4,4''''-Azobis[2,2':6',2''-terpyridine] and its Metal Complexes

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By two different routes, 4,4''''-azobis[2,2':6',2''-terpyridine] was synthesized. Its ruthenium complexes show interesting metal-to-ligand charge transfer (MLCT) absorption maxima in the electronic spectra. They represent the first ruthenium complexes of terpyridine units to give blue solutions.

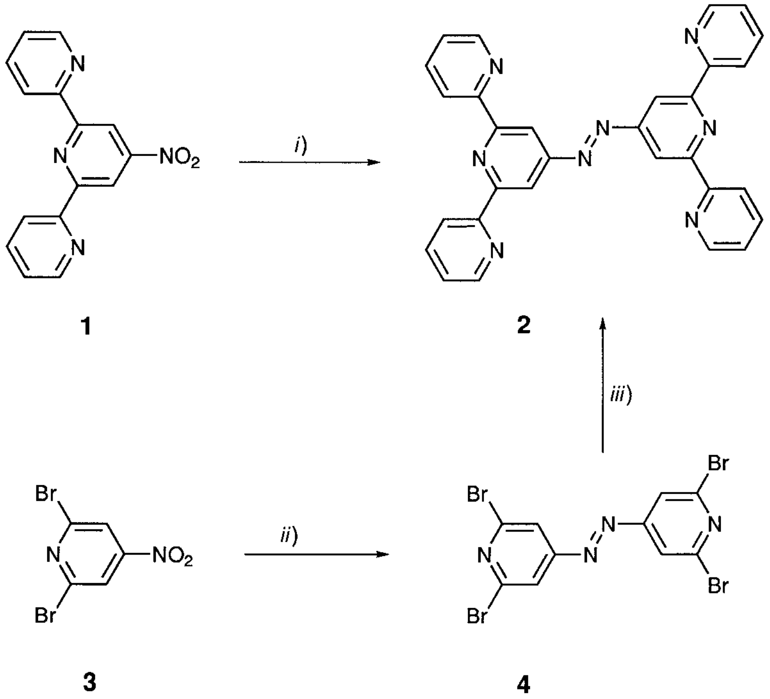
Dendrimers, in general, and metallodendrimers, in particular, are a subject of great interest [1]. Oligopyridines incorporated in metallodendrimers are mainly based on 2,2'-bipyridine (bpy) and 2,2':6',2''-terpyridine (tpy) and can be synthesized convergently or divergently. Bpy ligands have been attached to oligoamines [2] or to the *Fréchet*-type dendrimers [3]. In the terpyridine series, most of the metallodendrimers contain spacers such as phenylene [4] or acetylene groups [5]. Alternatively, the tpy units have been attached together or to a bpy ligand with an ether bridge. This chemistry has been extensively investigated [6].

There exist, to the best of our knowledge, only a few examples of metal complexes or dendrimers containing an azo group as the spacer. In one case, a *Fréchet*-type dendrimer was attached to azobenzene to investigate the isomerization from the (*E*)- to the (*Z*)-form [7]. In the other case, *Jiang* and *Aida* found that a large aryl ether azodendrimer undergoes (*Z*)- to (*E*) isomerization at the interior azo unit upon exposure to weak infrared (IR) light with a wave number of *ca.* 1600 cm^{-1} [8]. The 4,4''-azo-bis[2,2'-bipyridine] has also been synthesized, and some of its metal complexes were reported [9][10]. Alternatively, azobenzene was attached to the surface of dendrimers to obtain photoswitchable supramolecular systems [11][12]. Recently, *Nishihara* and co-workers reported the synthesis of azobenzene-bridged bis[terpyridine] ligand and some of its rhodium complexes [13].

We report here the synthesis of ruthenium complexes containing the azo group as a spacer directly linked to the two tpy units. We have already reported the synthesis of 4'-nitro-2,2':6',2''-terpyridine (**1**) [14][15] which is of interest due to the versatile synthetic accessibility of the nitro group. While the nitro group can easily be reduced to an amine [14][15], it can also be reduced to the azo compound **2** by relatively weak reducing agents such as $NaBH_4$ [16] or $SnCl_2 \cdot 2\,H_2O$ [17] in 40 and 33% yields, respectively (*Scheme 1*).

