Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supporting Information
for

Mono- and dinuclear ruthenium(II) 1,6,7,12-tetraazaperylene complexes

Thomas Brietzke, Wulfhard Mickler, Alexandra Kelling and Hans-Jürgen Holdt*

Crystallographic information

[**2**]$(PF_6)_2 \cdot 0.5CH_3CN \cdot 0.5$toluene

The complex [**2**]$(PF_6)_2 \cdot 0.5CH_3CN \cdot 0.5$toluene crystallises with one half of a molecule toluene (disordered around the inversion center). The disorder models gave unsatisfactory results. Therefore, the data were corrected for disordered solvent using the SQUEEZE option in PLATON[1].

[**3**]$(PF_6)_2 \cdot 2$toluene

The solvent molecules toluene in [**3**]$(PF_6)_2 \cdot 2$toluene were refined over two position, with occupancy ratios of 80:20 and 70:30 and a set of geometrical restraints/constraints. (The methyl aryl distances were restrained to standard values by DFIX-instructions and the aromatic rings were constrained to a regular hexagon [d = 1.39] by AFIX 66 - instructions.)

Table S 1 Selected Bond Lengths (Å) and Angles (deg) for [**2**]$(PF_6)_2 \cdot 0.5CH_3CN \cdot 0.5$toluene, [**3**]$(PF_6)_2 \cdot 2$toluene and [**4**]$(PF_6)_2 \cdot 3$acetone$\cdot 0.5H_2O$ as well as the ruthenium and tape distances of the according dimer.

Compound	[**2**]$(PF_6)_2 \cdot 0.5CH_3CN \cdot 0.5$toluene	[**3**]$(PF_6)_2 \cdot 2$toluene	[**4**]$(PF_6)_2 \cdot 3$acetone$\cdot 0.5H_2O$
Ru-N(1)	2.057(2)	2.047(2)	2.065(3)
Ru-N(4)	2.062(3)	2.056(3)	2.053(3)
Ru-N(5)	2.048(3)	2.062(3)	2.054(3)
Ru-N(6)	2.060(2)	2.069(2)	2.057(3)
Ru-N(7)	2.073(3)	2.063(3)	2.061(3)
Ru-N(8)	2.056(3)	2.061(3)	2.065(3)
N(1)-Ru-N(4)	79.10(10)	79.15(10)	79.19(13)
N(5)-Ru-N(6)	78.52(10)	78.57(10)	78.37(11)
N(7)-Ru-N(8)	78.42(10)	77.98(10)	78.27(12)
Ru···Ru	10.83	10.37	10.50
tape···tape[a]	3.40(8)	3.38(7)	3.37(3)

[a] Distances are between the calculated plains (MERCURY) of the tape moieties using the non-hydrogen atoms only.

[1] A. L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

UV-Vis absorption

Table S 2 Full absorption Data[a] of the synthesized mono- and dinuclear ruthenium(II)-complexes.

