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Synthesis of a novel rigid molecule family for the investigation of electron and energy transfer

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Dedicated to Professor Dick Stufkens, University of Amsterdam

Contents

Abstract

Three new rigid bridging ligands for metal complexation (**7** = **bmb**, **8** = **bqb** and **11** = **btb**) were prepared from a rigid triptycene spacer connected to two bipyridine ligands using a Horner–Emmons type reaction. The triptycene spacer is substituted by methoxy groups in the case of **bmb** and in the case of **bqb** by a benzoquinone substituent. The corresponding metal complexes (ruthenium and/

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or osmium) were synthesised and the different luminescence behaviour was tested. They show great potential for the investigation of intramolecular electron and energy transfer reactions. The dinuclear metal complex **Ru–bqb–Os** is an interesting system in which the bridging ligand **bqb** acts as a redox switch, able to tune the conductivity for energy or electrons across the bridge.

Keywords: Energy transfer; Electron transfer; Molecular devices; Bipyridyl complexes; Bridging ligands; Dinuclear metal complexes

1. Introduction

Photoinduced energy- and electron transfer processes in supramolecular species [1–8] are the object of broad interest since they are of importance for the construction of light-harvesting systems [1,5,6,9], sensors [10,11], charge-separation devices [1–3,5,6,12], and information storage systems [13]. To guarantee progress in this field the availability of molecular components or in other words building blocks having well-defined properties and structures is necessary. In the case when light- and/or redox active units are involved in such devices, much attention is presently focussed on $M(N–N)_3^{n+}$ complexes as building blocks, where M is a metal ion of the second or third transition rows (Ru^{II}, Re^{I}, and Os^{II}) [14]. Ru^{II}- and Re^{I}-metal complexes are often used as photosensitizers in which their excitation energy is the driving force to induce the energy- or electron transfer process [15]. The Os^{II} containing metal complex normally plays the role of a detector (light emission from the osmium centre) for the arriving energy quantitiy. N–N is a bidentate bpy- or phen-type ligand (bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline) [16]. The N–N ligands are often modified in such a way that they are substituted by donor- or acceptor groups. Such modification leads to fine-tuning of the sensitizer properties of the incorporated metal complexes. To observe such transfer processes between metal complexes they must be connected by a bridging ligand [17]. Several bridging ligands based on two bpy-type chelating units (directly coupled [18], linked by flexible spacers like $–(CH_2)_n–$ chains [19], or by rigid spacers like –HC=CH–bco–HC=CH– [20] and –HC≡CH–bco–HC≡CH– [21] (bco = bicyclo[2.2.2]octane) or -(phenylene)$_n$-connectors [22] have been used. Other rodlike, rigid spacers with two phenanthroline-type chelators have been studied and described in the literature [23]. Such spacers determine the spatial arrangement of the whole molecule. The chemical nature of the connectors plays a very important role for the following reasons: (a) the coordinating site of the bridging ligand itself directly influences the spectroscopic and redox properties of the two metal based units; (b) the nature of the spacer determines the electronic communication namely the rate of energy- and/or electron transfer processes between the donor and acceptor part of the molecule. Such a dependency is expressed in the so-called attenuation factor [β], the lowering of the conductibility for the transfer of electrons per molecular unit of the connecting chain [24]; (c) the spacer influences the geometrical topology of the molecular device. Furthermore, the spacer can have a more sophisticated function than that of a simple connector. It could contain supplementary functions addressable by external stimuli like photons, redox processes, change in magnetic properties and so on. Application of such a stimulus directly influences the transfer process. Either the stimulus influences the rate of the energy- or electron transfer process or in a extreme case the stimulus opens the chain for a transfer or the transfer is interrupted. In such a case we can speak of a bridging ligand containing an ON/OFF switch. In Fig. 1, such a device is depicted.

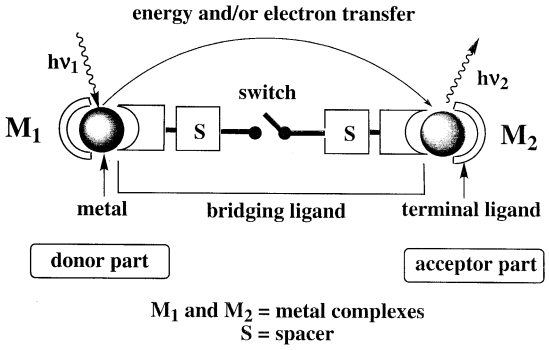
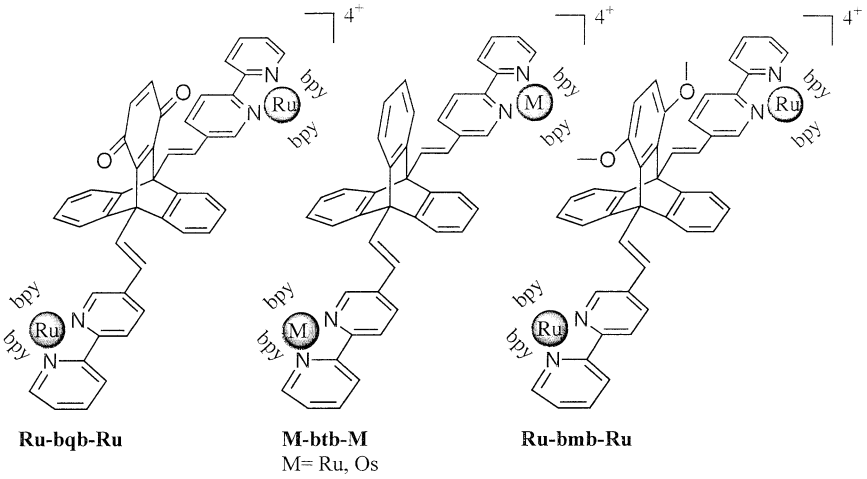


Fig. 1. Schematic representation for dinuclear metal complexes with tunable bridging ligands.

In this context, we tried to design new non-conjugated ligand systems maintaining a well-defined distance in between the two metal centres and in one case containing a redox active switching unit. The triptycene moiety was chosen out of various other possibilities. One reason for this choice was the short and relatively easy synthesis for such a ligand system. Further, a spacer consisting of a quinone moiety could provide the possibility to tune electron- or energy transfer. So both transfer reactions could be strongly influenced by this spacer, depending upon whether it is in the oxidised or in the reduced form. A redox active bridge should therefore be able to control energy and electron transfer reactions in between two complexed metal centres. In Scheme 1 the dinuclear metal complexes with the new bridging ligands are depicted.

The study and description of photoactive molecular devices are often strongly focused on the discussion of the photophysical phenomena found in such devices. The effort, which is necessary to prepare an ideal



Scheme 1. The complexes of the new rigid molecule family.

molecular device, will often be ignored. Therefore, the present overview will be mainly focused on aspects like synthesis and characterisation of the new bridging ligands and their metal complexes.

