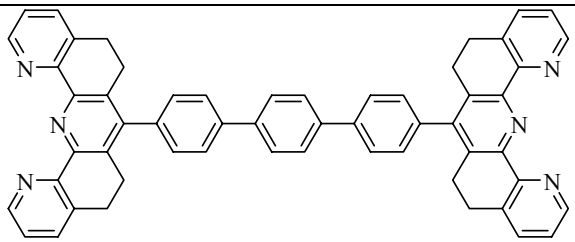
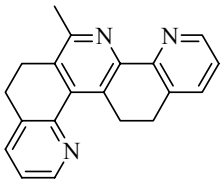
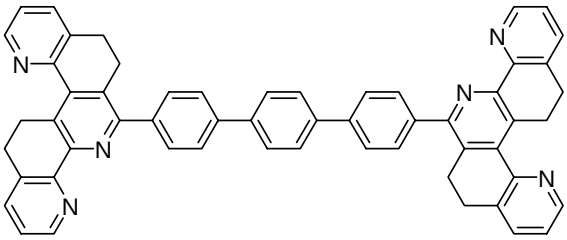
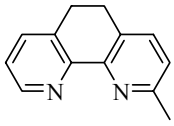
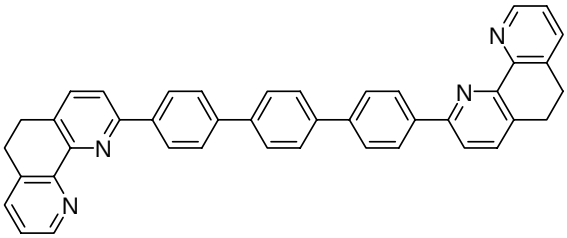
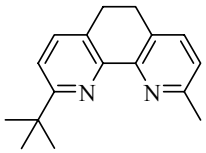
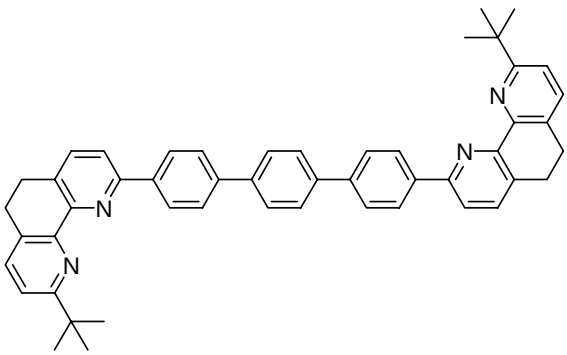
In our first attempts to prepare bridged ditopic ligands we have chosen the Suzuki cross-coupling reaction.[15] Previously, this method has been utilized by Sauvage for the synthesis of bridged oligopyridines.[16] A mixture of benzene-1,4-diboronic acid (**3**), two equivalents of the corresponding substituted bi- or terpyridines (**1**) or (**2**) and $Pd(PPh_3)_4$ (5–10 % mol) in a biphasic solution (toluene, MeOH, 2 M Na_2CO_3) is refluxed for 16–48 h (**Scheme 1**). Work-up and flash column chromatography affords the bridged ligands (**4**) and (**5**) in good yields (**Table 1**, **Table 2**).[16]



1 (4-Br-C_6H_4) **3** **4** (*para*-linked product)
2 (3-Br-C_6H_4) **5** (*meta*-linked product)

Scheme 1

Table 1. Synthesis of *para*-linked oligopyridines (**4**).

entry	R **1**	ditopic oligopyridine (**4**)	reaction time yield
4a			48 h 52%
4b			48 h 99%
4c			24 h 92%
4d			24 h 58%

