Synthesis of Highly Charged Ruthenium(II)–Quaterpyridinium Complexes: A Bottom-Up Approach to Monodisperse Nanostructures

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Received 6 September 2006

Abstract: Tris-homoleptic ruthenium(II)–quaterpyridine and –quaterpyridinium complexes, possessing geometric dimensions in the nanoscale, have been synthesized. The diameters range from 1.82 to 4.55 nm according to molecular modeling. The new complexes are highly charged (either +8 or +14) and luminescent and represent examples for the 'bottom-up' approach to monodisperse nanostructures.

Key words: 4,4′:2′,2″:4″,4‴-quaterpyridine, ruthenium(II)–quaterpyridine, ruthenium(II)–quaterpyridinium complexes, high-pressure-assisted synthesis, photosensitizer

The d block metal–4,4′:2′,2″:4″,4‴-quaterpyridine and -quarterpyridinium complexes,[1] which are also referred to as 2,2′:4,4″:4′,4‴-quaterpyridyl or tetrapyridine and tetrapyridinium complexes,[1,2] have gained importance during the last two decades in several research domains: (a) in fundamental research in inorganic chemistry as extended ligand of various d block metal cations, such as iron(II),[3] ruthenium(II),[3–14] osmium(II),[15,16] rhenium(I), palladium(II), and platinum(II);[16] (b) as redox catalysts and electron carriers (relays) at composite electrodes;[4,9,11] (c) as components in supramolecular assemblies;[7,11,12,14,16] (d) as in situ luminescence sensors of pH[8] and DNA intercalators[5] (with the prospect of photodynamic therapy); and (e) advanced nonlinear optical materials.[3,13]

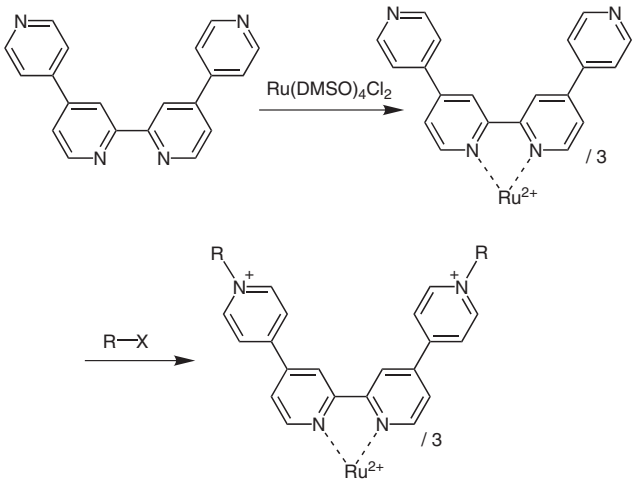
Ruthenium(II)–quaterpyridinium complexes were successfully employed as sensitizer-relay assemblies for the photocatalytic reduction of water to dihydrogen[1] and carbon dioxide to methane and other volatile hydrocarbons.[17]

Most recently, ruthenium(II)–quaterpyridinium complexes have proved to be prospective channel blockers of mycobacterial porins (model bacterium: *Mycobacterium smegmatis*).[18]

Here, we describe the synthesis of tris-homoleptic ruthenium(II)–quaterpyridinium complexes. Since all tris-homoleptic ruthenium(II) complexes principally exhibit D_3 symmetry,[19] which can be slightly distorted when intricate ligand systems are employed,[2] The size (diameter) of the desired ruthenium(II)–quaterpyridinium complexes should range from ca. 2–5 nm in order to block mycobacterial porin channels. Furthermore, we were aiming at unusually high charges for ruthenium(II)–polypyridine complexes since it can be expected that the binding of the desired ruthenium(II)–quaterpyridinium complexes within the model porin MspA[20] from *M. smegmatis* is aided by the presence of up to 14 positive charges. Additionally, possible applications of ruthenium(II)–quaterpyridinium complexes in the field of artificial photosynthesis will also profit from highly charged (nano-sized) sensitizer-relay assemblies.[17]

A completely novel application for nano-sized ruthenium(II) complexes, representing completely monodisperse nanoparticles possessing D_3 symmetry, is their use as calibration materials in atomic force microscopy (AFM) experiments. Due to the size of the AFM tip, this technique exhibits a strong tendency to generate images of nanostructures that are larger than the investigated original sample.[21] In this case, the use of precision materials for calibration can help to eliminate this systematic error.

Two strategies exist for the synthesis of ruthenium(II)–quaterpyridinium complexes: strategy A, synthesis of a ruthenium(II)–tris(quaterpyridine) that possesses six tertiary aromatic pyridine moieties, followed by quaternization of the non-ruthenium(II)-bound sp^2 nitrogens (Scheme 1);[1,17] or strategy B, selective quaternization of the two terminal pyridine rings of 4,4′:2′,2″:4″,4‴-

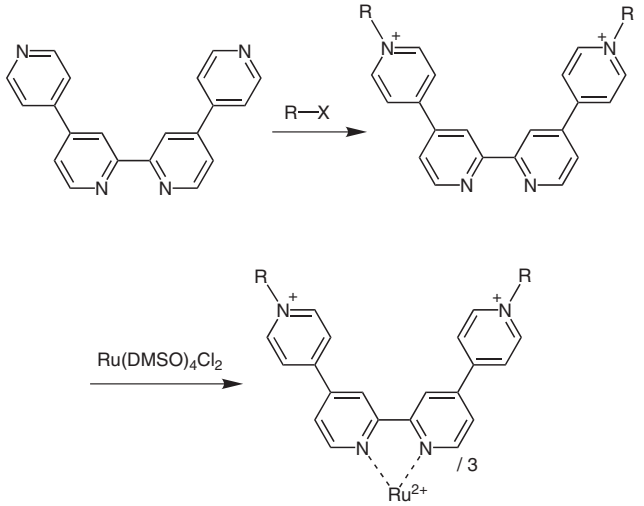


Scheme 1 4,4′:2′,2″:4″,4‴-Quaterpyridine complexation of ruthenium(II), followed by quaternization (strategy A)

SYNTHESIS 2007, No. 4, pp 0505–0514
Advanced online publication: 22.01.2007
DOI: 10.1055/s-2007-965901; Art ID: M05806SS

quaterpyridine,[22] followed by the synthesis of the ruthenium(II)–tris(quaterpyridinium) complex (Scheme 2).

The quaternization of the two external pyridine moieties of 4,4′:2′,2″:4″,4‴-quaterpyridine (strategy B) works especially well, if methylation of the external pyridine systems is performed. However, as indicated by preliminary experiments in our research group, the selectivity was less than desired when larger substituents were selected.

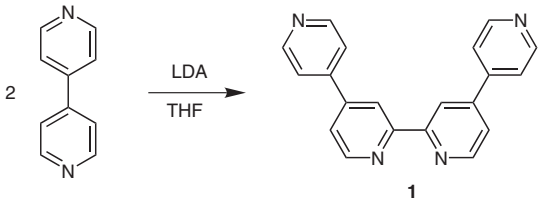


Scheme 2 4,4′:2′,2″:4″,4‴-Quaterpyridine quaternization of ruthenium(II), followed by complexation (strategy B)

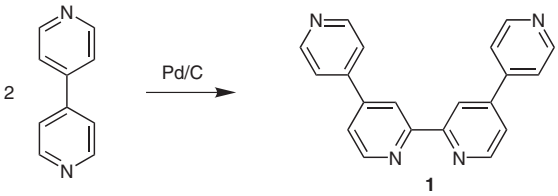
Therefore, the work described here has been performed according to strategy A: The syntheses of 4,4′:2′,2″:4″,4‴-quaterpyridine from 4,4′-bipyridine and then of tris(4,4′:2′,2″:4″,4‴-quarterpyridine-*N*′,*N*″)ruthenium(II) dichloride $[Ru(qpy)_3]Cl_2$ were optimized. Since tris-homoleptic ruthenium(II)–quaterpyridinium complexes featuring bulky groups were the desired group of target molecules, a facile synthetic method had to be developed because thermal activation proved to be insufficient. We applied high pressure and moderate temperature in order to achieve superior results. These experiments were guided by the simple paradigm that S_N2 reactions profit from high-pressure conditions due to a decrease in their activation energy. The latter is caused by a diminished entropic effect at high pressure.[23] Although organic chemistry at high pressure has been available for many years,[24] its distinct advantages are still not widely recognized and/or utilized. It is hoped that this report will provide further evidence for its usefulness as well as its easy and safe application in an organic laboratory.