2. Results and discussion

2.1. Preparation of the bridging ligands

During the synthesis of the ligands, there were two crucial steps which are well described in literature but caused unexpected problems. Firstly the Diels–Alder reaction from substituted anthracenes to form bridged molecules and secondly the Horner–Emmons reaction showed unusual behaviour.

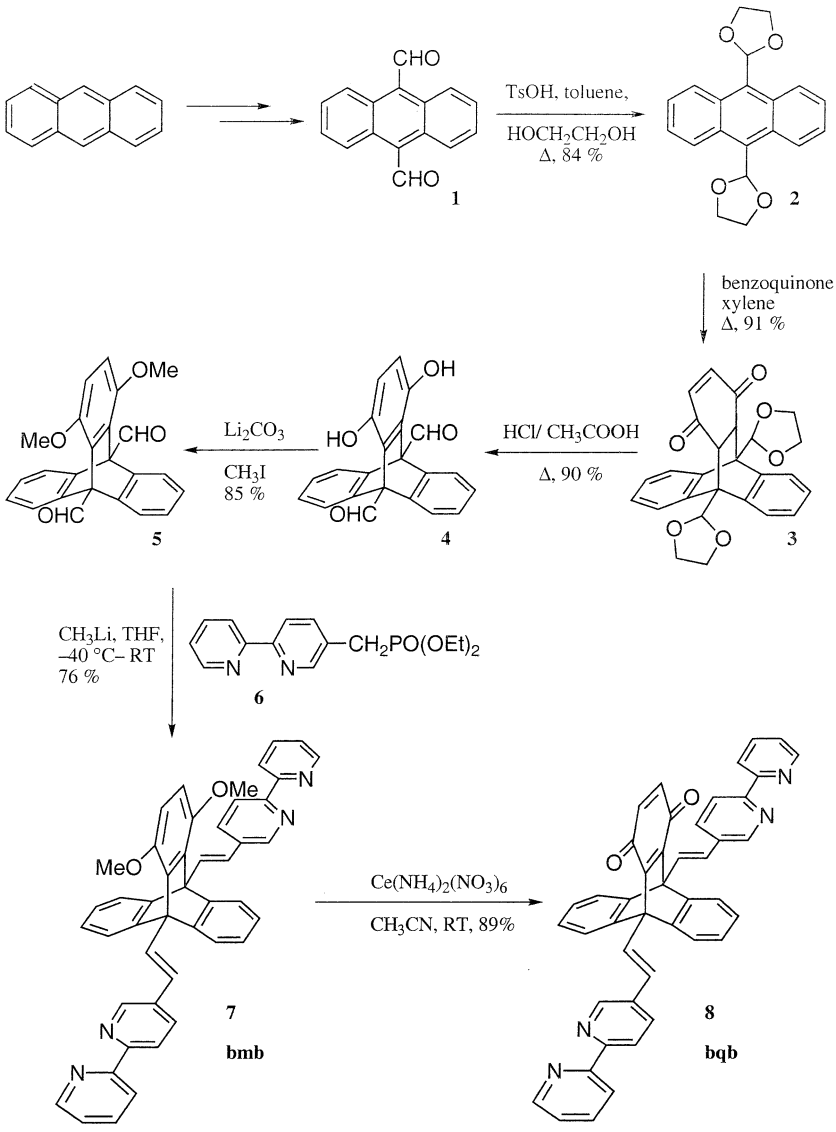
Due to the two aldehyde groups in 9,10-position in molecule **1**, the electron density in the anthracene is too poor to undergo a Diels–Alder reaction. Neither did the precursor 9,10-bis-chloromethyl-anthracene or the coupled, fully aromatic product between **1** and **6** react with benzoquinone or maleic anhydride. Adding a protection group to the aldehydes could eliminate the strong M-effect. In this way a Diels–Alder coupling to such a substituted anthracene was possible. Scheme 2 gives an overview about the synthesis of **bmb** and **bqb**. The Horner–Emmons reaction showed the second unexpected behaviour: while **1** reacts easily with **6** at room temperature using NaH as a base, bridged anthracenes did not do this. A deprotected Diels–Alder adduct between **2** and cyclopentadiene carboxylic acid methyl ester reacted in refluxing toluene using potassium-*tert*-butoxyde [25], however triptycene moieties did not. After several attempts using different strong bases, for example *n*-BuLi, the reaction to **bmb** (**7**) was achieved when a methyl lithium solution above −40 °C was used.

The molecule **1** was prepared following a two step literature procedure [26,27]. The two aldehyde groups were protected using ethylene glycol in toluene with *p*-toluenesulphonic acid as catalyst. However, a much longer reaction time was required (2 days instead of 3–4 h). Diels–Alder reaction between **2** and benzoquinone in refluxing xylene furnished **3**. The intramolecular proton shift and the deprotection were promoted simultaneously in refluxing acetic acid/concentrated HCl mixture [28]. In order to avoid deprotonation and side reactions during the coupling reaction, the hydroquinone groups were selectively protected using methyl iodide under basic conditions to give **5**. Coupling between bipyridine **6** and **5** was carried out using methyl lithium as base at −40 °C. Oxidation to the quinone **bqb** (**8**) was effected with a Ce^{IV} salt [29].

The unsubstituted triptycene spacer (**9**) was obtained by a benzyne addition to **2** [30]. The benzyne intermediate was created in situ using anthranilic acid and isopropyl nitrite. In order to avoid a potential hazard of explosion, as well as observed side reactions, the addition of both substances to the solution was carried out very slowly to keep the benzyne concentration very low. The solubility and polarity of **2** and **9**, also **1** and **10**, are nearly identical, so separation was rather difficult. The two following steps via **10** to **btb** (**11**) were carried out as mentioned above (**4** resp. **7**). However, the yield of the final ligand was lower than that of **7**. Due to similar solubility, separation from the single coupled product was difficult and some product was lost during recrystallisation. Scheme 3 gives an overview of the synthesis of the non-substituted bridging ligand **btb**.