Alternatively, 2,6-dibromo-4-nitropyridine (**3**) was reduced to the azo compound **4**, which was then converted to **2** by a 4-fold *Stille* coupling reaction [18]. The structure of **4** was determined by X-ray crystal-structure analysis and was found to have the (*E*)-

Scheme 1



i) $NaBH_4$, EtOH, 1 h, 78°, 40%. *ii*) $SnCl_2 \cdot 2\,H_2O$, H_2O, 100°, 2 h; 49%. *iii*) (2-Pyridyl)$SnBu_3$ (4 mol-equiv.), [$Pd(PPh_3)_4$] (0.08 mol-equiv.), toluene, 110°, 16 h; 45%.

configuration (*Fig. 1*)[1]). Compound **4** is a planar molecule with both pyridine rings in almost the same plane.

The azo compound **2** is an orange microcrystalline solid that gives a green complex upon reaction with Fe^{2+}. In the ^1H-NMR spectrum of **2**, five signals were observed. The signal for H–C(3′) at δ 9.00 is more shifted to lower field than in 4′-(methylsulfonyl)-2,2′:6′,2″-terpyridine (δ 8.88) [14] or 4′-chloro-2,2′:6′,2″-terpyridine (δ 8.48) [14], indicating the electron-withdrawing ability of the azo group. Only the nitro group causes a shift to still lower field (δ 9.17) [15].

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[1]) Crystal-structure determination of $C_{10}H_4Br_4N_4$: crystal size 0.09 × 0.32 × 0.40 mm, M_r 499.806; monoclinic, space group $P2_1/c$, $a = 4.4862(5)$, $b = 7.5506(6)$, $c = 19.7032(15)$ Å, $V = 665.4(1)$ Å^3, $F(000) = 464$, $Z = 2$, $D_c = 2.49$ g cm^{-3}; unit-cell parameters were determined by the least-squares method on 25 independent reflections. Data collection was carried out on a four-circle *Enraf-Nonius-CAD4* diffractometer with monochromated MoK_α radiation (λ 0.71069 Å); T 293 K. The ω-2θ technique was used to measure 1809 reflections, range $2° \leq \theta \leq 30.44°$. Three standard reflections monitored every hour during data collection showed a decay of 4.72%. To solve and refine the structure, 1585 unique data with $I \geq 3\sigma(I)$ were used. The usual corrections were applied. The absorption correction was determined by means of Ψ scans; max/min transmission 1.0/0.23. The structure was solved by direct methods with the program SIR92 [19]. Anisotropic least squares refinement was carried out on all non-H-atoms with the program CRYSTALS [20]. The H-atoms are in calculated positions with a fixed distance of 0.96 Å: scattering factors were taken from the International Tables for X-Ray Crystallography [21].