compound	λ [nm] (ε [10^{-4}M^{-1}cm^{-1}])
$[Ru(bpy)_2bpym]^{2+}$	286 (55.9±0.7), 427 (11.2±0.1)
$[Ru(dmbpy)_2bpym]^{2+}$	258 (27.6±2.2), 284 (50.7±3.9), 424 (10.6±0.8)
$[Ru(tmbpy)_2bpym]^{2+}$	206 (62.6±0.1), 267 (42.6±0.1), 288 (61.1±0.1), 418 (14.0±0.2)
$[Ru(dtbbpy)_2bpym]^{2+}$	249 (27.6±1.0), 258 (28.3±1.1), 286 (52.7±2.2), 421 (10.8±0.3)
$[Ru(dtbbpy)_2tpphz]^{2+}$	247 (51.6±0.4), 283 (92.7±0.2), 363 (18.5±0.3), 382 (26.8±0.4), 440 (16.2±0.1)
$[Ru(bpy)_2dbneil]^{2+}$	257 (53.2±1.0), 285 (79.0±2.1), 329 (45.7±0.8), 418 (23.4±0.3), 440 (25.6±0.1), 491 (6.1±0.2), 593 (19.3±0.1)
$[Ru(dmbpy)_2dbneil]^{2+}$	233 (61.6±0.3), 259 (58.0±0.2), 284 (84.0±0.1), 328 (46.1±0.2), 381 (24.7±0.3), 423 (25.3±0.2), 444 (25.5±0.2), 608 (21.1±0.2)
$[Ru(tmbpy)_2dbneil]^{2+}$	290 (79.4±0.4), 392 (25.1±0.2), 422 (23.9±0.2), 446 (21.3±0.3), 618 (18.4±0.2)
$[Ru(dtbbpy)_2dbneil]^{2+}$	259 (55.7±1.5), 285 (82.1±2.0), 328 (45.1±1.2), 392 (24.3±0.7), 423 (25.6±0.7), 441 (24.5±0.7), 610 (20.0±0.5)
$[Ru(bpy)_2tape]^{2+}$	245 (60.8±3.4), 284 (61.8±3.5), 396 (18.7±0.7), 421 (19.4±0.8), 609 (14.0±0.5)
$[Ru(phen)_2tape]^{2+}$	262 (78.3±1.3), 389 (20.5±0.5), 420 (19.2±0.4), 441 (15.0±0.2), 606 (12.7±0.2)
$[Ru(dmbpy)_2tape]^{2+}$	283 (55.3±0.6), 399 (17.4±0.4), 421 (17.0±0.4), 625 (12.5±0.3)
$[Ru(tmbpy)_2tape]^{2+}$	247 (50.0±1.5), 287 (60.2±1.8), 399 (18.4±0.5), 418 (17.0±0.4), 640 (12.4±0.4)
$[Ru(dtbbpy)_2tape]^{2+}$	284 (60.2±3.0), 399 (18.5±0.7), 422 (18.0±1.0), 626 (13.2±0.1)
$[\{Ru(bpy)_2\}_2(\mu\text{-bpym})]^{4+}$	244 (43.1±0.1), 281 (89.1±0.1), 413 (25.2±0.1), 594 (6.2±0.1)
$[\{Ru(dmbpy)_2\}_2(\mu\text{-bpym})]^{4+}$	280 (96.2±1.5), 416 (29.9±0.5), 612 (7.9±0.1)
$[\{Ru(tmbpy)_2\}_2(\mu\text{-bpym})]^{4+}$	285 (99.0±2.9), 412 (28.9±1.4), 619 (7.2±0.1)
$[\{Ru(dtbbpy)_2\}_2(\mu\text{-bpym})]^{4+}$	255 (49.2±1.1), 281 (101.0±1.6), 415 (31.9±0.6), 617 (7.6±0.3)
$[\{Ru(dtbbpy)_2\}_2(\mu\text{-tpphz})]^{4+}$	247 (66.1±1.8), 283 (183.2±5.3), 352 (31.8±1.1), 371 (38.7±1.2), 446 (41.2±1.0)
$[\{Ru(bpy)_2\}_2(\mu\text{-dbneil})]^{4+}$	245 (68.6±3.0), 286 (128.7±4.5), 420 (44.6±2.0), 699 (31.9±1.4)
$[\{Ru(dmbpy)_2\}_2(\mu\text{-dbneil})]^{4+}$	249 (68.5±2.1), 285 (130.9±2.9), 422 (44.9±1.5), 716 (35.3±1.1)
$[\{Ru(tmbpy)_2\}_2(\mu\text{-dbneil})]^{4+}$	255 (74.1±1.9), 290 (134.6±2.5), 421 (40.4±1.2), 729 (33.5±0.9)
$[\{Ru(dtbbpy)_2\}_2(\mu\text{-dbneil})]^{4+}$	249 (68.7±0.6), 286 (131.2±1.8), 423 (44.5±0.8), 721 (33.3±0.7)
$[\{Ru(bpy)_2\}_2(\mu\text{-tape})]^{4+}$	252 (65.9±0.5), 284 (102.8±0.5), 398 (29.1±0.2), 746 (28.8±0.5)
$[\{Ru(phen)_2\}_2(\mu\text{-tape})]^{4+}$	262 (135.0±3.8), 223 (106.8±3.0), 393 (32.9±0.7), 744 (23.7±0.4).
$[\{Ru(dmbpy)_2\}_2(\mu\text{-tape})]^{4+}$	254 (63.7±0.8), 282 (100.5±1.7), 402 (30.6±0.4), 772 (30.1±0.5)
$[\{Ru(tmbpy)_2\}_2(\mu\text{-tape})]^{4+}$	255 (69.6±2.3), 287 (100.3±3.4), 406 (32.1±1.1), 789 (28.6±0.9)
$[\{Ru(dtbbpy)_2\}_2(\mu\text{-tape})]^{4+}$	253 (68.8±±2.2), 284 (112.1±3.8), 403 (35.4±0.9), 774 (32.6±0.1).