2.2. Preparation of the metal complexes

Due to the poor solubility in high boiling ethers, the bis ruthenium complexes of **bqb** (**8**) was prepared in 1:1



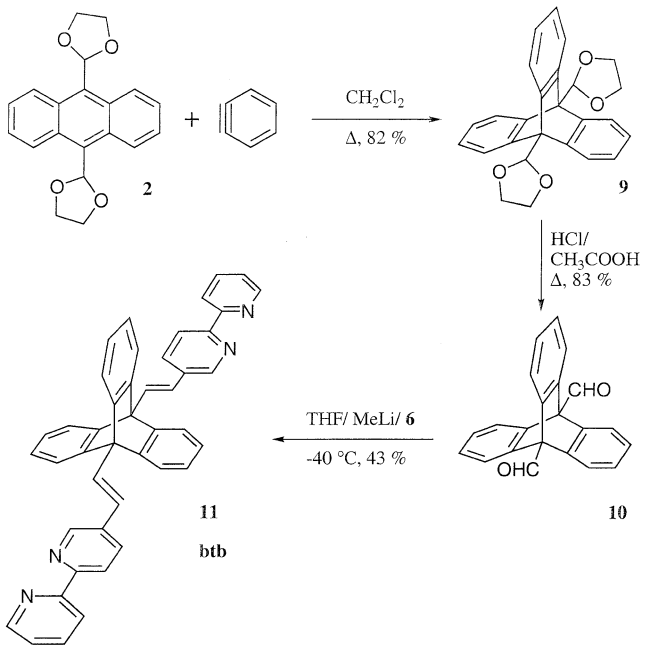
Scheme 2.

and **bmb** (**7**) was obtained in a 2:1 mixture of methoxyethanol and trichloroethanol, respectively. The bis osmium complexes as well as the bis ruthenium complexes of **btb** were synthesised using a standard microwave technique [31]. The mixed ruthenium osmium complex of **btb** was obtained starting from the mono osmium complex, a side product of the synthesis of **Os–btb–Os**, successfully separated by preparative thin layer chromatography.

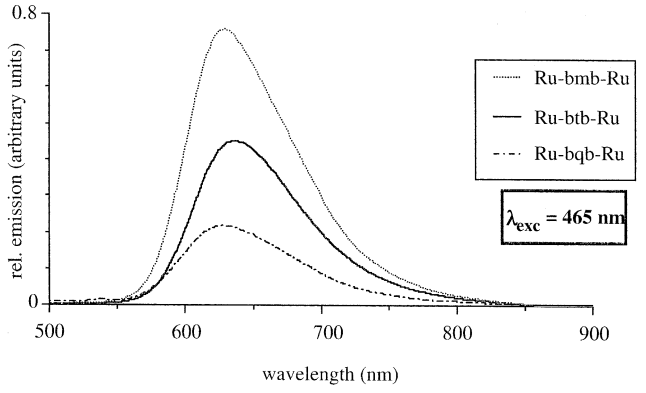
2.3. Discussion of the photophysical properties

In the UV-part of the spectra of the ruthenium complexes an intense absorption band (about 280 nm) can be attributed to a ^{1}LC transition from the bpy ligand. Moderately intense metal-to-ligand charge transfer (^{1}MLCT) bands are observed for all complexes in the 400–550 nm region. In the osmium complexes, spin-orbit coupling gives rise to broad and weak absorption at wavelengths higher than 600 nm, corresponding to the forbidden, formally ^{3}MLCT transition. Isoabsorptive solutions at identical concentrations can be observed for all three metal complexes at 465 nm.

The emission of the three bis-ruthenium complexes (**Ru–btb–Ru**, **Ru–bqb–Ru** and **Ru–bmb–Ru**) was compared in order to check the influence of the triptycene bridge to the emission of the metal complex moieties. The three emission maxima are at 627 (**Ru–bmb–Ru**), 635 (**Ru–btb–Ru**) and 629 nm (**Ru–bqb–Ru**). The ratio between the relative emission is 3.7:2:1 as shown in Scheme 4. The donor effect of the methoxy-substituents on the triptycene part of the **bmb** bridging ligand induces



Scheme 3.



Scheme 4. Emission spectra of the different dinuclear ruthenium complexes.

higher emission with respect to the unsubstituted **btb** ligand. On the other hand the emission is strongly quenched by the quinone moiety in the **bqb** system.

Due to the redox active properties of the quinone moiety emission tuning can be obtained [5,32,33]. The electronic energy level of the quinone moiety (part of the bridging ligand) in the metal complex Ru–bqb–Os ($E^0 = +0.96$ V for single substituted benzoquinone [34]) is positive enough to act as a quencher for the Ru-based ^{3}CT excited state. Little or no phosphorescence from the Os-based ^{3}CT level can be observed. After a two electron-reduction in acidic solutions the quinone moiety is transformed into a hydroquinone moiety. The reduction potential is now more negative and the energy level of the hydroquinone moiety plays the role of an intermediate in the energy transfer process. As a consequence, the emission from the excited osmium based ^{3}CT level increases. The situation can be shown in Fig. 2.

In the case of the three complexes of the **btb** family (**Ru–btb–Ru**, **Os–btb–Os** and **Ru–btb–Os**), effective quenching of the luminescence of the ruthenium centred moiety is obvious. In the heteronuclear complex **Ru–btb–Os**, the emission of the ruthenium unit is more than 10 times less intense than in the homonuclear **Ru–btb–Ru** complex (see Scheme 5).

On the other hand, the osmium centred emission is slightly stronger than in the homonuclear **Os–btb–Os** complex. This is partially due to a superposition of the osmium centred emission with part of the remaining ruthenium centred emission. Nonetheless the emission of the osmium unit is still stronger than that from the usual mono-osmium complex of this type [20a]. These two observations are a clear sign for an energy transfer from the ruthenium to the osmium unit [20a,21].

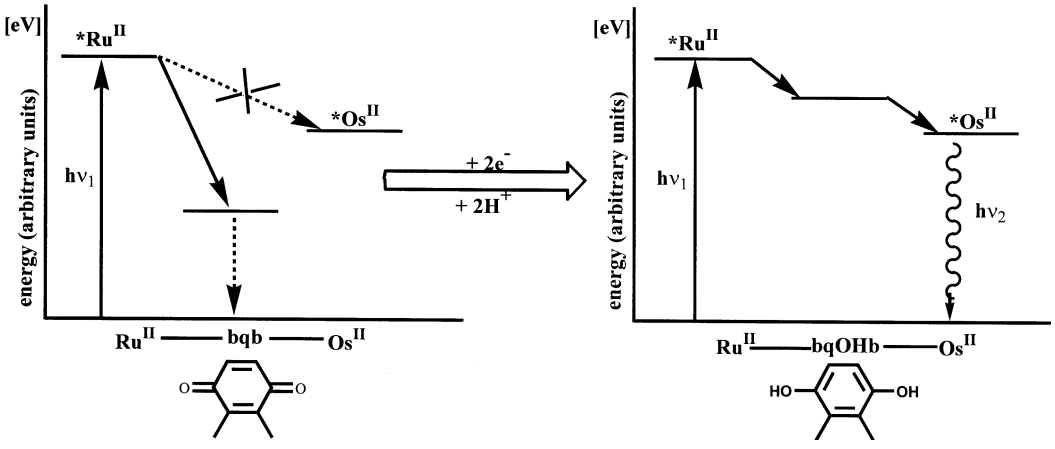
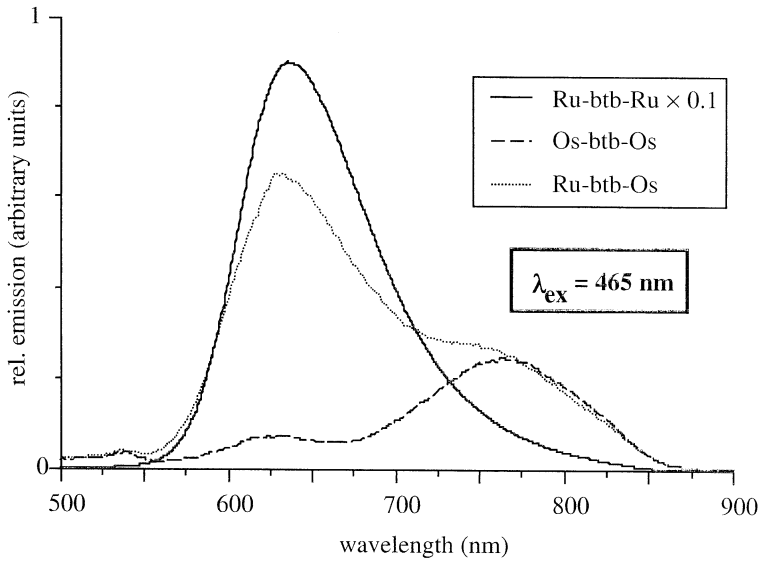