First we examined the optimization of the synthesis of 4,4′:2′,2″:4″,4‴-quaterpyridine (**1**). According to literature studies, there are three straightforward pathways to 4,4′:2′,2″:4″,4‴-quaterpyridine. All three syntheses start from 4,4′-bipyridine. Pathways A and B lead to 4,4′:2′,2″:4″,4‴-quaterpyridine (**1**) in higher yields, because they can be completed in one stage; pathway C comprises of three stages: the formation of the pyridinium *N*-oxide, reaction with phosphorus oxychloride to give a 4-(2-chloropyridin-4-yl)pyridine[25] and reductive coupling to give 4,4′:2′,2″:4″,4‴-quaterpyridine (**1**).

Pathway A involves lithium diisopropylamide mediated coupling of 4,4′-bipyridine (Scheme 3);[1,26,27] the general mechanism of this reaction remains unclear. Pathway B, involves heating and oxidative coupling of a mixture of 4,4′-bipyridine and palladium on carbon catalyst (Scheme 4).[13,22]

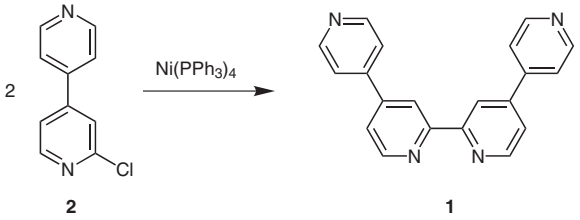


Scheme 3 Synthesis of 4,4′:2′,2″:4″,4‴-quaterpyridine from 4,4′-bipyridine employing lithium diisopropylamide as coupling reagent



Scheme 4 Synthesis of 4,4′:2′,2″:4″,4‴-quaterpyridine from 4,4′-bipyridine on the surface of palladium(0) on carbon

Pathway C utilizes the tetrakis(triphenylphosphine)nickel(0) mediated reductive coupling of 4-(2-chloropyridin-4-yl)pyridine (**2**) to give 4,4′:2′,2″:4″,4‴-quaterpyridine (**1**) (Scheme 5). Examples of the successful application of these symmetric coupling reactions of two halogenated aromatic systems are provided.[28–30]



Scheme 5 Synthesis of 4,4′:2′,2″:4″,4‴-quaterpyridine from 4-(2-chloropyridin-4-yl)pyridine employing tetrakis(triphenylphosphine)nickel(0) as coupling agent

A thorough comparison of the three approaches yielded the following yields: pathway A: 14%, which was lower than previous results;[25,26] pathway B: 36%, in agreement with the previously optimized procedure;[13] and C: 14%. The latter result is predominantly caused by the low yields obtained in the two-stage synthesis of 4-(2-chloropyridin-4-yl)pyridine (**2**).[25] The tetrakis(triphenylphosphine)nickel(0) mediated reductive coupling reaction has a yield of 79%, which is typical for this coupling reaction of non-sterically hindered electron-poor aromatic systems.

In order to improve pathway B, we introduced a dipolar aprotic solvent (DMF) to the catalytic dehydrogenation and coupling reaction of 4,4′-bipyridine at palladium (10% on carbon). The presence of a solvent permits better control of the heat exchange during the reaction and facilitates the desorption of the reaction product from the palladium surface.[31] After refluxing the mixture (at 154 °C, instead of 250 °C[13]) for 48 hours, typical yields ranged from 40–44%. This represents a considerable improvement compared to the yield of 36%, which was obtained without the use of a solvent. Note that the influence of oxygen (air) on the coupling reaction was negligible. Another interesting finding is that when ethylene glycol was used as solvent, 4,4′:2′,2″:4″,4‴-quaterpyridine could only be isolated in 2–3% yield.

Next we optimized of the synthesis of tris(4,4′:2′,2″:4″,4‴-quarterpyridine-*N*′,*N*″)ruthenium(II) dichloride $[Ru(qpy)_3]Cl_2$ (**3**) (Scheme 6). As we intended to add rather large and positively charged groups by quaternization of the sp^2 nitrogens of the pyridine moieties in 4,4′:2′,2″:4″,4‴-quarterpyridine, the optimization of the synthesis of $Ru(qpy)_3^{2+}$ was the next logical step.

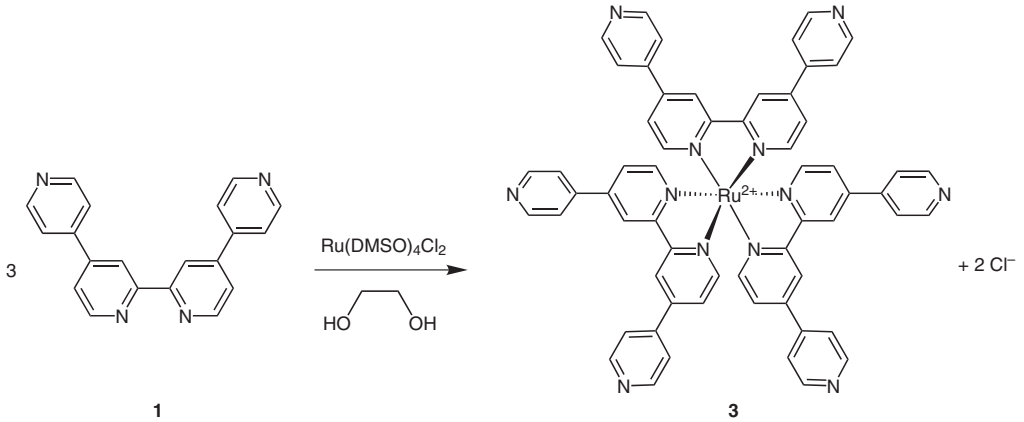
Refluxing 4,4′:2′,2″:4″,4‴-quarterpyridine (**1**) and the mixture of ruthenium(II) complexes commonly abbreviated as $[Ru(DMSO)_4]Cl_2$[32] for 14 hours gave **3** in only 33% yield after workup and subsequent recrystallization.[1,26] Our procedure follows the synthesis by Dürr and Thiery closely, but avoids the filtration of the reaction mixture. Instead, the solvent is removed under high vacuum and the inevitable bis-complex $[Ru(qpy)_2]Cl_2$ **3** is removed by filtration using Sephadex G25 as the stationary phase. These minor changes resulted in a remarkable increase in yield, typically, 85 ±5% have been obtained.

Naturally, we also tried to improve the yield of **3** even further by employing high-pressure reaction conditions up to 69 bar (1000 psi), but this failed. According to our findings, heat is a far more important factor than pressure in overcoming the kinetic barrier for the formation of this particular tris-homoleptic ruthenium(II) complex. This behavior is somewhat surprising since is not likely that significant steric hindrance would be found in this case. However, the formation of the tris-homoleptic complex might be hindered due to competing coordination of the external pyridine moieties.