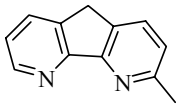
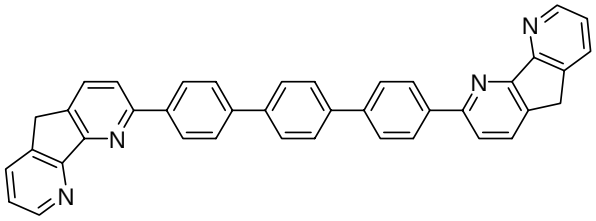
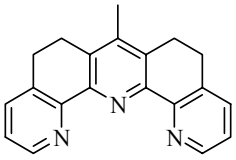
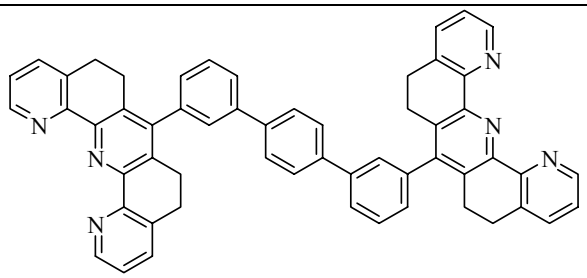
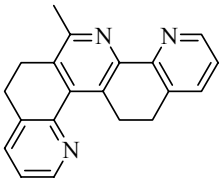
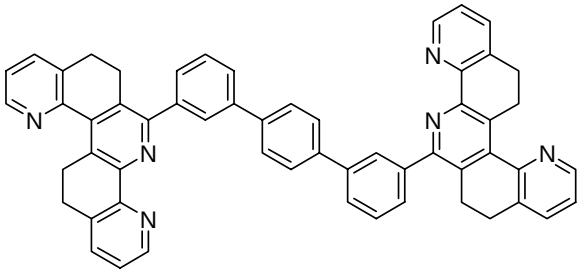
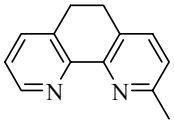
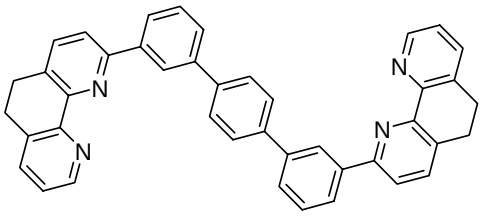
4e			16 h 90%

Table 2. Synthesis of *meta*-linked oligopyridines (**5**).

entry	R **2**	ditopic oligopyridine (**5**)	reaction time yield
5a			18 h 43%
5b			24 h 99%
5c			48 h [a] 34%

a) In the case of **5c** a modified procedure according to Snieckus was applied (DME/EtOH, 2 M Na_2CO_3).[17]

Recently, we have reported on the selective preparation of U-shaped terpyridines, such as **1a** and **2a**, and their use as tritopic ligands in the formation of novel Pt(II)-complexes.[13] Employing the protocol developed by Lowe[18] we have synthesized the binuclear complexes (**6**) and (**7**) (**Figure 1**). Binuclear platinum(II) complexes are known to possess interesting photophysical properties.[19]

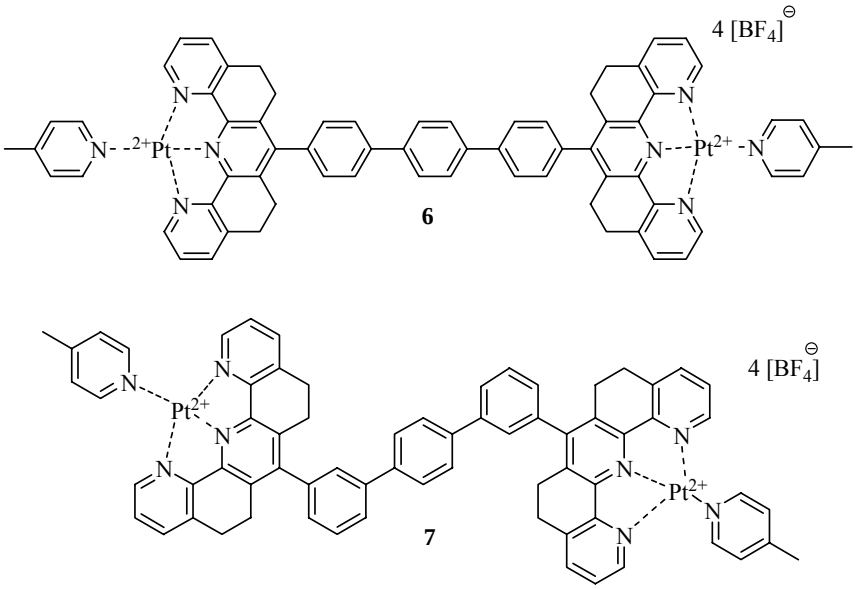


Figure 1. Binuclear Pt(II)-complexes (**6**) and (**7**).