Fig. 2. Energy level diagram showing the energy transfer process in the complex **Ru–bqb–Os** before and after reduction of the benzoquinone spacer.



Scheme 5. Emission spectra of the complex family of **btb** (**11**).

3. Conclusion

The triptycene ligand **btb** allows an easy access to ligand systems with well-defined distances in between two metal centres due to the short and relatively easy synthesis of the triptycene spacer. Even an elongation of the spacer using two triptycene units could be realised. The good solubility of these ligands enables better metal complexation and shows therefore an easier way to access heteronuclear complexes [26,27]. The first experiments showed similar behaviour to the complexes of this type on emission already published [20a,21]. Also homonuclear complexes of the triptycene type ligands (**Ru–bqb–Ru** and **Ru–bmb–Ru**) showed interesting behaviour due to changes in luminescence. Combined with the fact that the quinone moiety could be electrochemically altered, a new electrochemical switch based on two different metal centres could be obtained [5,32,33].

4. Experimental

4.1. General remarks

M.p. were measured on a Büchi 520 capillary apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded at 300 MHz using a Varian Gemini 300 spectrometer. Chemical shifts are quoted in parts per million (ppm) and are referenced to the residual solvent peak. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants are quoted to the nearest 0.5 Hz. MS and HRMS were recorded either on a VG Micromass 7070E (Matrix NBA) or on a HP5988 (ionisation energy 70 eV). Electro Spray Ionisation measurements were measured on a Finnigan MAT 900S. Elemental analysis was performed by CIBA in Marly (Switzerland). IR spectra were recorded using a Perkin–Elmer 16 PC Fourier transform spectrometer with major absorbances only being quoted. UV–vis measurements were carried out on a Perkin–Elmer Lambda 5 instrument. A modified microwave oven was used as described [31]. All solvents were purified by standard techniques or used as supplied from commercial sources as appropriate [35].

4.1.1. General work-up for metal complexes

After removal of the solvent under reduced pressure, the residue was dissolved in water and extracted with CH_2Cl_2 in order to remove remaining ligand. The aq. phase was then warmed to 70 °C when the complex was precipitated with an excess of NH_4PF_6. The complexes were purified as described previously [23b]. 9,10-Anthracene-dicarboxaldehyde (**1**) [26,27] and compound **6** [20a,36,37] were prepared following known literature procedures. The precursors for the complexations, $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and $Os(bpy)_2C1_2$ were synthesised following known procedures [38–40].

4.2. 9,10-Anthracenedi-(1,3)-carboxalane (2)

Ethylene glycol (6.70 g, 100 mmol), 9,10-anthracene-dicarboxaldehyde (**1**) (4.67 g, 20 mmol) and a half spatula of *p*-toluenesulphonic acid in 400 ml $C_6H_5CH_3$ were refluxed for 48 h in a 1 l round bottom flask equipped with a Dean–Stark apparatus. The $C_6H_5CH_3$ was then removed using the Dean–Stark apparatus until crystallisation occurred. The cooled solution was filtered. The crystals obtained were washed with Et_2O and

dried at 50 °C, resulting 5.44 g (17 mmol/ 84%). The sample for elemental analysis was recrystallised from EtOAc.

R_f (SiO_2, Et_2O/TEA 10:1 v/v): 0.50; m.p.: 295–296 °C (dec.); ^{1}H-NMR (300 MHz, $CDC1_3$): δ 8.56 (4H, m, CH_{ant} 1, 4, 5 and 8); 7.47 (4H, m, CH_{ant} 2, 3, 6 and 7); 7.06 (2H, s, CHO_2); 4.49 (4H, m, CH_2O); 4.24 (4H, m, CH_2O); ^{13}C-NMR (75.44 MHz, $CDC1_3$): δ 130.7 (C_{ar}); 127.9 (C_{ar} 9,10); 125.4 (CH_{ar}); 124.7 (CH_{ar}); 101.8 (CH_{aliph}); 65.3 (CH_2O); MS (FAB): *m/z* 323 [$M^+ + 1$], 322 [M^+], 251 [$M^+ - CH(OCH_2)_2$], 206 [9-anthracene-carboxaldehyde], 178 [anthracene], 154, 136, 107, 89, 73, 51; IR (KBr, ν (cm^{-1})): 3096, 2950, 2876, 1456, 1446, 1432, 1348 (CHO_2 oop), 1282, 1258, 1190, 1134, 1100 (C–O–C), 1038, 1022, 972, 936, 888, 792, 754, 702, 636, 598, 464; Elemental analysis for $C_{20}H_{18}O_4$ (322.36): Calc.: C, 74.52; H, 5.63. Found: C, 74.29; H, 5.66%.

4.3. Benzoquinone-anthracene-9,10-dicarboxalane (*3*)

9,10-Anthracenedi-(1,3)-carboxalane (1.76 g, 5.5 mmol) (**2**), 690 mg (6.4 mmol) benzoquinone and half a spatula of hydroquinone were refluxed in 40 ml C_8H_{10} for 3 h. After adding 210 mg (2.2 mmol) maleic anhydride the mixture was refluxed a further hour. After evaporation of the solvent the residue was dissolved in 100 ml CH_2Cl_2, three times extracted with 60 ml 3 M NaOH, followed by 60 ml water and the organic phase was dried over $MgSO_4$. After evaporation of the solvent, the slightly yellow residue was heated to reflux in 40 ml Et_2O for 30 min. From the cooled solution, the solid was filtered off and washed with Et_2O to furnish 2.15 g (5.0 mmol/91%) white powder.