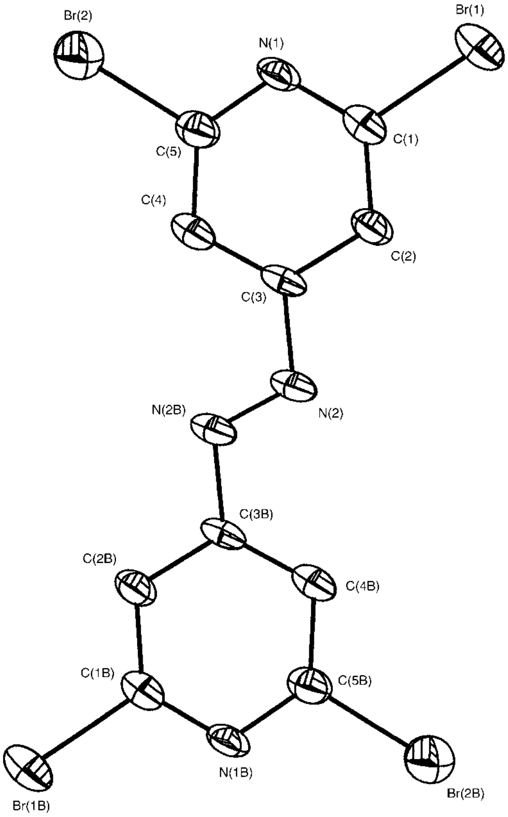

Fig. 1. *Solid-state crystal structure of* **4**

Two ruthenium complexes of ligand **2** were prepared by standard methods [15], to exemplify its reactivity and properties. Compound **2** was reacted with (2,2′:6′,2″-terpyridin-4′-ol)ruthenium trichloride ([Ru(HO-tpy)Cl_3]) [15] and (4′-chloro-2,2′:6′,2″-terpyridine)ruthenium trichloride ([Ru(Cl-tpy)Cl_3] [15]) in MeOH to give the two complexes **5** and **6** in 39 and 53% yield, respectively (*Scheme 2*). We assume that both complexes **5** and **6** contain the (*E*)-azo function due to steric hinderance. This view is supported by the fact that **4**, a precursor of **2**, exhibits already the (*E*)-configuration. Both complexes are symmetric and exhibit ten signals in the ^{1}H-NMR spectra, five for each of the ligands **2** and 2,2′:6′,2″-terpyridin-4′-ol or 4′-chloro-2,2′:6′,2″-terpyridine, respectively. In complex **5**, the H−C(3‴)[2]) signal of the 2,2′:6′,2″-terpyridin-4′-ol ligand was observed at δ 8.34, while in complex **6**, H−C(3‴)[2]) appeared at δ 8.91, which is consistent with the electron-releasing (OH) and -withdrawing (Cl) groups. The H−C(3′) signal of the azobis[terpyridine] ligand was observed at δ 9.37 (**5**) and 9.44 (**6**), respectively (*Fig. 2*).

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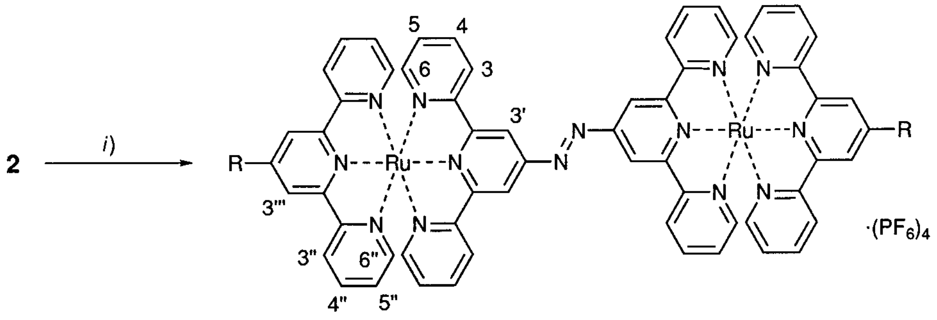
[2]) In the ^{1}H-NMR spectra, the numbering of the ligands 2,2′:6′,2″-terpyridin-4′-ol and 4′-chloro-2,2′:6′,2″-terpyridine of **5** and **6**, respectively, is arbitrary (see *Scheme 2*).

Scheme 2



5[2]) R = OH
6[2]) Cl

i) [Ru(HO-tpy)Cl_3], *N*-ethylmorpholine, MeOH, 64°, 1 h; **5** (39%). [Ru(Cl-tpy)Cl_3], *N*-ethylmorpholine, MeOH, 64°, 1 h; **6** (53%).

Usually, ruthenium complexes of tpy ligands are red to orange and exhibit the metal-to-ligand charge transfer (MLCT) band in the range 460–550 nm. Compared with that, the MLCT absorption in the electronic spectra of the complexes **5** and **6** was shifted to lower energy and appeared at 633 and 578 nm, respectively (*Fig. 3*). The π-π absorption of the azo group was observed in both complexes at 470 nm. Complexes **5** and **6** are the first examples of blue ruthenium(II) complexes containing tpy ligands.

Ruthenium(II) complexes **5** and **6** are electrochemically oxidized in MeCN solution, each exhibiting an oxidation wave corresponding to the Ru^{II}/Ru^{III} process. The potential of the ruthenium(II) complexes **5** and **6** (*vs.* ferrocene/ferrocenium internal reference) are 0.886 and 0.975 V, respectively, which are in accord with other ruthenium complexes of tpy ligands.

In conclusion, we have synthesized 4,4''''-azobis[2,2':6',2''-terpyridine] (**2**) and prepared some metal complexes. The azo (*E*)/(*Z*) isomerism of the metal complexes may be used as a redox-responsive molecular switch in the photochemistry (*cf.* [22]). Therefore, the isomerization and photochemistry of **2** and its complexes are currently under investigation in our group.