Furthermore, the bipyridine-type ligands (**5b**) and (**5c**) are well suited for synthesis of binuclear Ru(II)-complexes (**8**) and (**5**) (**Figure 2**).[17] The synthesis has been carried out by a modification of Meyer's protocol.[20-21]

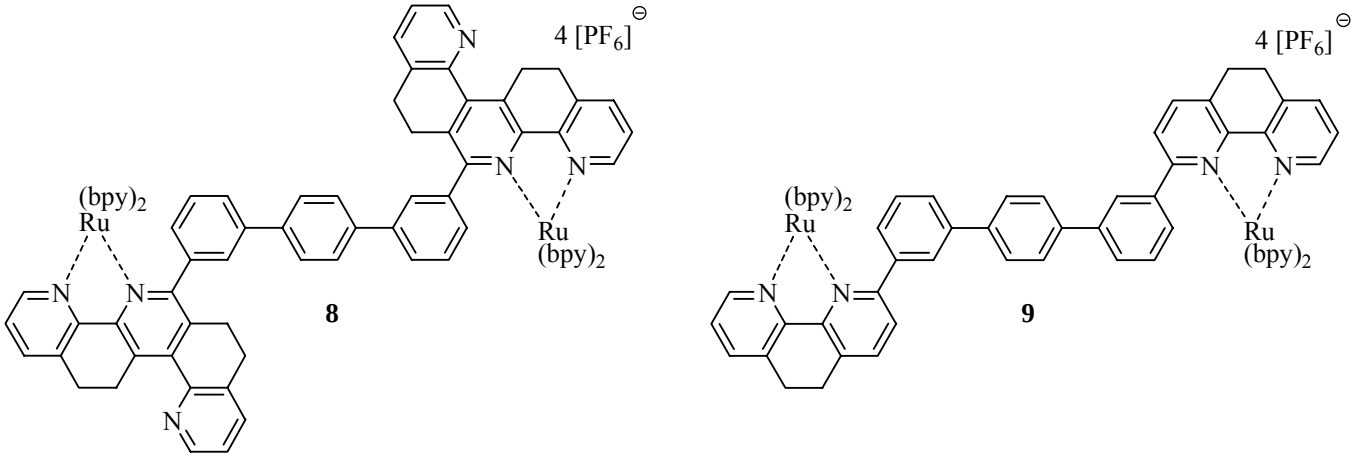


Figure 2. Binuclear Ru(II)-complexes (**8**) and (**9**).

EXPERIMENTAL

All reagents were purchased from commercial sources and used without further purification unless specified. All solvents were dried and distilled according to standard procedures and stored under argon. Chromatographic separation was performed on aluminum oxide (neutral, Akt. III, Fa. Macherey & Nagel, 0.063–0.200 nm). Melting points were obtained on a Büchi SMP-20 mp apparatus and are uncorrected.

IR spectra were measured on a Nicolet 510 P FT-IR spectrophotometer. All NMR spectra were recorded on a Bruker ARX 200 instrument at 200 MHz (^{1}H NMR) and 50 MHz (^{13}C NMR); chemical shifts are reported in ppm relative to TMS. MS was carried out using a Finnigan MAT 8230 (FAB-MS, *m*-nitrobenzyl alcohol matrix) or a Micromass Quattro LCZ apparatus (electrospray, acetonitrile, 10^{-4} mol/L). Elemental analyses were obtained on a Perkin-Elmer M240 analyzer. UV spectra were measured on a Shimadzu UV-2101 PC spectrophotometer (acetonitrile, 10^{-5} mol/L). Bi- and terpyridine derivatives (**1**) and (**2**) were synthesized by procedures known to the literature.[22-24]

General procedure for the Suzuki cross-coupling reaction.[24] To a stirred solution of the bromophenyl-substituted bi- or terpyridine (**1**) or (**2**) (1.0 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in toluene (7 mL) under an atmosphere of argon was added an aqueous solution of Na_2CO_3 (2 M, 1 mL, 2 mmol) and benzene-1,4-diboronic acid (**3**) (83 mg, 0.5 mmol) in methanol (7 mL). The vigorously stirred mixture was refluxed for 16–48 h, then cooled, and partitioned between CH_2Cl_2 (20 mL) and aqueous Na_2CO_3 (2 M, 20 mL) containing 1 mL of a concentrated NH_3 solution. The organic layer was separated and the residual aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated to dryness. Chromatography on neutral Al_2O_3 (CH_2Cl_2 / MeOH, 50:1) yielded the pure products.