R_f (SiO_2, C_6H_{14}/EtOAc 8:2 v/v): 0.16; m.p.: 223 °C; ^{1}H-NMR (300 MHz, $CDC1_3$): δ 7.60 (3H, m, CH_{ar} 2, 3, 6 and 7); 7.38 (1H, bs, CH_{ar} 2, 3, 6 and 7); 7.14 (4H, m, CH_{ar} 1, 4, 5 and 8); 6.31 (1H, d, $CH_{benzoquinone}$); 6.08 (1H, s, CHO_2); 5.88 (1H, s, CHO_2); 5.78 (1H, d, $CH_{benzoquinone}$); 4.80–4.20 (5H, m, CH_2O); 4.06 (2H, m, CH_2O); 3.83 (1H, m, CH_2O); 3.49 (1H, d, CH_{aliph}); 3.27 (1H, d, CH_{aliph}); ^{13}C-NMR (75, 44 MHz, $CDC1_3$): due to hindered rotation very complicated; MS (FAB): *m/z* 431 [$M^+ + 1$], 357, 321 [M^+ – benzoquinone], 307, 249, 205, 178 [anthracene]; IR (KBr, ν (cm^{-1})): 3036, 2992, 2962, 1780, 1684 (C=O), 1600, 1490, 1462, 1270, 1212, 1168, 1110 (C–O–C), 1084, 1050, 1026, 944, 888, 754; Elemental analysis for $C_{26}H_{22}O_6$ (430.46): Calc.: C, 72.55; H, 5.15. Found: C, 72.19; H, 5.18%.

4.4. Triptycenehydroquinone-9,10-dialdehyde (*4*)

Compound **3** (200 mg, 0.46 mmol) was refluxed in a mixture of 9 ml AcOH (98%) and 1 ml concd. HCl (37%) for 5 h. After evaporation of the solvent, 5 ml water was added to the residue. After 1 min treatment in an ultrasonic bath, the solid material was filtered off and dried, resulting 143 mg (0.42 mmol) brown–yellow powder (90%).

R_f (SiO_2, THF/TEA: 10:1 v/v): 0.46; m.p.: 281–282 °C (dec.); ^{1}H-NMR (300 MHz, [d_6]DMSO): δ 11.00 (2H, s, CHO); 9.66 (2H, s, OH); 7.98 (4H, dd, CH_{ar} 1, 4, 5 and 8, $\vartheta_\delta = 5.5$, 3.5 Hz); 7.10 (4H, dd, CH_{ar} 2, 3, 6 and 7, $\vartheta_\delta = 5.5$, 3.5, Hz); 6.49 (2H, s, $CH_{hydro-quinone}$); ^{13}C-NMR (75.44 MHz, [d_6]DMSO): δ 199.1 (CHO); 144.8 ($C_{hydroquinone}$); 143.9 ($C_{hydroquinone}$); 130.0 (C_{ar}); 125.3 (CH_{ar}); 123.1 (CH_{ar}); 115.4 ($CH_{hydroquinone}$); 59.1 (C_{aliph}); MS (EI): *m/z* 342 [M^+], 313 [M^+ – CHO], 285 [M^+ – 2CHO], 239, 226, 202, 119; IR (KBr, ν (cm^{-1})): 3464 (O–H), 2870 and 2760 (CHO_{fermi}), 1726 (C=O), 1482, 1452, 1412, 1260, 1218, 1162, 1052, 810, 744; HRMS: $C_{22}H_{14}O_4$: Calc.: 342.0892. Found: 342.0893%.

4.5. 1,4-Dimethoxytriptycene-9,10-dialdehyde (*5*)

Compound **4** (200 mg, 0.59 mmol), 400 mg (2.90 mmol) K_2CO_3 and 825 mg (5.85 mmol/0.38 ml) MeI were refluxed in 30 ml C_3H_6O for 3 h. After the addition of 3 ml water, the volume of the solution was reduced to 1/4, 30 ml CH_2C1_2 was added. After extraction with water (30 ml) the organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The solid material was suspended in 20 ml Et_2O and heated to reflux for 1 h. After filtration, 185 mg (0.50 mmol) colourless material was obtained (85%).

R_f (SiO_2, THF/TEA 10:1 v/v): 0.77; m.p.: > 305 °C; ^{1}H-NMR (300 MHz, $CDC1_3$): δ 10.99 (2H, s, CHO); 8.02 (4H, dd, CH_{ar} 1, 4, 5 and 8, $\vartheta_\delta = 5.5$, 3.5 Hz); 7.07 (4H, dd, CH_{ar} 2, 3, 6 and 7, $\vartheta_\delta = 5.5$, 3.5 Hz); 6.65 (2H, s, $CH_{hydroquinone}$); 3.75 (6H, s, OCH_3); ^{13}C-NMR (75.44 MHz, $CDC1_3$): δ 197.9 (CHO); 149.1 (COMe); 143.8 (C_{ar}); 134.1 ($C_{hydroquinone}$); 125.5 (CH_{ar}); 123.5 (CH_{ar}); 112.2 ($CH_{hydroquinone}$); 58.5 (C_{aliph}); 57.1 (OCH_3); MS (EI): *m/z* 370 [M^+], 341 [M^+ – CHO], 312 [M^+ – 2CHO], 283 [triptycene], 239, 200, 113; IR (KBr, ν (cm^{-1})): 3064, 3000, 2968, 2940, 2838 and 2760 (CHO_{fermi}), 1732 (C=O); 1490, 1450, 1258, 1220 (C–O–C_{asym}), 1184, 1152, 1090, 1068 (C–O–C_{sym}), 1032, 800, 744; Elemental analysis for $C_{24}H_{18}O_4$ (370.41) 0.33·H_2O: Calc.: C, 76.58; H, 5.00. Found: C, 76.58; H, 4.92%.

4.6. 1,4-Dimethoxytriptycene-9,10-di((*E*)ethenyl-5-(2,2′)-bipyridine) (*7*)

To 9 ml dry THF in a 100 ml three necked round bottom flask with dropping funnel and septum 1.0 ml of a MeLi-solution (1.6 M in ether) was added under Ar atmosphere at −40 °C. After 5 min stirring a solution of 387 mg (1.36 mmol) of bipyridine **6** in 25 ml dry THF

was added through the dropping funnel and stirred for 45 min, while the solution turned dark.

Dialdehyde **5** (185 mg, 0.50 mmol) dissolved in 30 ml dry THF, was added over a period of 10 min through the septum and the solution was allowed to warm up to room temperature (r.t.) overnight. After slow addition of 10 ml water, the volume of the mixture was diminished to 1/4, when a brownish solid precipitated. The suspension was dissolved in 100 ml CH_2Cl_2, extracted three times with 70 ml 1 M HCl, washed with 70 ml water and dried ($MgSO_4$). After evaporation of the solvent in vacuo there remained 265 mg (0.39 mmol/78%) brownish powder, which was used without further purification. Recrystallisation for analysis from C_3H_6O furnished a white powder.