[a] Absorption spectra in acetonitrile at 21.5±0.5 °C. Complexes as PF_6^- salts.

Electrochemistry

Table S 3 Potentials for the redox Processes[a] of the synthesized mono- and dinuclear ruthenium(II)-complexes.

compound	$E_{1/2}^{ox}$ (ΔE_p)	$E_{1/2}^{red}$ (ΔE_p)
$[Ru(bpy)_2bpym]^{2+}$	+1.36 (81)	−1.01 (73), −1.45 (70), −1.69 (73), −2.06 (irr.)
$[Ru(dmbpy)_2bpym]^{2+}$	+1.31 (81)	−1.04 (61), −1.54 (66), −1.73 (81), −2.08 (irr.)
$[Ru(tmbpy)_2bpym]^{2+}$	+1.24 (81)	−1.07 (75), −1.69 (65), −1.98 (irr.)
$[Ru(dtbbpy)_2bpym]^{2+}$	+1.31 (71)	−1.03 (73), −1.54 (63), −1.78 (61), −2.10 (irr.)
$[Ru(dtbbpy)_2tpphz]^{2+}$	+1.22 (71)	−1.00 (112), −1.47 (68), −1.68 (irr.), −1.85 (irr.), −2.13 (irr.)
$[Ru(bpy)_2dbneil]^{2+}$	+1.45 (65)	−0.40 (55), −0.55 (51), −0.93 (71), −1.55 (irr.), −1.70 (irr.), −2.14 (irr.)
$[Ru(dmbpy)_2dbneil]^{2+}$	+1.36 (65)	−0.47 (56), −0.58 (51), −0.97 (65), −1.65 (irr.), −1.78 (irr.)
$[Ru(tmbpy)_2dbneil]^{2+}$	+1.36 (91)	−0.52 (50), −0.59 (49), −1.02 (65)
$[Ru(dtbbpy)_2dbneil]^{2+}$	+1.37 (96)	−0.43 (59), −0.54 (56), −0.93 (56), −1.66 (irr.), −1.94 (irr.)
$[Ru(bpy)_2tape]^{2+}$	+1.39 (66)	−0.34 (68), −0.97 (67), −1.58 (76)
$[Ru(phen)_2tape]^{2+}$	+1.40 (59)	−0.34 (83), −0.92 (68), −1.54 (88), −1.86 (irr.), −2.08 (irr.)
$[Ru(dmbpy)_2tape]^{2+}$	+1.30 (71)	−0.36 (71), −0.94 (71), −1.66 (81), −1.94 (irr.)
$[Ru(tmbpy)_2tape]^{2+}$	+1.25 (69)	−0.39 (71), −0.95 (83), −1.84 (irr.)
$[Ru(dtbbpy)_2tape]^{2+}$	+1.31 (76)	−0.36 (68), −0.93 (65), −1.67 (61), −1.93 (59)
$[\{Ru(bpy)_2\}_2(\mu\text{-bpym})]^{4+}$	+1.57 (69), +1.79 (66)	−0.38 (69), −1.06 (66), −1.53 (irr.), −1.79 (irr.), −1.94 (irr.)
$[\{Ru(dmbpy)_2\}_2(\mu\text{-bpym})]^{4+}$	+1.46 (75), +1.66 (65)	−0.44 (71), −1.12 (75), −1.65 (irr.), −1.88 (irr.), −1.99 (irr.)