4,4''-Di-(5,6,8,9-tetrahydroquino[8,7-*b*][1,10]phenanthrolin-7-yl)-[1,1';4',1'']terphenyl (4a). Terpyridine (**1a**) (252 mg, 0.57 mmol) and **3** (47 mg, 0.29 mmol) afforded **4a** (118 mg, 52 %) as a brownish powder, mp >250 °C after recrystallization from methanol. ^{1}H NMR ($CDCl_3$/MeOD, 20:1): 2.72–2.83 (m, 8 H), 2.89–3.03 (m, 8 H), 7.21–7.35 (m, 8 H), 7.55–7.65 (m, 4 H), 7.76–7.87 (m, 4 H), 8.54 (d, ^3J = 4.7 Hz, 4 H). ^{13}C NMR ($CDCl_3$/MeOD, 20:1): 25.6 (t), 27.6 (t), 124.3 (d), 127.9 (d), 128.0 (d), 129.5 (d), 136.3 (s), 136.6 (d), 140.0 (s), 140.7 (s), 148.5 (d), 150.3 (s), 152.1 (s). FAB-MS (NBA matrix); *m/z* (%): 797 (20) $[M+H]^+$, 307 (15), 279 (16), 219 (15), 154 (100), 136 (85). Anal. Calcd for $C_{56}H_{40}N_6$: C 84.40 H 5.06 N 10.55. Found C 84.45 H 5.09 N 10.43.

4,4''-Di-(7,8,13,14-tetrahydroquino[8,7-*k*][1,8]phenanthrolin-6-yl)-[1,1';4',1'']terphenyl (4b). Terpyridine (**1b**) (190 mg, 0.42 mmol) and **3** (36 mg, 0.21 mmol) afforded **4b** (159 mg, 95 %) as brownish powder, mp >290 °C after recrystallization from methanol. ^{1}H NMR (CF_3OOD): 2.98–3.06 (m, 4 H), 3.17–3.23 (m, 4 H), 3.28–3.35 (m, 4 H), 3.61–3.72 (s, 4 H), 7.33–7.82 (m, 12 H), 7.89–8.02 (m, 4 H), 8.45 (d, ^3J = 7.7 Hz, 2 H), 8.54–8.64 (m, 4 H), 8.83 (d, ^3J = 5.7 Hz, 2 H). FAB-MS (NBA matrix); *m/z* (%): 796 (100) M^+, 436 (49), 356 (98), 281 (48), 207 (41). Anal. Calcd for $C_{56}H_{40}N_6$: C 84.40 H 5.06 N 10.55. Found C 84.41 H 5.02 N 10.52.

4,4''-Di-(5,6-dihydro-[1,10]-phenanthrolin-2-yl)-[1,1';4',1'']terphenyl (4c). Bipyridine (**1c**) (336 mg, 1.00 mmol) and **3** (83 mg, 0.50 mmol) afforded **4c** (271 mg, 92 %) as an orange-brown solid, mp > 290 °C after recrystallization from methanol. ^{1}H NMR ($CDCl_3$/MeOD, 20:1): 2.87–3.03 (m, 8 H), 7.28–7.35 (m, 2 H), 7.64–7.68 (m, 4 H), 7.76–7.80 (m, 10 H), 8.27 (d, ^3J = 8.2 Hz, 4 H), 8.70 (d, ^3J = 4.65 Hz, 2H). ^{13}C NMR ($CDCl_3$): 27.4 (t), 27.8 (t), 121.2 (d), 124.3 (d), 127.0 (d), 127.5 (d), 127.8 (d), 128.0 (d), 133.0 (s), 134.9 (s), 137.2 (d), 138.5 (s), 140.1 (s), 141.3 (s), 148.4 (d), 151.0 (s), 151.7 (s), 156.6 (s). FAB-MS (NBA matrix); *m/z* (%): 591 (100) $[M+H]^+$, 281 (4), 154 (35, 136 (47), 90 (18). Anal. Calcd for $C_{42}H_{30}N_4$: C 85.40 H 5.12 N 9.48. Found C 85.37 H 5.10 N 9.53.