R_f (SiO_2, THF/TEA 10:1 v/v): 0.26; m.p.: >305 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.98 (2H, d, CH_{bpy} 6, $\vartheta_\delta = 1.5$ Hz); 8.71 (2H, dt, CH_{bpy} 6′, $\vartheta_\delta = 5$, $\vartheta_\tau = 1$ Hz); 8.66 (2H, d, CH–C, $\vartheta_\delta = 17.5$ Hz); 8.51 (2H, d, CH_{bpy} 3, $\vartheta_\delta = 8$ Hz); 8.46 (2H, dd, CH_{bpy} 3′, $\vartheta_\delta = 8$, 1 Hz); 8.15 (2H, dd, CH_{bpy} 4, $\vartheta_\delta = 8.5$, 2 Hz); 7.85 (2H, td, CH_{bpy} 4′, $\vartheta_\tau = 7.5$, $\vartheta_\delta = 2$ Hz); 7.73 (4H, dd, CH_{ar} 1, 4, 5 and 8, $\vartheta_\delta = 5.5$, 3.5 Hz); 7.33 (2H, m, CH_{bpy} 5′); 7.08 (4H, dd, CH_{ar} 2, 3, 6 and 7, $\vartheta_\delta = 5.5$, 3.5 Hz); 7.02 (2H, d, CH–C_{bpy}, $\vartheta_\delta = 17.5$ Hz); 6.63 (2H, s, $CH_{hydroquinone}$); 3.80 (6H, s, OCH_3); ^{13}C-NMR (75.44 MHz, $CDC1_3$): δ 156.0 (C_{bpy}); 155.1 (C_{bpy}); 150.9 (COMe); 149.3 (CH_{bpy}); 147.6 (CH_{bpy}); 146.7 (C_{ar}); 137.9 ($C_{hydroquinone}$); 136.9 (CH_{ar}); 133.7 (CH_{ar}); 131.7 (CH_{ar}); 130.3 (CH_{ar}); 125.1 (CH_{Ant}); 124.1 (CH_{Ant}); 123.6 (CH_{ar}); 121.1 (CH_{ar}); 121.0 (CH_{ar}); 113.4 ($CH_{hydroquinone}$); 57.6 (OCH_3); 57.2 (C_{aliph}); MS (FAB): *m/z* 675 [M^+], 338, 289, 239, 181 [bpy–CH=CH]; IR (KBr, ν (cm^{-1})): 3050, 2992, 2936, 2834, 1734, 1640, 1588, 1550, 1482, 1456, 1382, 1256 (C–O–C_{asym}), 1060 (C–O–C_{sym}), 1038, 992, 780, 760, 734; Elemental analysis for $C_{46}H_{34}N_4O_2$ (674.81) 0.50·H_2O: Calc.: C, 80.80; H, 5.16; N, 8.20. Found: C, 80.70; H, 5.30; N, 8.03%.

4.7. 1,4-Triptycenequinone-9,10-di((*E*)ethenyl-5-(2,2′)-bipyridine) (*8*)

A solution of 400 mg (0.70 mmol) $Ce^{IV}(NH_4)_2(NO_3)_6$ in 5 ml water was added to a suspension of 120 mg (0.18 mmol) **7** in 30 ml MeCN and stirred for 4 h at r.t. After evaporation of the solvent, the residue was dissolved in 70 ml CH_2C1_2 and washed with 70 ml water. The aq. phase was re-extracted with 30 ml CH_2C1_2, the combined organic layers were dried in ($MgSO_4$) and the solvents evaporated in vacuo, resulting in 103 mg (0.16 mmol/89%) pure orange product.

R_f (SiO_2, Et_2O/TEA 10:1 v/v): 0.66; m.p.: >220 °C (dec.); ^{1}H-NMR (300 MHz, $CDC1_3$): δ 8.92 (2H, d, CH_{bpy} 6, $\vartheta_\delta = 2.0$ Hz); 8.71 (2H, dd, CH_{bpy} 6′); 8.54 (2H, d, CH_{bpy} 3, $\vartheta_\delta = 8.5$ Hz); 8.49 (2H, d, CH_{bpy} 3′, $\vartheta_\delta = 8$ Hz); 8.36 (2H, d, CH–C, $\vartheta_\delta = 17.5$ Hz); 8.28 (2H, dd, CH_{bpy} 4, $\vartheta_\delta = 8$, 2 Hz); 7.87 (2H, td, CH_{bpy} 4′, $\vartheta_\tau = 8$, $\vartheta_\delta = 1.5$ Hz); 7.72 (4H, dd, CH_{ar} 1, 4, 5 and 8, $\vartheta_\delta = 5.5$, 3 Hz); 7.35 (2H, m, CH_{bpy} 5′); 7.15 (4H, dd, CH_{ar} 2, 3, 6 and 7, $\vartheta_\delta = 5.5$, 3 Hz); 6.95 (2H, d, CH–C_{bpy}, $\vartheta_\delta = 17.5$ Hz); 6.51 (2H, s, $CH_{quinone}$); ^{13}C-NMR (75.44 MHz, $CDC1_3$): δ 185.4 (C=O); 155.6 (C_{bpy}); 155.2 (C_{bpy}); 154.5 (C_{bpy}); 149.1 (CH_{bpy}); 148.0 (CH_{bpy}); 145.1 (C_{ar}); 137.2 (CH_{ar}); 135.4 (CH_{ar}); 133.9 (CH_{ar}); 132.9 ($C_{quinone}$); 125.7 (CH_{ar}); 125.4 (CH_{ar}); 124.6 (CH_{ar}); 123.8 (CH_{ar}); 121.3 (CH_{ar}); 121.0 (CH_{ar}); 57.9 (C_{aliph}); MS (FAB): *m/z* 647 [$M^+ + 2$], 529, 485, 441, 329, 307, 176; ESI: $C_{44}H_{29}N_4O_2$ [$M+H^+$]: Calc.: 645.2290. Found: 645.2294%.

4.8. 9,10-Triptycenedi-(1,3)-carboxalane (*9*)

In a 50 ml two-necked flask 400 mg (1.24 mmol) 9,10-anthracene-dicarboxalane (**2**) were refluxed in 20 ml dry CH_2C1_2 under an Ar atmosphere. A solution of 176 mg (1.28 mmol) anthranilic acid in 4 ml C_3H_6O and a solution of 220 mg (1.44 mmol) isopentyl nitrite in 4 ml dry CH_2C1_2 were added simultaneously during 3 h through a septum using a double syringe pump. The reaction was protected by a safety shield (*caution*: the intermediate benzyne is known as an explosive, but we did not have any problems during several reactions). After addition the solution was refluxed for a further hour. After removal of the solvent, 120 mg (1.24 mmol) maleic anhydride and 40 ml $C_6H_5CH_3$ were added and the mixture was refluxed for 2 h. After removal of the solvent in vacuo, 100 ml EtOAC was added and the organic layer was extracted three times with 150 ml 3 M NaOH and 70 ml saturated brine. After drying over $MgSO_4$ the solvent was removed in vacuo. The crude product was dissolved in a little CH_2C1_2, SiO_2 was added and the solvent was removed. The residue was put on a column (SiO_2, C_6H_{14}/EtOAc 8:2 v/v, $h = 18$ cm, $d = 2$ cm). The product remaining on the column was washed out using MeOH and CH_2C1_2. Removal of the solvent yielded 407 mg (1.02 mmol/82%) of yellow crystals.