$[\{Ru(tmbpy)_2\}_2(\mu\text{-bpym})]^{4+}$	+1.39 (75), +1.60 (65)	−0.49 (71), −1.16 (76), −1.81 (irr.), −2.06 (irr.), −2.17 (irr.)
$[\{Ru(dtbbpy)_2\}_2(\mu\text{-bpym})]^{4+}$	+1.46 (106), +1.68 (71)	−0.42 (71), −1.09 (71), −1.69 (101), −1.89 (irr.), −2.00 (irr.)
$[\{Ru(dtbbpy)_2\}_2(\mu\text{-tpphz})]^{4+}$	+1.24 (72)	−0.67 (73), −1.26 (68)
$[\{Ru(bpy)_2\}_2(\mu\text{-dbneil})]^{4+}$	+1.49 (60), +1.65 (56)	−0.16 (65) −0.56 (71), −1.17 (irr.), −1.44 (irr.), −1.67 (irr.), −1.76 (irr.)
$[\{Ru(dmbpy)_2\}_2(\mu\text{-dbneil})]^{4+}$	+1.39 (60), +1.57 (59)	−0.21 (71), −0.61 (71), −1.34 (71), −1.60 (irr.), −1.72 (irr.), −1.83 (irr.),
$[\{Ru(tmbpy)_2\}_2(\mu\text{-dbneil})]^{4+}$	+1.33 (71), +1.52 (76)	−0.24 (71), −0.64 (65), −1.38 (71), −1.69 (65), −1.96 (irr.)
$[\{Ru(dtbbpy)_2\}_2(\mu\text{-dbneil})]^{4+}$	+1.37 (100), +1.52 (71)	−0.19 (65), −0.60 (65), −1.35 (71), −1.60 (55), −1.75 (irr.), −1.85 (irr.)
$[\{Ru(bpy)_2\}_2(\mu\text{-tape})]^{4+}$	+1.48 (64), +1.64 (63)	+0.03 (64), −0.50 (63), −1.48 (irr.), −1.83 (irr.)
$[\{Ru(phen)_2\}_2(\mu\text{-tape})]^{4+}$	+1.44 (68), +1.65 (66)	−0.00 (68), −0.53 (76), −1.37 (irr.), −1.86 (irr.)
$[\{Ru(dmbpy)_2\}_2(\mu\text{-tape})]^{4+}$	+1.34 (71), +1.55 (71)	−0.02 (75), −0.55 (75), −1.60 (91), −1.88 (irr.)
$[\{Ru(tmbpy)_2\}_2(\mu\text{-tape})]^{4+}$	+1.29 (59), +1.49 (56)	−0.05 (66), −0.59 (68), −1.81 (irr.), −2.09 (irr.)
$[\{Ru(dtbbpy)_2\}_2(\mu\text{-tape})]^{4+}$	+1.31 (95), +1.55 (86)	−0.01 (71), −0.53 (81), −1.60 (85), −1.92 (irr.)

[a] The potentials are given in V *vs* SCE in CH_3CN (internal standard Fc/Fc^+), ΔE_p in mV and the supporting electrolyte is 0.1 M $^nBu_4PF_6$ at room temperature. Complexes as PF_6^- salts. Potentials of irreversible processes were determined by square wave voltammetry.