Finally we optimized of the size of the ruthenium(II)–quaterpyridinium complexes possessing the charges +8 and +14. The optimization of the structure of the complexes structures was performed employing a modified MM2 force field.[2] The requirements of the ruthenium(II) complexes were: (a) Tris-homoleptic structures [(slightly distorted) D_3 symmetries], which would permit the existence of 8 or 14 positive charges per molecule. (b) Diameters ranging from approximately 2 to 4.5 nm. (c) Flexible bonds, which allow a certain amount of motion of the complexes' substituents with respect to each other. This requirement is especially important for the use of these ruthenium(II) complexes as mycobacterial channel blockers. (d) The synthesis should start from $Ru(qpy)_3^{2+}$. (e) Finally, the synthesis of the substituents themselves should be possible in a straightforward manner. The diameters of the target complexes, obtained from the MM2 calculation and optimization, are summarized in Table 1.

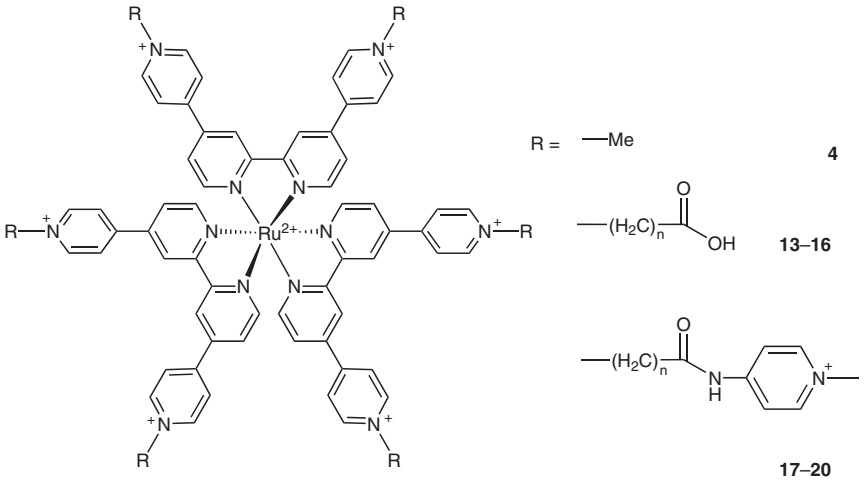
ω-Bromo-*N*-(1-methylpyridinium-4-yl)alkanamide iodides **9–12** were synthesized by a one-pot method (Scheme 7). The reaction of ω-bromoalkanoic acids (C1–C4) with 4-aminopyridine in dimethyl sulfoxide at 60 °C using the well-established *N*,*N*′-dicyclohexylcarbodiimide/*N*-hydroxysuccinimide system[33,34] yielded ω-bromo-*N*-(pyridin-4-yl)alkanamides **5–8**, which were methylated employing iodomethane in situ. This one-pot reaction led to the desired products **9–12**, which were used to assemble our highly charged (14+) target ruthenium(II) complexes.

Ruthenium(II)–tris(4,4′:2′,2″:4″,4‴-quarterpyridine) complexes $[Ru(QP\text{-}R)_3]Cl_8$ and $[Ru(QP\text{-}R)_3]Cl_{14}$ were synthesized by high-pressure synthesis, which yielded excellent results (Scheme 8). Reacting the ω-bromoalkanoic acids (C1–C4) with $[Ru(qpy)_3]Cl_2$ **3** in methanol at 80 °C/69 bar gave the ruthenium(II)–quaterpyridinium complexes **13–16** in near quantitative yields. It is noteworthy that there was no NMR or UV/Vis spectroscopical evidence for the occurrence of incomplete quaternization reactions or dihalobis(quaterpyridinium)ruthenium(II) complexes $[Ru(QP\text{-}R)_2X_2]^{4+}$.[1,19,26]

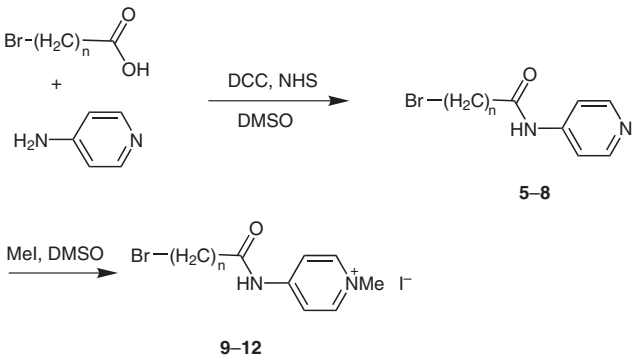


Scheme 6 Synthesis of tris(4,4′:2′,2″:4″,4‴-quarterpyridine-*N*′,*N*″)ruthenium(II) dichloride $[Ru(qpy)_3]Cl_2$

Table 1 Target Ruthenium(II)–Tris(quaterpyridinium) Complexes from MM2 Calculations