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Experimental Part

General. All reagents were used as supplied. Column chromatography (CC): silica gel (0.060–0.200 mm) from *Chemie Uetikon*, aluminium oxide (type *507 C* neutral; 100–125 mesh) from *Fluka*. Electro-chemical measurements: *Ecochemie-Autolab-PGSTAT-20 Potentiostat.* M.p.: *Büchi 535* apparatus; not corrected. UV/VIS Spectra: *Perkin-Elmer Lambda-19* spectrometer; λ_{max} (log ε) in nm. NMR Spectra: *Bruker AM-250* spectrometer; δ in ppm rel. to $SiMe_4$, *J* in Hz. MALDI-TOF-MS: *Perspective-Biosystems Voyagers-RP* biospectrometry workstation; *m/z*.

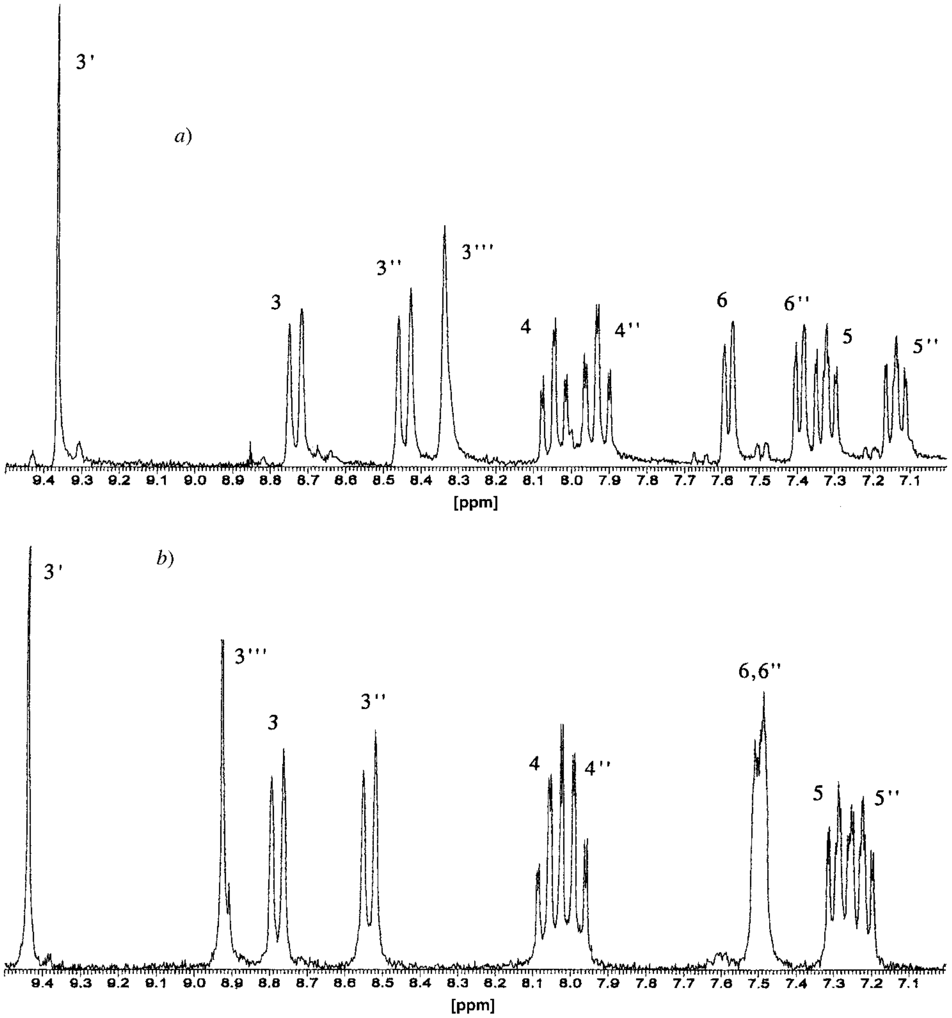

Fig. 2. *^{1}H-NMR Spectra* (CD_3CN) *of the Ru^{II} complexes* a) **5** *and* b) **6**[2])