R_f (SiO_2, Et_2O): 0.77, (SiO_2, EtOAc/C_6H_{14} 8:2 v/v): 0.09; m.p.: >305 °C; ^{1}H-NMR (300 MHz, $CDC1_3$): δ 7.66 (4H, m, CH_{arom}); 7.57 (2H, m, CH_{arom}); 6.97 (6H, m, CH_{arom}); 6.31 (2H, d, CHO_2); 4.47 (4H, m, CH_2O); 4.34 (4H, m, CH_2O); ^{13}C-NMR (75.44 MHz, $CDC1_3$): δ 145.4, 145.3 and 142.8 (C_{arom}); 124.8, 124.6, 124.5, 124.3, 124.2, 123.0, 122.9 (CH_{arom}); 104.3 (CHO_2); 64.8 and 64.7 (CH_2O); 55.5 (C_{aliph}); MS (EI): *m/z* 398 [M^+], 325 [$M^+ - CH(OCH_2)_2$], 265, 252 [$M^+ - 2CH(OCH_2)_2$], 126, 73, 45; IR (KBr, ν (cm^{-1})): 3062, 2958, 2886, 2856, 1456, 1404, 1386, 1218, 1134, 1108 (C–O–C), 1032, 1002, 940, 746, 638; HRMS: $C_{26}H_{22}O_4$: Calc.: 398.1518. Found: 398.1508%.

4.9. 9,10-Triptycenedialdehyde (**10**)

Triptycenedicarboxalane (**9**) (450 mg, 1.13 mmol) were refluxed in 25 ml AcOH (98%) and 2.6 ml concd. HCl (37%) for 3 h. The green solution was evaporated to dryness, the residue was redissolved in 40 ml CH_2Cl_2, extracted twice with 40 ml 1 M NaOH followed by 40 ml water and dried over $MgSO_4$. Removal of the solvent yielded 292 mg (0.94 mmol/83%) of yellow crystals.

R_f (SiO_2, THF/TEA 10:1 v/v): 0.76, (SiO_2, EtOAc/C_6H_{14} 8:2 v/v): 0.39; m.p: >293 V(slow dec.); ^{1}H-NMR (300 MHz, $CDC1_3$): δ 11.17 (2H, s, CHO); 7.68 (6H, dd, CH_{arom}); 7.10 (6H, dd, CH_{arom}); ^{13}C-NMR (75.44 MHz, $CDCl_3$): δ 200.2 (CHO); 143.2 (C_{arom}); 125.8 (CH_{arom}); 122.8 (CH_{arom}); 60.1 (C_{aliph}); MS (EI) *m/z*: 310 [M^+], 281 [$M^+ - CHO$], 253, 224, 200, 176, 150, 126, 113, 87, 73, 50; IR (KBr, ν (cm^{-1})): 3052, 3000, 2922, 1730 (C=O), 1466, 1446, 1358, 1336, 1232, 1190, 1172, 1032, 1002, 882, 838, 730; HRMS: $C_{22}H_{14}O_2$: Calc.: 310.0994. Found: 310.0993%.

4.10. Triptycene-9,10-di((*E*)ethenyl-5-(2,2′)-bipyridine) (**11**)

The crude product mixture was obtained according to the synthesis of **7**, using **10** instead of **5**. The suspension was dissolved in 100 ml CH_2C1_2 and extracted three times with 70 ml 3 M HCl. The aq. phase was neutralised with NaOH (40%) and extracted with three times 100 ml CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product (210 mg) was refluxed in 20 ml C_3H_6O. From the cooled solution, 131 mg (0.21 mmol, 43%) slightly yellow powder was obtained after filtration.

R_f (SiO_2, Et_2O/TEA 10:1 v/v): 0.63; m.p: >305 °C; ^{1}H-NMR (300 MHz, $CDC1_3$): δ 8.98 (2H, d, CH_{bpy} 6, $\vartheta_\delta = 2$ Hz); 8.73 (2H, dd, CH_{bpy} 6′, $\vartheta_\delta = 4$, 1 Hz); 8.57 (2H, d, CH_{bpy} 3, $\vartheta_\delta = 8$ Hz); 8.49 (2H, d, CHbpy 3′, $\vartheta_\delta = 8$ Hz); 8.28 (2H, dd, CH_{bpy} 4, $\vartheta_\delta = 8$, 2 Hz); 7.86 (2H, td, CH_{bpy} 4′, $\vartheta_\tau = 7.5$, $\vartheta_\delta = 1.8$ Hz); 7.70 (2H, d, CH–C, $\vartheta_\delta = 17.5$ Hz); 7.65 (6H, dd, CH_{ar} 1 and 4, $\vartheta_\delta =$ 5.5, 3.5 Hz); 7.33 (2H, m, CH_{bpy} 5′); 7.19 (2H, d, CH–C_{bpy}, $\vartheta_\delta = 17.5$ Hz); 7.10 (6H, dd, CH_{ar} 2 and 3, $\vartheta_\delta =$ 5.5, 3.5 Hz); ^{13}C-NMR (75.44 MHz, $CDCl_3$): δ 155.9 (C_{bpy}); 155.8 (C_{bpy}); 149.3 (CH_{bpy}); 148.1 (CH_{bpy}); 146.8 (C_{ar}); 137.0 (CH_{ar}); 135.7 (CH_{ar}); 133.6 (CH_{ar}); 132.7 (CH_{bpy}); 125.2 (CH_{Ant}); 124.3 (CH_{ar}); 123.9 (CH_{ar}); 122.7 (CH_{Ant}); 121.2 (CH_{ar}); 55.6 (C_{aliph}); MS (FAB): *m/z* 615 [M^+], 574, 530, 486, 442, 307, 154; HRMS: $C_{44}H_{30}N_4$: Calc.: 614.2470. Found: 614.2470%.

4.11. Metal complexes

4.11.1. [(bpy)$_2$Ru–bqb–Ru(bpy)$_2$](PF$_6$)$_4$

To a solution of 20 mg (0.031 mmol) **bqb** (**8**) in 4 ml $C_2H_2Cl_3OH$ 34 mg (0.065 mmol/2.1 equiv.) $Ru(bpy)_2C1_2 \cdot 2H_2O$ dissolved in 8 ml methoxyethanol was added and the mixture was heated for 4 × 2 min in a modified microwave oven (380 W). After a common work-up, the complex was precipitated a second time from C_3H_6O instead of a purification on preparative plate, yielding 45 mg (0.022 mmol/70%) red powder.