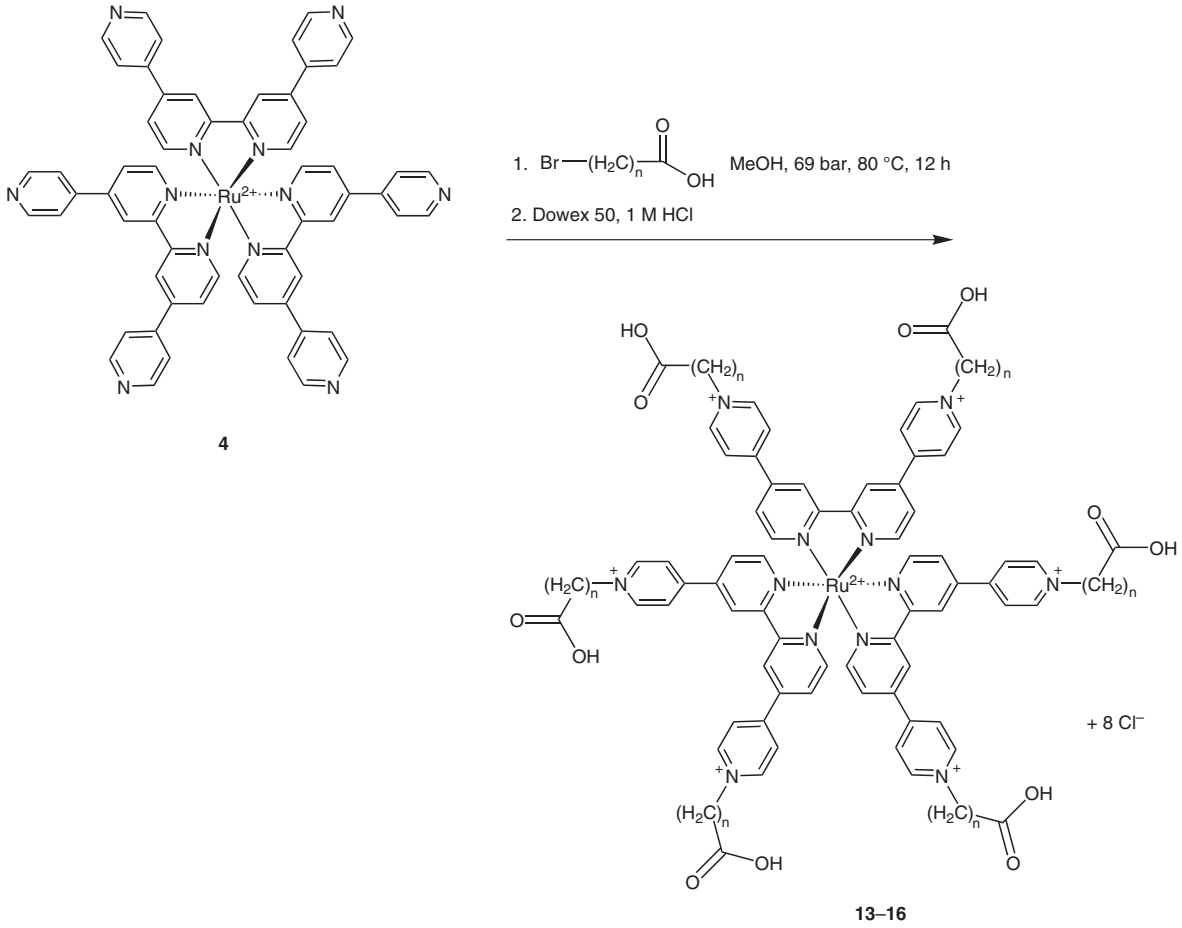
Compound	Complex, sum formula	n	R	Diameter (nm)
3	$Ru(qpy)_3^{2+}$ $C_{60}H_{42}Cl_2N_{12}Ru$	–	–	1.82
4	$Ru(QP\text{-}Me)_3^{8+}$ $C_{66}H_{60}Cl_8N_{12}Ru$	–	Me	2.11
13	$Ru(QP\text{-}C_1)_3^{8+}$ $C_{72}H_{60}Cl_8N_{12}O_{12}Ru$	1	CH_2CO_2H	2.43
14	$Ru(QP\text{-}C_2)_3^{8+}$ $C_{78}H_{72}Cl_8N_{12}O_{12}Ru$	2	$(CH_2)_2CO_2H$	2.92
15	$Ru(QP\text{-}C_3)_3^{8+}$ $C_{84}H_{84}Cl_8N_{12}O_{12}Ru$	3	$(CH_2)_3CO_2H$	2.99
16	$Ru(QP\text{-}C_4)_3^{8+}$ $C_{90}H_{96}Cl_8N_{12}O_{12}Ru$	4	$(CH_2)_4CO_2H$	3.18
17	$Ru(QP\text{-}C_1\text{-}py)_3^{14+}$ $C_{108}H_{102}Cl_{14}N_{24}O_6Ru$	1	$CH_2CO(4\text{-}py^+Me)$	3.76
18	$Ru(QP\text{-}C_2\text{-}py)_3^{14+}$ $C_{114}H_{114}Cl_{14}N_{24}O_6Ru$	2	$(CH_2)_2CO(4\text{-}py^+Me)$	3.89
19	$Ru(QP\text{-}C_3\text{-}py)_3^{14+}$ $C_{120}H_{126}Cl_{14}N_{24}O_6Ru$	3	$(CH_2)_3CO(4\text{-}py^+Me)$	4.09
20	$Ru(QP\text{-}C_4\text{-}py)_3^{14+}$ $C_{126}H_{138}Cl_{14}N_{24}O_6Ru$	4	$(CH_2)_4CO(4\text{-}py^+Me)$	4.55



Scheme 7 *N*,*N*′-Dicyclohexylcarbodiimide/*N*-hydroxysuccinimide mediated amide formation and in situ methylation

The synthesis of the highly charged (+14), nanometer-sized ruthenium(II)–tris(quaterpyridinium) complexes **17–20** was carried out at room temperature under high pressure (Scheme 9). Again, yields very close to 100% were reached.

In Table 2, the some important photophysical parameters of the newly synthesized highly charged ruthenium(II) complexes are summarized. The occurrence of distinct ^{3}MLCT transitions in the visible range of the UV/Vis spectrum can be regarded as proof of the existence of a ligand field around the ruthenium(II) center cation, which possesses D_3 symmetry, as it is typical for all tris-homoleptic ruthenium(II) complexes.[19] In agreement with the paradigms developed by Balzani and co-workers[19] and the literature available on ruthenium(II)–quaterpyridinium



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13–16

Scheme 8 High-pressure synthesis of ruthenium(II)–quaterpyridinium complexes

complexes,[1–16] a distinct red shift is observed for all complexes **13**–**20**.

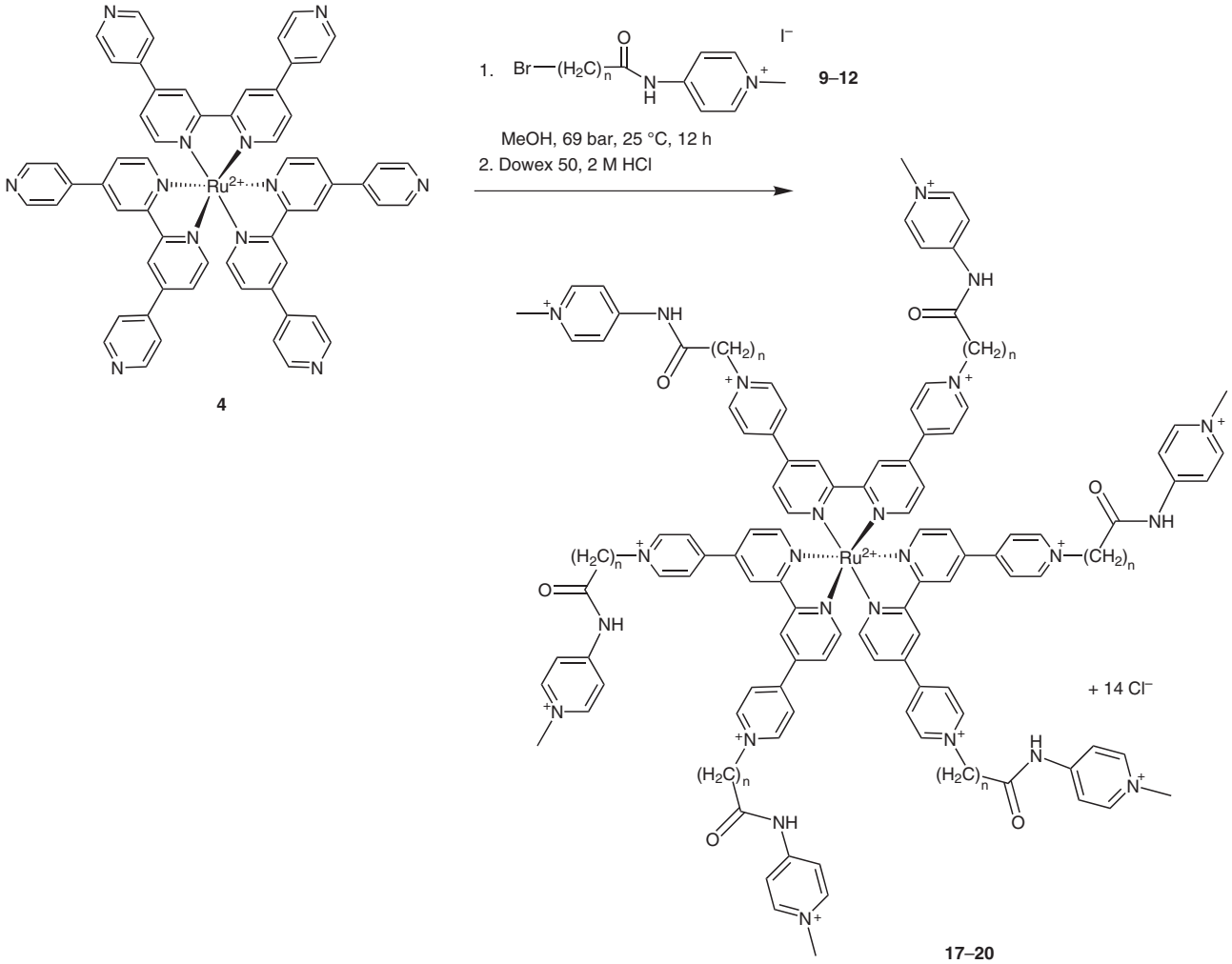
The luminescence occurring from the ^{3}MLCT states is bathochromically shifted as well, compared to $Ru(bpy)_3^{2+}$ in H_2O ($\lambda_{max,em}$ = 613 nm[19]).