4,4′′′′-Azobis[2,2′:6′,2″-terpyridine] (**2**). A suspension of 4′-nitro-2,2′:6′,2″-terpyridine (**1**; 100 mg, 0.36 mmol) and $NaBH_4$ (40 mg, 1.08 mmol) in EtOH (20 ml) was heated under reflux for 1 h. After cooling to r.t., EtOH was evaporated and H_2O (30 ml) added. The aq. phase was extracted with CH_2Cl_2 (3 × 30 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. CC (aluminium oxide, CH_2Cl_2/AcOEt 1:1) followed by recrystallization in EtOH gave 50 mg (40%) of **2**. Yellow microcrystalline solid. M.p. 303–304°. UV (MeCN): 243 (4.20), 281 (4.22), 350 (sh, 3.50); min. 222 (4.08), 261 (4.12). ^{1}H-NMR ($CDCl_3$): 9.00 (*s*, 4 H, H–C(3′)); 8.79 (*d*, *J* = 7.80, 4 H, H–C(6)); 8.69 (*d*, *J* = 7.80, 4 H, H–C(3)); 7.91 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H–C(4)); 7.40 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H–C(5)). ^{13}C-NMR ($CDCl_3$): 159.53, 157.53, 149.33, 146.10, 137.03, 124.18, 121.44, 114.18. MALDI-TOF-MS: 492 (M^+). Anal. calc. for $C_{30}H_{20}N_8$: C 73.16, H 4.09, N 22.75; found: C 73.20, H 4.90, N 22.39.

4,4′-Azobis[2,6-dibromopyridine] (**4**). To a soln. of tin(II) chloride dihydrate (1.68 g, 7.44 mmol) in 10% KOH soln. (50 ml), 2,6-dibromo-4-nitropyridine (**3**; 1.0 g, 3.55 mmol) was added, and the mixture was heated for 2 h under reflux. The aq. phase was then extracted with CH_2Cl_2 (6 × 50 ml) and the combined org. phase

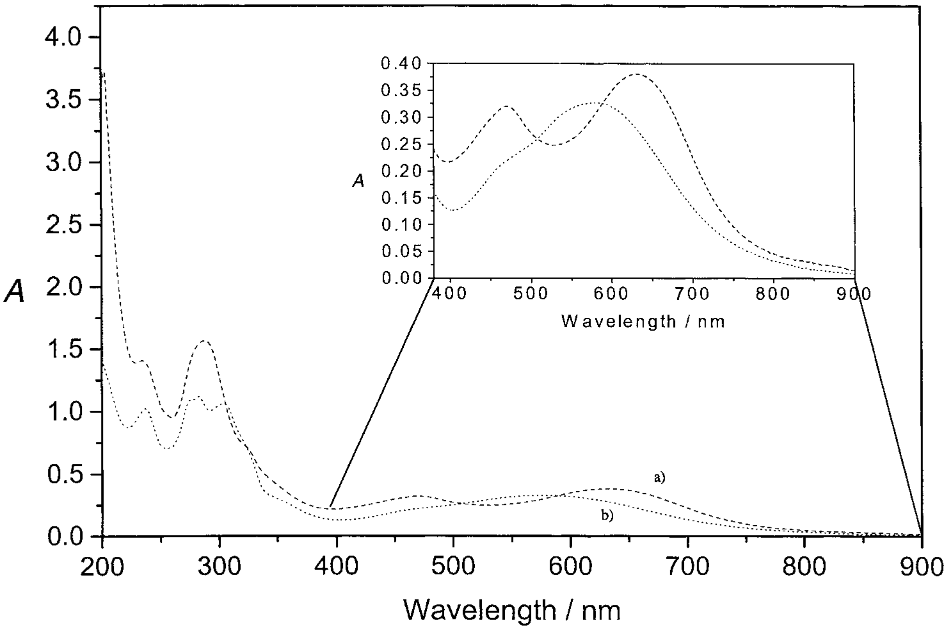

Fig. 3. *UV/VIS Spectra* (CD_3CN) *of the Ru*^{II} *complexes* a) **5** *and* b) **6**

dried ($MgSO_4$) and evaporated. CC (silica gel, CH_2Cl_2/hexane 3 : 2) followed by recrystallization in EtOH gave 400 mg (45%) of **4**. Orange crystals. M.p. 145°. ^1H-NMR ($CDCl_3$): 7.91 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 158.35, 142.10, 120.33. MALDI-TOF-MS: 500 (M^+). Anal. calc. for $C_{10}H_4Br_4N_4$: C 24.03, H 0.81, N 11.21; found: C 24.53, H 1.32, N 11.33.