4,4''-Di-(9-*tert*-butyl-5,6-dihydro-[1,10]-phenanthrolin-2-yl)-[1,1';4',1'']terphenyl (4d). Bipyridine (**1d**) (382 mg, 1.00 mmol) and **3** (83 mg, 0.50 mmol) afforded **4d** (199 mg, 58 %) as a brown powder, mp > 260 °C after recrystallization from methanol. ^{1}H NMR ($CDCl_3$/MeOD, 20:1): 1.52 (s, 18 H), 2.95–3.05 (m, 4 H), 7.35 (d, ^3J = 8.0 Hz, 2 H), 7.52 (d, ^3J = 8.0 Hz, 2 H), 7.64 (d, ^3J = 8.0 Hz, 2 H), 7.76–7.84 (m, 10 H), 8.29–8.34 (m, 2 H). FAB-MS (NBA matrix); *m/z* (%): 702 (98) M^+, 687 (93), 671 (22), 646 (30), 590 (6), 507 (8), 350 (13), 343 (34). Anal. Calcd for $C_{50}H_{46}N_4$: C 85.43 H 6.60 N 7.97. Found C 85.48 H 6.62 N 8.05.

4,4'-Di-(5*H*-cyclopenta[2,1-b3,4-*b*']phenanthrolin-2-yl-[1,1';4',1'']terphenyl (4e). Bipyridine (**1e**) (322 mg, 1.00 mmol) and **3** (83 mg, 0.5 mmol) afforded **4e** (253 mg, 90 %) as a brown powder, mp > 290 °C after recrystallization from methanol. FAB-MS (NBA matrix); *m/z* (%): 562 (74) M^+, 438 (30), 396 (65), 320 (100), 281 (19), 244 (40). Anal. Calcd for $C_{40}H_{26}N_4$: C 85.38 H 4.66 N 9.96. Found C 85.31 H 4.64 N, 10.05.

3,3''-Di-(5,6,8,9-tetrahydroquino[8,7-*b*][1,10]phenanthrolin-7-yl)-[1,1';4',1'']terphenyl (5a). Terpyridine (**2a**) (413 mg, 0.94 mmol) and **3** (80 mg, 0.48 mmol) afforded **5a** (164 mg, 43 %) as a brownish powder, mp > 250 °C after recrystallization from methanol. ^{1}H NMR ($CDCl_3$/MeOD, 20:1): 2.77–2.85 (m, 8 H), 2.91–2.97 (m, 8 H), 7.21–7.29 (m, 6 H), 7.53–7.68 (m, 8 H), 7.72–7.80 (m, 6 H), 8.79 (d, ^3J = 4.7 Hz, 4 H). ^{13}C NMR ($CDCl_3$): 25.9 (t), 27.8 (t), 123.9 (d), 127.0 (d), 127.5 (d), 128.1 (d), 129.9 (d), 132.8 (s), 133.7 (s), 136.6 (d), 138.3 (s), 140.2 (s), 141.4 (s), 148.0 (s), 149.2 (d), 150.9 (s), 152.6 (s). FAB-MS (NBA matrix); *m/z* (%): 797 (8) $[M+H]^+$, 197 (15), 154 (18), 1345 (45). Anal. Calcd for $C_{56}H_{40}N_6$: C 84.40 H 5.06 N 10.55. Found C 84.33 H 5.08 N 10.60.