All the tris-homoleptic ruthenium complexes were analyzed using a Bruker Esquire 3000 liquid chromatography electrospray quadrupole ion trap instrument (Table 3) and the compounds were fully characterized by IR and ^{1}H and ^{13}C NMR (Table 4). As it becomes apparent from Table 3, we succeeded in the destructionless ionization and detection of the tris-homoleptic complexes **3**, **4**, and **13**–**16**. The complexes show various amounts (0, 1, 2) of complexing chlorines. For the higher-charged (+14) ruthenium(II) complexes **17**–**20**, we were unable to obtain MS signals corresponding to the tris-homoleptic structures. Instead, we observed two characteristic signals, indicating the existence of two pathways during electrospray MS ionization and detection:

(a) For all four complexes, masses corresponding to the bis-heteroleptic complexes [Ru(QP-C_n-py)$_2$$Cl_2$] were found, demonstrating the occurrence of the loss of one ligand and replacement of the coordination sites at ruthenium(II) by two chlorides.

(b) The second pathway consists of the loss of all six substituents formerly bound to the external nitrogen atoms of the ruthenium(II)–quaterpyridinium complexes, thus regenerating the starting complex $Ru(qpy)_3^{2+}$. The signal $[C_{60}H_{42}N_{12}Ru]^+$ (*m*/*z* = 1032.2) is strongly indicative of this behavior.

By applying high pressure in key synthetic steps, tris-homoleptic ruthenium(II)–quarterpyridinium complexes possessing geometric dimensions on the nano scale have been synthesized. Due to their size, high charges (+8 or +14), and luminescent properties, these compounds will be tested for various applications in the near future. Among other applications, they will serve as mycobacterial channel blockers and monodisperse 'bottom-up' nanostructures for protein-binding experiments. Based on the properties of ruthenium(II)–tris(dimethylquaterpyridinium) octachloride **4**, we expect that the new complexes will feature suitable photoelectrochemical properties for solar energy conversion experiments as well.



Scheme 9 High-pressure synthesis of highly charged ruthenium(II)–quaterpyridinium complexes

Table 2 MLCT Typical for Tris-hololeptic Ruthenium Complex with D_3 Structure and Emission

Compound	Absorption λ_{max} (nm) [log ε ($M^{-1}cm^{-1}$)]			Fluorescence $\lambda_{max,em}$ (nm)
	Π–Π*	d–Π*	^{3}MLCT	^{3}MLCT
3[a]	247 [5.12]	307 [4.98]	474 [4.53]	638
4[a]	254 [4.77]	319 [4.08]	487 [4.20]	668
13	257 [4.84]	323 [4.41]	491 [4.23]	662
14	258 [5.04]	316 [4.48]	490 [4.27]	669
15	248 [4.85]	309 [4.59]	479 [4.21]	663
16	257 [5.03]	306 [4.55]	481 [4.19]	659
17	248 [5.01]	317 [4.61]	490 [4.14]	664
18	253 [5.03]	311 [4.63]	492 [4.04]	667
19	250 [5.00]	315 [4.48]	490 [4.22]	661
20	252 [4.98]	314 [4.58]	491 [4.60]	671

[a] Data are in agreement with literature values.[1]

Table 3 MS Data of the Ruthenium(II)–Tris(quaterpyridinium) Complexes

Compound	Complex sum formula	ES-MS [identified ion]	
		Calcd	Found
3	$Ru(qpy)_3^{2+}$ $C_{60}H_{42}Cl_2N_{12}Ru$	1032.3 $[C_{60}H_{42}N_{12}Ru]^+$	1032.3
4	$Ru(QP\text{-}Me)_3^{8+}$ $C_{66}H_{60}Cl_8N_{12}Ru$	1192.4 $[C_{60}H_{42}Cl_2N_{12}Ru]^+$	1192.4
13	$Ru(QP\text{-}C_1)_3^{8+}$ $C_{72}H_{60}Cl_8N_{12}O_{12}Ru$	1379.3 $[C_{72}H_{60}ClN_{12}O_{12}Ru]^+$	1379.3
14	$Ru(QP\text{-}C_2)_3^{8+}$ $C_{78}H_{72}Cl_8N_{12}O_{12}Ru$	1540.4 $[C_{78}H_{72}Cl_2N_{12}O_{12}Ru]^+$	1540.4
15	$Ru(QP\text{-}C_3)_3^{8+}$ $C_{84}H_{84}Cl_8N_{12}O_{12}Ru$	1589.5 $[C_{84}H_{84}ClN_{12}O_{12}Ru]^+$	1589.5
16	$Ru(QP\text{-}C_4)_3^{8+}$ $C_{90}H_{96}Cl_8N_{12}O_{12}Ru$	1673.6 $[C_{90}H_{96}Cl_8N_{12}O_{12}Ru]^+$	1673.6
17	$Ru(QP\text{-}C_1\text{-}py)_3^{14+}$ $C_{108}H_{102}Cl_{14}N_{24}O_6Ru$	1392.4 $[C_{72}H_{68}Cl_2N_{16}O_4Ru]^+$	1392.4, 1032.3
18	$Ru(QP\text{-}C_2\text{-}py)_3^{14+}$ $C_{114}H_{114}Cl_{14}N_{24}O_6Ru$	1448.5 $[C_{80}H_{84}Cl_2N_{16}O_4Ru]^+$	1448.5, 1032.3
19	$Ru(QP\text{-}C_3\text{-}py)_3^{14+}$ $C_{120}H_{126}Cl_{14}N_{24}O_6Ru$	1505.6 $[C_{80}H_{84}Cl_2N_{16}O_4Ru]^+$	1505.6, 1032.3
20	$Ru(QP\text{-}C_4\text{-}py)_3^{14+}$ $C_{126}H_{138}Cl_{14}N_{24}O_6Ru$	1560.6 $[C_{84}H_{92}Cl_2N_{16}O_4Ru]^+$	1560.6, 1032.3