Stacking interaction in solution

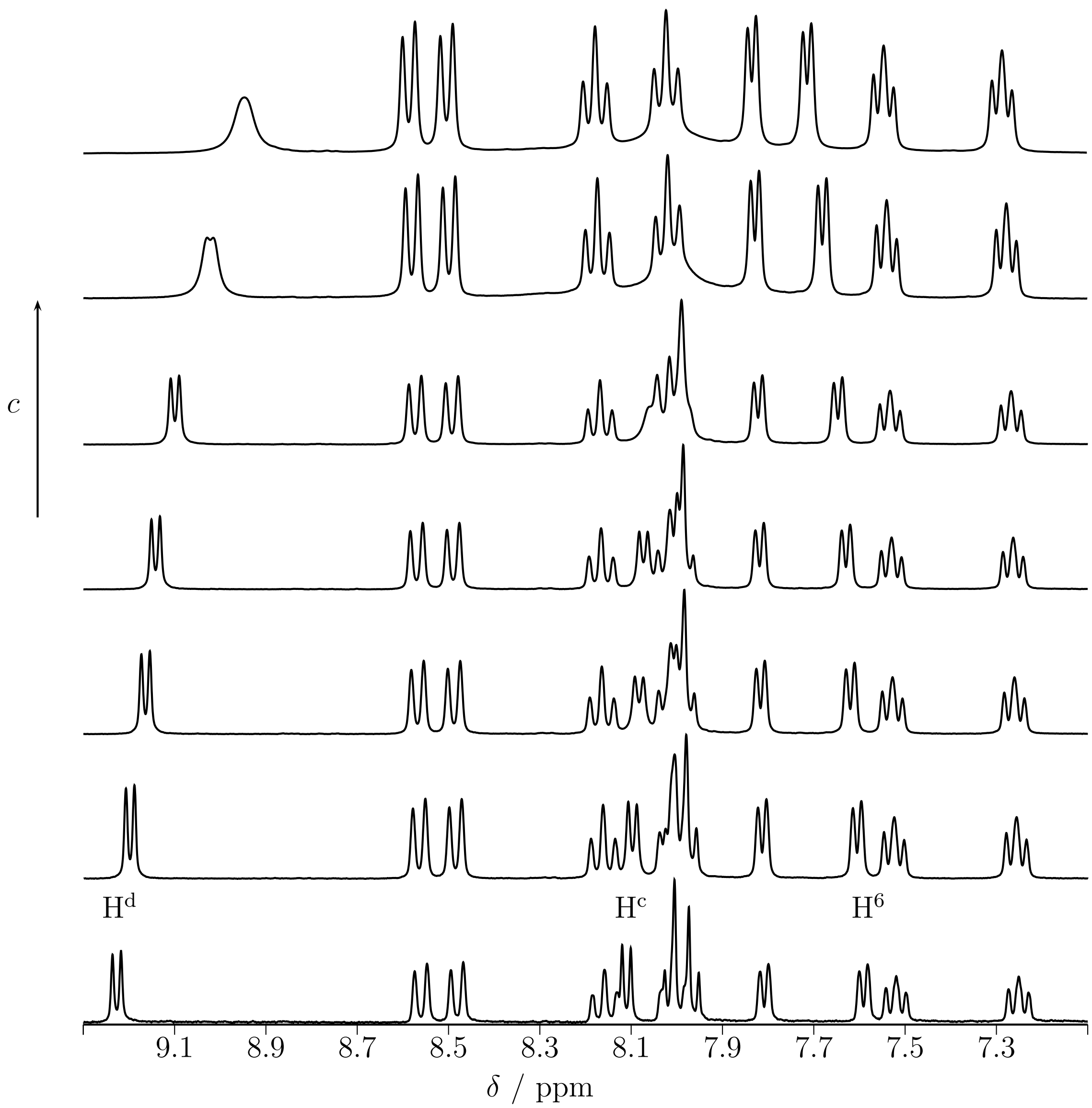

Fig. S 1 ^{1}H NMR spectra of $[Ru(bpy)_2tape](PF_6)_2$ in CD_3CN at various concentrations, from top to bottom: 19.8, 14.5, 10.0, 7.4, 6.0, 4.0 and 2.0 mM.