3,3''-Di-(7,8,13,14-tetrahydrochino[8,7-*k*][1,8]phenanthrolin-6-yl)-[1,1';4',1'']terphenyl (5b). Terpyridine (**2b**) (441 mg, 1.00 mmol) and **3** (83 mg, 0.50 mmol) afforded **5b** as a yellow solid (394 mg,

99 %), mp 244 °C after recrystallization from methanol. ^{1}H NMR ($CDCl_3$/MeOD, 20:1): 2.79–2.95 (m, 12 H), 3.63 (t, ^3J = 7.1 Hz, 4 H), 7.19–7.27 (m, 4 H), 7.47–7.68 (m, 10 H), 7.69–7.72 (m, 4 H), 7.87 (s, 2 H), 8.58 (d, ^3J = 4.8 Hz, 2 H), 8.59 (d, ^3J = 4.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$): 26.4 (t), 26.9 (t), 28.3 (t), 29.2 (t), 123.6 (d), 123.8 (d), 127. 0 (2 d), 127.9 (d), 128.6 (d), 128.9 (d), 131.4 (s), 132.9 (s), 134.6 (s), 135.7 (d), 135.9 (2 d), 140.4 (s), 140.8 (s), 141.0 (s), 141.2 (s), 147.4 (d), 148.6 (d), 151.1 (s), 152.4 (s), 152.9 (s), 156.7 (s). FAB-MS (NBA matrix); *m/z* (%): 797 (10) $[M+H]^+$, 795 (1), 798 (8), 709 (1), 614 (1), 438 (2), 279 (19), 133 (23). Anal. Calcd for $C_{56}H_{40}N_6$: C 84.40 H 5.06 N 10.55. Found C 84.47 H 5.09 N 10.45.

3,3''-Di-(5,6-dihydro-[1,10]-phenanthrolin-2-yl)-[1,1';4',1'']terphenyl (5c). To a stirred solution of bipyridine (**2c**) (586 mg, 1.74 mmol) and $Pd(PPh_3)_4$ (150 mg, 0.13 mmol) in DME (12 mL) under an atmosphere of argon was added an aqueous solution of Na_2CO_3 (2 M, 5.2 mL) and **3** (145 mg, 0.87 mmol) in ethanol (2 mL) within 15 min. The vigorously stirred mixture was refluxed for 24 h. After addition of $Pd(PPh_3)_4$ (150 mg, 0.13 mmol) the mixture was refluxed for further 24 h. The solvent was evaporated and the residue was diluted with CH_2Cl_2 (30 mL) and water (20 mL). The organic phase was seperated and the aqueous layer extracted with CH_2Cl_2 (2 x 30 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated.[17] Chromatography on Al_2O_3 (EtOAc; CH_2Cl_2/MeOH 100:1) afforded **5c** (226 mg, 34 %) as yellow powder, mp 142 °C after recrystallization from methanol. ^{1}H NMR ($CDCl_3$): 2.95–3.11 (m, 8 H), 7.28–7.35 (m, 2 H), 7.48–7.91 (m, 14 H) 8.16–8.24 (m, 2 H), 8.39–8.43 (m, 2 H), 8.77 (dd, ^4J = 1.7 Hz, ^3J = 4.7 Hz, 2 H). ^{13}C NMR ($CDCl_3$): 27.7 (t), 28.0 (t), 120.9 (d), 123.9 (d), 125.8 (d), 126.6 (d), 127.8 (d), 128.0 (d), 129.6 (d), 133.4 (s), 134.8 (s), 136.1 (d), 137.1 (d), 140.5 (s), 140.7 (s), 141.4 (s), 149.0 (d), 152.1 (s), 152.5 (s), 156.4 (s). FAB-MS (NBA matrix); *m/z* (%): 591 (100) $[M+H]^+$, 207 (15), 154 (52), 136 (57). Anal. Calcd for $C_{42}H_{30}N_4$: C 85.40 H 5.12 N 9.48. Found C 85.46 H 5.17 N 9.59.