Table 4 Characterization of the Optimized Compounds **3**, **4**, and **13–20**

Product[a]	FT-IR (KBr) (cm^{-1})	^1H NMR (400 MHz, $CDCl_3$) δ, ^3J (Hz)	^{13}C NMR (400 MHz, $CDCl_3$) δ (Hz)
3	3340, 2940, 2810, 2750, 2610, 2410, 2390, 1550, 1115, 1030	9.51 (d, *J* = 4, 6 H), 8.857 (d, *J* = 6, 6 H), 8.84 (d, *J* = 5, 6 H), 8.08 (dd, *J* = 7, 12 H), 8.03 (d, *J* = 6, 12 H)	157.31, 150.765, 146.11, 142.42, 125.35, 121.62
4		9.25 (d, *J* = 8, 6 H), 8.93 (d, *J* = 7, 6 H), 8.87 (s, *J* = 7, 6 H), 8.20 (d, *J* = 9, 12 H), 8.08 (d, *J* = 8, 12 H), 4.44 (s, 18 H)	158.82, 150.86, 147.23, 146.43, 136.23, 125.68, 121.86, 63.42
13	3340, 2945, 2810, 2755, 2610, 2410, 2390, 1550, 1115, 1030	10.01 (s, 6 H), 9.28 (d, *J* = 7, 12 H), 9.09 (d, *J* = 8, 6 H), 9.00 (d, *J* = 6, 6 H), 8.25 (d, *J* = 7, 12 H), 8.13 (s, *J* = 6, 6 H), 4.04 (s, *J* = 4, 12 H)	174.12, 157.37, 152.86, 149.50, 146.87, 146.36, 126.86, 126.00, 125.91, 59.49
14	3340, 2945, 2810, 2755, 2610, 2410, 2390, 1550, 1115, 1030	9.87 (s, 6 H), 9.41 (d, *J* = 8, 12 H), 9.07 (d, *J* = 6, 6 H), 8.93 (d, *J* = 6, 6 H), 8.23 (d, *J* = 8, 12 H), 8.08 (s, *J* = 6, 6 H), 4.91 (t, *J* = 8, 12 H), 2.08 (t, *J* = 4, 12 H)	171.59,157.34,152.97,150.27,148.99,146.15,129.28, 126.48, 125.95, 56.43, 34.49
15	3340, 2945, 2810, 2755, 2610, 2410, 2390, 1550, 1115, 1030	9.80 (s, 6 H), 9.28 (d, *J* = 6, 6 H), 9.13 (d, *J* = 8, 12 H), 8.70 (d, *J* = 7, 12 H), 8.19 (d, *J* = 8, 12 H), 4.25 (t, d *J* = 7, 12 H), 3.38 (m, *J* = 10, 12 H), 2.08 (t, *J* = 7, 12 H)	175.22,157.27,152.65,148.22,145.61,144.20, 126.25,124.54,123.56,68.29,27.44, 21.76
16	3340, 2945, 2810, 2755, 2610, 2410, 2390, 1550, 1115, 1030	9.60 (s, *J* = 8, 6 H) 9.00 (s, *J* = 6, 6 H) 8.90 (d, *J* = 9, 12 H), 8.21 (d, *J* = 8, 12 H), 8.07 (d, *J* = 8, 12 H), 4.75 (t, *J* = 7, 12 H), 3.38 (m, *J* = 10, 12 H), 2.31 (m, *J* = 9, 12 H), 2.08 (t, *J* = 7, 12 H)	174.02, 154.00, 152.34, 149.86, 145.52, 143.34, 126.12, 125.50, 122.13, 6103, 33.31, 30.84, 21.15
17	3345, 2940, 2810, 2750, 2610, 2410, 2395, 1550, 1115, 1030	9.32 (d, *J* = 7, 6 H), 9.06 (d, *J* = 6, 6 H), 8.88 (d, *J* = 6, 6 H), 8.43 (d, *J* = 5, 6 H), 8.21 (d, *J* = 5, 6 H), 8.10 (d, *J* = 5, 12 H), 8.03 (d, *J* = 6, 12 H), 7.18 (d, *J* = 6, 6 H), 7.00 (d, *J* = 6, 6 H), 6.80 (d, *J* = 4, 6 H, NH), 4.42 (s, 12 H), 3.94 (s, 18 H)	174.02, 154.00, 152.34, 149.86, 145.52, 143.34, 126.12, 125.50, 122.13, 61.03, 33.31, 30.84, 21.15

Table 4 Characterization of the Optimized Compounds **3**, **4**, and **13–20** (continued)

Product[a]	FT-IR (KBr) (cm^{-1})	^1H NMR (400 MHz, $CDCl_3$) δ, ^3J (Hz)	^{13}C NMR (400 MHz, $CDCl_3$) δ (Hz)
18	3345, 2940, 2810, 2750, 2610, 2410, 2395, 1550, 1115, 1030	9.48 (s, 6 H), 9.25 (d, *J* = 8, 6 H), 8.87 (d, *J* = 8, 6 H), 8.16 (m, *J* = 4, 24 H), 8.07 (m, *J* = 4, 24 H), 6.77 (d, *J* = 6, 6 H, NH), 3.93 (s, 12 H), 3.85 (s, 18 H), 2.89 (s, 12 H)	180.12, 159.80, 157.60, 146.70, 143.70, 139.90, 125.55, 121.87, 109.18, 108.74, 48.78, 44.20
19	3345, 2940, 2810, 2750, 2610, 2410, 2395, 1550, 1115, 1030	9.28 (d, *J* = 7, 6 H), 9.04 (d, *J* = 6, 6 H), 8.89 (d, *J* = 6, 6 H), 8.41 (d, *J* = 7, 6 H), 8.24 (d, *J* = 6, 6 H), 8.11 (d, *J* = 6, 12 H), 8.02 (d, *J* = 6, 12 H), 7.14 (d, *J* = 6, 6 H), 6.95 (d, *J* = 7, 6 H), 6.80 (d, *J* = 6, 6 H, NH), 3.94 (t, *J* = 4, 12 H), 3.84 (s, 18 H), 2.86 (t, *J* = 4, 12 H), 2.32 (t, *J* = 4, 12 H)	179.82, 158.64, 155.98, 150.64, 143.23, 139.94, 125.44, 121.75, 109.21, 109.03, 108.77, 47.90, 44.50, 34.21
20	3345, 2940, 2810, 2750, 2610, 2410, 2395, 1550, 1115, 1030	9.50 (s, 6 H), 9.27 (d, *J* = 7, 6 H), 9.01 (d, *J* = 7, 6 H), 8.15 (m, *J* = 4, 24 H), 8.04 (m, *J* = 4, 24 H), 6.77 (d, *J* = 5, 6 H, NH), 4.43 (s, 12 H), 3.84 (s, 18 H), 2.87 (s, 12 H), 2.71 (s, 12 H), 2.06 (s, 12 H)	179.40, 159.31, 151.63, 150.20, 145.90, 135.70, 122.06, 119.18, 104.20, 108.75, 58.86, 48.20, 30.30, 28.88

[a] Satisfactory microanalyses obtained: C ±0.04, H ±0.03, N ±0.05.

Solvents (ACS grade) and inorganic chemicals were purchased from Aldrich and Acros Organics. DMF was further purified by azeotropic distillation of DMF–toluene–H_2O (85:10:5), anhydrous and amine-free DMF was collected when reaching 152 °C at the top of a 20-cm vigreux column. All other chemicals and chromatography materials were either purchased from Aldrich, or Acros Organics and used without further purification. H_2O was of bidistilled quality. Compound 2 was prepared by following a published procedure.[25] All high-pressure reactions were performed in a Parr reactor (50 mL volume). All vacuum distillations were performed using a Büchi rotavap equipped with a solvent recovery system and pressure control. Further instrumentation: 400 MHz NMR (Varian), FT-IR (Nicolet 870), MS: Bruker Esquire 3000, Melting point apparatus (Fisher), Carlo Erba Strumentatione (CHN).

Compounds **4**, **13–20** underwent decomposition when heated above 350 °C without melting. Compounds **9–12** melted partially under decomposition in the temperature interval between 140 °C and 150 °C. Compounds **1**, **9–12** gave satisfactory microanalyses: C ±0.04, H ±0.03, N ±0.05.