Ruthenium(II) Complexes **5** *and* **6**: *General Procedure.* Azo-bis[terpyridine] **2** (20 mg) and *N*-ethylmorpholine (0.1 ml) were added to a suspension of [Ru(Cl-tpy)Cl_3] or [Ru(HO-tpy)Cl_3] (2 mol-quiv.) in MeOH (20 ml), and the mixture was heated for 1 h. The resulting soln. was filtered through *Celite*, and then excess ammonium hexafluorophosphate was added to the filtrate. The precipitate was collected by filtration, washed with ice-cold MeOH (5 ml), H_2O (5 ml), and finally Et_2O (5 ml), and then air-dried. CC (silica gel, MeCN/ammonia 30 : 1) followed by recrystallization by diffusion of Et_2O into the MeCN soln. of **5** or **6** gave the pure compounds.

[μ-(4,4''''-Azobis[2,2':6',2''-terpyridine]-$\kappa N^1,\kappa N^{1'},\kappa N^{1''}$*:* $\kappa N^{1'''},\kappa N^{1''''},\kappa N^{1'''''}$*)]bis(2,2':6',2''-terpyridin-4-ol-*$\kappa N^1,\kappa N^{1'},\kappa N^{1''}$*)diruthenium(4+) Tetrakis[hexafluorophosphate(1−)]* (**5**): 22 mg (39%). UV (MeCN): 234 (4.99), 288 (5.04), 470 (4.35), 633 (4.43); min. 228 (4.99), 260 (4.83), 397 (4.18), 526 (4.24). ^1H-NMR (CD_3CN)^2): 9.37 (*s*, 4 H, H−C(3')); 8.73 (*d*, *J* = 7.80, 4 H, H−C(3)); 8.45 (*d*, *J* = 7.80, 4 H, H−C(3'')); 8.34 (*s*, 4 H, H−C(3''')); 8.05 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H−C(4)); 7.95 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H−C(4'')); 7.58 (*d*, *J* = 7.80, 4 H, H−C(6)); 7.39 (*d*, *J* = 7.80, 4 H, H−C(6'')); 7.32 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H−C(5)); 7.15 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H−C(5'')). MALDI-TOF-MS: 1338 ($[M + PF_6]^+$), 1193 (M^+), 843 ($[M -$ Ru(tpyOH)$]^+$). Anal. calc. for $C_{60}H_{42}F_{12}N_{14}O_2P_2Ru_2 \cdot H_2O$: C 48.01, H 2.95, N 13.06; found: C 47.83, H 2.30, N 12.79.

[μ-[4,4''''-Azobis[2,2':6',2''-terpyridine]-$\kappa N^1,\kappa N^{1'},\kappa N^{1''}$*:* $\kappa N^{1'''},\kappa N^{1''''},\kappa N^{1'''''}$*)]bis(4'-chloro-2,2':6',2''-terpyridine-*$\kappa N^1,\kappa N^{1'},\kappa N^{1''}$*)diruthenium(4+) Tetrakis[hexafluorophosphate(1−)]* (**6**). 31 mg (53%). UV (MeCN): 237 (4.87), 283 (4.91), 304 (4.89), 470 (sh, 4.18), 578 (4.37); min. 222 (4.80), 256 (4.71), 292 (4.86), 403 (3.96). ^1H-NMR (CD_3CN)^2): 9.44 (*s*, 4 H, H−C(3')); 8.91 (*s*, 4 H, H−C(3''')); 8.78 (*d*, *J* = 7.80, 4 H, H−C(3)); 8.53 (*d*, *J* = 7.80, 4 H, H−C(3'')); 8.05 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H−C(4)); 7.99 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H−C(4'')); 7.50 (*m*, 8 H, H−C(6), H−C(6'')); 7.29 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H−C(5)); 7.22 (*ddd*, *J* = 8.30, 7.80, 1.95, 4 H, H−C(5'')). MALDI-TOF-MS: 1375 ($[M + PF_6]^+$), 1230 (M^+), 1195 ($[M - Cl]^+$),861 ($[M -$ Ru(tpyCl)$]^+$). Anal. calc. for $C_{60}H_{40}Cl_2F_{12}N_{14}P_2Ru_2 \cdot H_2O$: C 46.86, H 2.75, N 12.75; found: C 46.40, H 2.10, N 12.45.

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