General procedure for the preparation of terpyridine-platinum complexes.[23, 24] To a suspension of diiodo(cycloocta-1,5-diene)platinum (55 mg, 0.10 mmol) in acetone (1 mL) was added silver tetrafluoroborate (40 mg, 0.21 mmol). The resulting mixture was stirred at rt until a colorless solution was obtained (20–30 min). The AgI precipitate was then removed by filtration. The solution was added to a suspension of a terpyridine (0.08 mmol) in acetonitrile (0.5 mL) and the reaction mixture was stirred at rt for another 30 min. The acetonitrile complex precipitating was collected by centrifugation, suspended in acetonitrile (1 mL) and treated with 4-picoline (20 μL) for 30 min to give a clear solution. The picoline complex was precipitated by addition of ether to give the crude complex, which was recrystallized from acetonitrile by slow diffusion of ether vapor.

[Pt_2(4a)(4-picoline)$_2$][BF_4]$_4$ (6). $PtCODI_2$ (55 mg, 0.1 mmol), $AgBF_4$ (42 mg, 0.2 mmol), **4a** (32 mg, 0.04 mmol) and 4-picoline (25 μL) afforded **6** as a yellow solid (51 mg, 74 %), mp > 250 °C after recrystallization from acetonitrile/ether. ^{1}H NMR (CD_3CN): 2.69 (s, 6 H), 3.01–3.12 (m, 8 H), 3.29–3.34 (m, 8 H), 7.53–7.83 (m, 16 H), 7.98–8.03 (m, 8 H), 8.17 (d, ^3J = 8.0 Hz, 4 H), 8.88 (d, ^3J = 6.4 Hz, 4 H). ^{13}C NMR (CD_3CN): 21.0 (q), 24.1 (t), 26.1 (t), 127.9 (d), 128.1 (d), 129.1 (d), 129.2 (d), 129.3 (d), 132.6 (s), 137.1 (s), 138.9 (s), 139.7 (s), 141.6 (s), 142.9 (d), 149.5 (s), 150.3 (d), 152.1 (d), 153.6 (s), 155.3 (s), 155.7 (s). ES-MS; *m/z*: 629 $[C_{62}H_{47}N_7Pt + 2BF_4]^{2+}$, 486 $[C_{68}H_{54}N_8Pt_2 + BF_4]^{3+}$, 343 $[C_{68}H_{54}N_8Pt_2]^{4+}$. UV/VIS; $\lambda_{max}(\varepsilon)$: 418 (19200), 396 (23700), 350 (31500), 317 (69200), 301 (67300), 2667 (45900), 238 (42900).

[Pt_2(5a)(4-picoline)$_2$][BF_4]$_4$ (7). $PtCODI_2$ (55 mg, 0.1 mmol), $AgBF_4$ (42 mg, 0.2 mmol), **4a** (32 mg, 0.04 mmol) and 4-picoline (25 μL) afforded **6** as a yellow solid (49 mg, 71 %), mp > 250 °C after recrystallization from acetonitrile/ether. ^{1}H NMR (CD_3CN): 2.69 (s, 6 H), 3.03–3.12 (m, 8 H), 3.25–3.34 (m, 8 H), 7.35–7.43 (m, 2 H), 7.54–7.88 (m, 14 H), 7.89–7.95 (m, 8 H), 8.16 (d, ^3J = 8.5 Hz, 4 H), 8.87 (d, ^3J = 6.5 Hz, 4 H). ^{13}C NMR (CD_3CN): 21.0 (q), 24.1 (t), 26.1 (t), 126.6 (d), 127.5 (d), 128.2 (d), 129.1 (d), 129.3 (d), 130.4 (d), 134.2 (s), 137.2 (s), 138.9 (s), 141.5 (s), 142.9 (d), 149.5 (s), 150.3 (d), 152.1 (d), 153.8 (s), 155.3 (s), 155.6 (s). ES-MS; *m/z*: 629 $[C_{62}H_{47}N_7Pt + 2BF_4]^{2+}$, 583 $[C_{56}H_{40}N_6Pt + 2BF_4]^{2+}$. UV/VIS; $\lambda_{max}(\varepsilon)$: 419 (10200), 397 (8400), 350 (15500), 317 (58700), 299 (58600), 267 (57500), 240 (42600).

***cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O.**[25] A mixture of $RuCl_3 \cdot 3H_2O$ (3.9 g, 14.9 mmol), 2:2'-bipyridine (4.7 g, 30 mmol) and LiCl (4.2 g, 1.0 mmol) in dry DMF (2 mL) was refluxed for 8 h under vigorous stirring. After cooling acetone (125 mL) was added and the reaction mixture was kept at 0 °C for 12 h. The green-black precipitate was filtered off, washed with water (3 x 12 mL) and ether (3 x 12 mL) and dried in vacuo to give the precursor complex (2.98 g, 48 %).

General procedure for the preparation of bipyridine-ruthenium complexes.[25-26] A mixture of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ (0.4 mmol) and the ditopic ligand (0.2 mmol) was refluxed in ethanol and water (7:2, 15 mL) for 24 h. After cooling to rt 2/3 of the solvent were evaporated. The Ru(II)-complex was obtained by the addition of NH_4PF_6 (4.5 eq.) in water (3 mL). The crude product was filtered off and purified by column chromatography on Al_2O_3 (toluene/acetonitrile, 1:1) followed by crystallization from the same solvents.

[Ru_2(bpy)$_4$(5b)][PF_6]$_4$ (8). Ditopic ligand (**5b**) (135 mg, 0.17 mmol), *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ (200 mg, 0.39 mmol) and NH_4PF_6 (116 mg, 0.71 mmol) afforded **8** (201 mg, 53 %) as a red solid, mp >250 °C after

recrystallization from acetonitrile/toluene. ^{1}H NMR (CD_3CN): 2.17–2.46 (m, 4 H), 2.68–2.90 (m, 4 H), 3.25–3.29 (m, 4 H), 3.96–4.07 (m, 4 H), 5.99–6.02 (m, 1 H), 6.29–6.36 (m, 1 H), 6.58–6.68 (m, 1 H), 6.84–6.92 (m, 3 H), 7.07–7.72 (m, 30 H), 7.87–7.97 (m, 6 H), 8.08–8.51 (m, 12 H), 8.72–8.74 (m, 2 H). FAB-MS (NBA matrix); *m/z* (%): 2059 (1) $[M - PF_6]^+$, 1912 (1) $[M - 2PF_6 - 2H]^+$, 1767 (1) $[M - 3PF_6 - 2H]^+$, 486 (1), 1307 (1), 998 (10), 968 (13), 822 (8), 642 (7), 537 (4), 460 (12), 362 (11), 279 (15), 154 (100). Anal. Calcd for $C_{96}H_{72}N_{14}F_{24}P_4Ru_2$: C 52.32 H 3.29 N 8.90. Found C 52.75 H 3.76 N 8.70. UV/VIS; $\lambda_{max}(\varepsilon)$: 456 (29700), 290 (119700), 239 (40000).

$[Ru_2(bpy)_4(5c)][PF_6]_4$ (9). Ditopic ligand (**5c**) (45 mg, 0.06 mmol), *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ (62 mg, 0.12 mg) and NH_4PF_6 (41 mg, 0.25 mmol) afforded **9** (46 mg, 38 %) as an orange-red solid, mp >250 °C after recrystallization from acetonitrile/toluene. ^{1}H NMR (CD_3CN): 3.31–3.42 (m, 8 H), 6.84–6.93 (m, 4 H), 7.14–7.47 (m, 23 H), 7.53–7.78 (m, 11 H), 7.82–8.16 (m, 12 H), 8.31–8.56 (m, 4 H). FAB-MS (NBA matrix); *m/z* (%): 1851 (99) $[M - PF_6 - 2H]^+$, 1707 (98) $[M - 2PF_6 - H]^+$). ES-MS; *m/z*: 521 $[C_{82}H_{62}N_{12}Ru_2+PF_6]^{3+}$, 354 $[C_{82}H_{62}N_{12}Ru_2]^{4+}$. Anal. Calcd for $C_{82}H_{62}N_{12}F_{24}P_4Ru_2$: C 49.31 H 3.13 N 98.41. Found C 49.03 H 3.12 N 8.75. UV/VIS; $\lambda_{max}(\varepsilon)$: 453 (14800), 289 (81500), 235 (19900).

ACKNOWLEDGEMENTS

We would like to thank the *Fonds der Chemischen Industrie*, the *Deutsche Forschungsgemeinschaft* and the *Grünenthal GmbH* for their financial support of this project.

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