4,4′:2′,2″:4″,4‴-Quarterpyridine (1); Procedure A

4,4′-Bipyridine (10.7 g, 0.0685 mol) was dissolved in anhyd THF (3 L) under a N_2 atmosphere. The soln was cooled to –58 °C (CO_2/EtOH bath). Then, freshly prepared LDA soln [*i*-Pr_2NH (15.0 g, 0.148 mol), anhyd Et_2O (250 mL) and 1.6 M BuLi in hexane (86 mL, 0.138 mol) under N_2] was added dropwise. The mixture was kept at –58 °C during the whole addition process, which took approx. 30 min. The mixture was then allowed to warm up to r.t. It developed a slight red color. After stirring for 30 min at r.t., the slight N_2 overpressure was removed and the mixture refluxed allowing contact with air through the reflux condenser. A color change to deep purple was observed. After 3 h of reflux, the soln was allowed to cool down to r.t. H_2O (200 mL) was added and the organic phase was separated and collected; the aqueous soln was extracted with CH_2Cl_2 (5 × 50 mL). The combined organic phases were dried (Na_2SO_4). After removal of the solvents under vacuum, a red oily residue was obtained. The product was purified by column chromatography (neutral alumina, CH_2H_2–MeOH, 97:3; R_f = 0.35). The product was further purified by recrystallization (acetone) to give a bright yellow solid; yield: 1.5 g (14%); mp 336 °C.

FT-IR (KBr): 3050, 1570, 1520, 800 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.88 (dd, ^3J = 1 Hz, 2 H,), 8.77 (m, ^3J = 1 Hz, 4 H), 8.73 (dd, ^3J = 1.4 Hz, 2 H), 7.92 (dd, ^3J = 2.8 Hz, 4 H), 7.83 (dd, ^3J = 2.4 Hz, 2 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 150.74, 150.64, 122.11, 121.50, 121.38, 118.11.

4,4′:2′,2″:4″,4‴-Quarterpyridine (1); Procedure B

4,4′-Bipyridine (5.0 g, 0.032 mol) were dissolved in DMF (70 mL) and Pd/C (0.70 g) were added to the soln. The mixture was stirred under reflux for 48 h. The solvent was removed and the residue was dissolved in $CHCl_3$ (50 mL), then the catalyst was filtered off. A bright yellow soln was obtained. $CHCl_3$ was distilled under vacuum, and the residue was recrystallized three times (acetone) to obtain a bright yellow product; yield: 2.2 g (44%); mp 336 °C.

4,4′:2′,2″:4″,4‴-Quarterpyridine (1); Procedure C

Soln I: Ph_3P (3.05 g, 0.0115 mol) and $NiCl_2 \cdot 6\,H_2O$ (0.70 g, 0.0029 mol) were dissolved in anhyd DMF (30 mL). The mixture was stirred intensely for 30 min under N_2 at 50 °C. A dark blue color emerged. Elemental Zn (0.20 g, 0.0031 mol) was added in one portion. The soln immediately became brownish and after an additional 30 min it became dark green.

Soln II: 4-(2-chloropyridin-4-yl)pyridine (**2**, 1.11 g, 0.0058 mol) was dissolved in anhyd DMF (10 mL) and purged with N_2 for 20 min.

Soln II was added dropwise to soln I over 10 min. The reaction temperature increased to 60 °C and was then kept at that temperature for 3 h. A dark brownish color indicated the end of the reductive coupling reaction. The mixture was cooled to r.t. and aq 35% NH_3 (100 mL) was added. The aqueous soln was then extracted with CH_2Cl_2 (10 × 20 mL). CH_2Cl_2 was removed under normal pressure and then DMF under high vacuum. After DMF was completely removed, Ph_3P was separated using column chromatography (silica gel, CH_2Cl_2, R_f = 0.96). The product was obtained by increasing the polarity of the mobile phase (CH_2Cl_2–MeOH, 95:5, R_f = 0.32); yield: 0.71 g (79%).

Tris(4,4′:2′,2″:4″,4‴-quarterpyridine-*N*′,*N*″)ruthenium(II) Dichloride (3)

$RuCl_3$ (0.20 g, 0.0010 mol) was dissolved in DMSO (10 mL) and refluxed under argon until the color of the soln turned to yellow. After cooling to r.t., ethylene glycol (30 mL) and 4,4′:2′,2″:4″,4‴-quarterpyridine (**1**, 1.2 g, 0.038 mol) were added. The mixture was refluxed under argon for 12 h. A dark red soln was obtained. The solvent was removed under high vacuum during 24 h. The dark red residue was dissolved in hot water (50 mL) and then allowed to cool to r.t. The soln was extracted CH_2Cl_2 (3 × 50 mL). The aqueous phases were collected and the solvent was removed. The dark phases were dissolved in EtOH–H_2O (90:10) and then purified by column chromatography (Sephadex G25). The complex was collected as bright red fraction, whereas the formed byproducts remaining on the column were clearly discernible by their violet colors. EtOH–

H_2O was removed under vacuum and the complex was refluxed in acetone (30 mL) for 1 h and then filtered while still hot. After drying under high vacuum for 24 h, red crystals were obtained and dried to give a red product; yield: 0.96 g (85%).

Tris(*N*,*N*‴-dimethyl-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-dium-*N*′,*N*″)ruthenium(II) Octachloride [Ru(QP-Me)$_3$]Cl$_8$ (4)

Ru(qpy)$_3$Cl$_2$ (**3**, 0.11 g, 0.1 mmol) was dissolved in DMF (50 mL) at r.t. and MeI (0.50 mL) was added to the soln. The mixture was then stirred under N_2 (69 bar) at 80 °C for 24 h. It was then allowed to cool to r.t., the solvent was removed under vacuum and the dark red residue was washed with acetone (3 × 20 mL). The product [Ru(QP-Me)$_3$]Cl$_2$I$_6$ was dried under vacuum; yield: 0.18 g (92%).

The complex was dissolved in hot H_2O (20 mL) and adsorbed on a chromatography column [Dowex-50, 15 g, preconditioned with aq 1 M HCl (20 mL) and flushed with H_2O (40 mL)]. [Ru(QP-Me)$_3$]Cl$_8$ was obtained using 1 M HCl as mobile phase. The H_2O–HCl was removed under high vacuum to give the product **4** as red crystals; yield: 0.13 g (99%).

2-Bromo-*N*-(1-methylpyridinium-4-yl)acetamide Iodide (9); Typical Procedure

A mixture of 2-bromoacetic acid (0.14 g, 0.001 mol), DCC (0.23 g, 0.0012 mol), and NHS (catalytic amount) in DMSO (10 mL) was stirred at 60 °C for 2 h, the soln turned to yellow. After cooling to r.t., a white precipitate (DCU) was filtered off and a yellow soln was obtained, to which 4-aminopyridine (0.10 g, 0.001 mol) was added at once. The soln was stirred at 80 °C for 6 h and its color turned dark brown. This soln, which contained **5** in 95% yield by ^{1}H NMR was directly reacted with MeI (0.30 mL). The mixture was stirred at 80 °C for 2 h and the solvent was removed under high vacuum to give a crude dark brown product. This was recrystallized twice (MeOH, ca. 10 mL) to give **9**; yield: 0.29 g (82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 4 Hz, 2 H), 8.03 (d, *J* = 4 Hz, 2 H), 6.81 (d, *J* = 6 Hz, 1 H), 3.85 (m, 2 H), 3.36 (s, 3 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 168.23, 168.02, 146.94, 107.65, 48.04, 28.41.

3-Bromo-*N*-(1-methylpyridinium-4-yl)propanamide Iodide (10)

Following the typical procedure for **9**, a soln of **6** was obtained in 92% yield (^{1}H NMR). Direct reaction with MeI following the typical procedure gave a crude dark brown product that was recrystallized twice (MeOH–EtOH, 1:1, ~10 mL) to give **10**; yield: 0.27 g (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 4 Hz, 2 H), 8.01 (d, *J* = 4 Hz, 2 H), 6.80 (d, *J* = 6 Hz, 1 H), 3.86 (s, 2 H), 3.34 (m, 3 H), 2.30 (t, *J* = 3 Hz, 2 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 173.71, 168.02, 146.94, 107.63, 48.01, 37.70, 28.40.

4-Bromo-*N*-(1-methylpyridinium-4-yl)butanamide Iodide (11)

Following the typical procedure for **9**, a soln of **7** was obtained in 94% yield (^{1}H NMR). Direct reaction with MeI following the typical procedure gave a crude dark brown product that was recrystallized twice (EtOH, ~8 mL) to give **11**; yield: 0.35 g (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 4 Hz, 2 H), 8.01 (d, *J* = 4 Hz, 2 H), 6.80 (d, *J* = 6 Hz, 1 H), 3.86 (s, 2 H), 3.15 (m, 3 H), 2.59 (t, *J* = 3 Hz, 2 H), 2.32 (m, 2 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 173.01, 168.01, 146.95, 107.60, 48.03, 34.50, 32.72, 28.51.

5-Bromo-*N*-(1-methylpyridinium-4-yl)pentanamide Iodide (12)

Following the typical procedure for **9**, a soln of **8** was obtained in 83% yield (^{1}H NMR). Direct reaction with MeI following the typical procedure gave a crude dark brown product that was recrystallized twice (EtOH, ~15 mL) to give **12**; yield: 0.35 g (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 4 Hz, 2 H), 8.03 (d, *J* = 4 Hz, 2 H), 6.81 (d, *J* = 6 Hz, 1 H), 3.85 (s, 2 H), 3.37 (s, 3 H), 2.59 (m, 2 H), 2.31 (m, 2 H), 1.68 (m, 2 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 173.01, 168.01, 146.95, 107.60, 48.02, 35.15, 33.02, 31.70, 24.11.

Tris[*N*,*N*‴-bis(carboxymethyl)-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-diium-*N*′,*N*″]ruthenium(II) Octachloride [Ru(QP-C$_1$)$_3$]Cl$_8$ (13); Typical Procedure

A mixture of complex **3** (0.11 g, 0.1 mmol) and 2-bromoacetic acid (0.20 g, 0.0014 mol) in MeOH (50 mL) was stirred under N_2 (69 bar) at 80 °C for 12 h. The mixture was allowed to cool to r.t. and the solvent was removed under vacuum. The dark red residue was washed with acetone (3 × 20 mL) and dried under high vacuum to give [Ru(QP-C$_1$)$_3$]Br$_6$Cl$_2$; yield: 0.19 g (97%).

The ion exchange (bromide for chloride) was achieved by using Dowex-50 as ion exchanger, as described in the procedure for **4**. Also here, the yield was very close to quantitative (99%).

Tris[*N*,*N*‴-bis(2-carboxyethyl)-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-diium-*N*′,*N*″]ruthenium(II) Octachloride [Ru(QP-C$_2$)$_3$]Cl$_8$ (14)

Following the typical procedure for **13**, using 3-bromopropionic acid (0.22 g, 0.0014 mol) and washing the dark red residue with acetone (3 × 20 mL), gave [Ru(QP-C$_2$)$_3$]Br$_6$Cl$_2$; yield 0.21 g (98.5%), which was converted into **14** as given in the typical procedure in almost quantitative yield.

Tris[*N*,*N*‴-bis(3-carboxypropyl)-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-diium-*N*′,*N*″]ruthenium(II) Octachloride [Ru(QP-C$_3$)$_3$]Cl$_8$ (15)

Following the typical procedure for **13**, using 4-bromobutanoic acid (0.24 g, 0.0014 mol) and washing the dark red residue with acetone–MeOH (90:10, 3 × 20 mL) gave [Ru(QP-C$_3$)$_3$]Br$_6$Cl$_2$; yield: 0.21 g (97.5%) which was converted into **15** as given in the typical procedure in almost quantitative yield.

Tris[*N*,*N*‴-bis(4-carboxybutyl)-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-diium-*N*′,*N*″]ruthenium(II) Octachloride [Ru(QP-C$_4$)$_3$]Cl$_8$ (16)

Following the typical procedure for **13**, using 5-bromopentanoic acid (0.26 g, 0.0014 mol) in MeOH (50 mL) and washing the dark red residue with acetone–MeOH (90:10, 3 × 20 mL) gave [Ru(QP-C$_4$)$_3$]Br$_6$Cl$_2$; yield: 0.21 g (96.2%), which was converted into **16** as given in the typical procedure in almost quantitative yield.

Tris(*N*,*N*‴-bis{[(1-methylpyridinium-4-yl)carbonyl]methyl}-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-diium-*N*′,*N*″}ruthenium(II) Tetradecachloride [Ru(QP-C$_1$-py)$_3$]Cl$_{14}$ (17); Typical Procedure

A mixture of complex **3** (0.11 g, 0.1 mmol) and compound **9** (0.40 g, 0.0011 mol) in MeOH (50 mL) was stirred under N_2 (69 bar) at 25 °C for 12 h. The solvent was removed under vacuum. The dark red residue was washed with hot acetone (3 × 20 mL) and dried under high vacuum to give [Ru(QP-C$_1$-py)$_3$]Cl$_2$Br$_6$I$_6$; yield: 0.30 g (93%). Anion exchange was performed as described in the procedure for **4** giving **17** in almost quantitative yield using 2 M HCl as mobile phase.

Tris(*N*,*N*‴-bis{2-[(1-methylpyridinium-4-yl)carbonyl]ethyl}-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-diium-*N*′,*N*″}ruthenium(II) Tetradecachloride [Ru(QP-C$_2$-py)$_3$]Cl$_{14}$ (18)

Following the typical procedure for **17**, using **10** (0.42 g, 0.0011 mol), gave [Ru(QP-C$_2$-py)$_3$]Cl$_2$Br$_6$I$_6$; yield: 0.31 g (93%), which

was converted into **18** as given in the typical procedure in almost quantitative yield.

Tris(*N*,*N*‴-bis{3-[(1-methylpyridinium-4-yl)carbonyl]propyl}-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-diium-*N*′,*N*″}ruthenium(II) Tetradecachloride [Ru(QP-C_3-py)$_3$]Cl_{14} (19)

Following the typical procedure for **17**, using **11** (0.43 g, 0.0011 mol), gave [Ru(QP-C_3-py)$_3$]$Cl_2Br_6I_6$; yield: 0.31 g (91%), which was converted into **19** as given in the typical procedure in almost quantitative yield.

Tris(*N*,*N*‴-bis{4-[(1-methylpyridinium-4-yl)carbonyl]butyl}-4,4′:2′,2″:4″,4‴-quarterpyridin-*N*,*N*‴-diium-*N*′,*N*″}ruthenium(II) Tetradecachloride [Ru(QP-C_4-py)$_3$]Cl_{14} (20)

Following the typical procedure for **17**, using **12** (0.44 g, 0.0011 mol), gave [Ru(QP-C_4-py)$_3$]$Cl_2Br_6I_6$; yield: 0.32 g (94%), which was converted into **19** as given in the typical procedure in almost quantitative yield.

Acknowledgment

Financial support from Kansas State University, Kansas NSF-EPSCoR (First Award #4166) and the Terry C. Johnson Center for Basic Cancer Research (Innovative Cancer Research Grant) is gratefully acknowledged. The authors thank Prof. Dr. John Tomich for the use of the Bruker Esquire 3000 liquid chromatography electrospray quadrupole ion trap instrument of the Biochemistry Core Facility at KSU. The authors also thank Prof. Dr. Dan Higgins for the use of a Fluoromax-2 fluorometer and an Agilent UV/Vis spectrometer.

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