R_f (SiO_2, $CH_3CN/CH_3OH/H_2O/KNO_3$: 40:10:10:1 v/v): 0.31; ^{1}H-NMR (300 MHz, CD_3CN): δ 8.58 (2H, d, CH_{bpy}); 8.52 (8H, m, CH_{bpy}); 8.46 (2H, CH_{bpy}); 8.35 (2H, dd, CH_{bpy}); 8.08 (8H, m, CH_{bpy}); 7.98 (2H, m, CH_{bpy}); 7.95 (2H, m, CH_{bpy}); 7.87 (2H, d, =CH–ant); 7.80 (4H, m, CH_{bpy}); 7.75 (6H, m); 7.56–7.32 (14H, m, $CH_{bpy} + CH_{ant}$ 1, 4, 5, 8) 7.18–7.04 (4H, m, CH_{ant} 2, 3, 6, 7) 6.79 (2H, d, =CH–bpy); 6.54 (2H, s, $CH_{quinone}$); MS (FAB): *m/z* 1911 [$M^+ - PF_6$], 1765 [$M^+ - 2PF_6$].

4.11.2. [(bpy)$_2$Ru–bmb–Ru(bpy)$_2$](PF$_6$)$_4$

bmb (**78**) (20 mg, 0.030 mmol) are dissolved in 7 ml hot ethylene glycol after adding one drop of concd. HCl. Then 32.4 mg (0.062 mmol/2.1 equiv.) $Ru(bpy)_2C1_2 \cdot 2H_2O$ were added and the mixture was heated for 4 × 2 min in a modified microwave oven (530 W). After a standard work-up and purification, there remained 27 mg (0.012 mmol/43%) of red crystals.

R_f (SiO_2, $CH_3CN/CH_3OH/H_2O/KNO_3$: 40:10:10:1 v/v): 0.32; ^{1}H-NMR (300 MHz, CD_3CN): δ 8.60 (2H, d, CH_{bpy}); 8.50 (10H, m, CH_{bpy}); 8.45 (2H, m, CH_{bpy}); 8.35 (2H, d, =CH–ant); 8.07 (8H, m, CH_{bpy}); 7.95 (2H, m, CH_{bpy}); 7.90 (2H, m, CH_{bpy}); 7.87 (2H, d, CH_{bpy}); 7.80–7.66 (8H, m, CH_{bpy}); 7.58 (2H, m, CH_{ant} 1, 4, 5, 8); 7.46 (6H, m, $CH_{bpy} + CH_{ant}$ 1, 4, 5, 8); 7.44–7.28 (6H, m, CH_{bpy}); 7.02 (4H, m, CH_{ant} 2, 3, 6, 7); 6.80 (2H, d, =CH–bpy); 6.72 (2H, s, $CH_{hydroquinone}$); 3.60 (6H, s, OCH_3); MS (FAB): *m/z* 1939 [$M^+ - PF_6$], 1795 [$M^+ - 2PF_6$], 1649 [$M^+ - 3PF_6$].

4.11.3. [(bpy)$_2$Ru–btb–Ru(bpy)$_2$](PF$_6$)$_4$

To a solution of 14 mg (0.023 mmol) **btb** (**11**) in 5.5 ml $C_2H_2Cl_3OH$ 24.9 mg (0.048 mmol/2.1 equiv.) $Ru(bpy)_2Cl_2 \cdot 2H_2O$ dissolved in 5.5 ml methoxyethanol were added. The mixture was heated for 3 × 2 min in a modified microwave oven (380 W). After a standard work-up and purification, 20 mg (0.010 mmol/43%) of red crystals were obtained.

R_f (SiO_2, $CH_3CN/CH_3OH/H_2O/KNO_3$: 40:10:10:1 v/v): 0.39; ^{1}H-NMR (300 MHz, CD_3CN): δ 8.59 (2H, t, CH_{bpy}); 8.52 (10H, d, CH_{bpy}); 8.48 (2H, m, CH_{bpy}); 8.12 (2H, m, CH_{bpy}); 8.10–8.02 (8H, m, CH_{bpy}); 8.01 (2H, td, CH_{bpy}); 7.94 (2H, dd, CH_{bpy}); 7.86–7.70 (8H, m, CH_{bpy}); 7.53 (2H, d, =CH–ant); 7.50–7.36 (16H, m, $CH_{bpy} + CH_{ar}$ 1, 4); 7.06 (6H, dd, CH_{ar} 2, 3); 6.98 (2H,

d, =CH–bpy); MS (FAB): *m/z* 1878 [$M^+ - PF_6$], 1736 [$M^+ - 2PF_6$], 1586 [$M^+ - 3PF_6$].

4.11.4. [(bpy)$_2$Os–btb–Os(bpy)$_2$](PF$_6$)$_4$ + [(bpy)$_2$Os–btb](PF$_6$)$_2$

btb (**11**) (20 mg, 0.032 mmol) are dissolved in 3 ml hot ethylene glycol after adding one drop of concd. HCl. After adding 34 mg (0.067 mol/2.05 equiv.) $Os(bpy)_2Cl_2$ the mixture was heated for 4×2 min in a modified microwave oven (530 W). After standard work-up and purification there remained 24 mg (0.011 mmol, 34%) of bis complex and 4 mg (0.003 mmol/10%) mono complex as dark olive crystals. The separation of the two complexes was controlled by TLC and appeared to give two clean products.

4.11.5. [(bpy)$_2$Os–btb–Os(bpy)$_2$](PF$_6$)$_4$

R_f (SiO_2, $CH_3CN/CH_3OH/H_2O/KNO_3$: 40:10:10:1 v/v): 0.32; ^{1}H-NMR (300 MHz, CD_3CN): δ 8.58 (2H, d, CH_{bpy}); 8.54 (2H, d, CH_{bpy}); 8.48 (8H, m, CH_{bpy}); 8.35 (2H, dd, CH_{bpy}); 7.94 (2H, d, CH_{bpy}); 7.93 (2H, m, CH_{bpy}); 7.90 (4H, d, CH_{bpy}); 7.87 (2H, m); 7.84 (2H, m); 7.81 (2H, td, ?); 7.74–7.61 (4×2H, dd each, CH_{bpy}); 7.51 (2H, d, =CH–ant); 7.45 (6H, m, CH_{ar} 1, 4): 7.41–7.27 (10H, m, CH_{bpy}); 7.06 (6H, m, CH_{ar} 2, 3); 6.96 (2H, d, =CH–bpy); MS (FAB): *m/z* 2054 [$M^+ - PF_6$], 1912 [$M^+ - 2PF_6$], 1765 [$M^+ - 3PF_6$].

4.11.6. [(bpy)$_2$Os–btbl(PF$_6$)$_2$

[$(bpy)_2$Os–btbl$(PF_6)_2$ was not further characterised, but was checked by the ratio of different integrals in the ^{1}H-NMR and was pure by TLC.

R_f (SiO_2, $CH_3CN/CH_3OH/H_2O/KNO_3$: 40:10:10:1 v/v): 0.19.

4.11.7. [(bpy)$_2$Ru–btb–Os(bpy)$_2$](PF$_6$)$_4$

[$(bpy)_2$Os–btb$](PF_6)_2$ (4 mg, 0.002 mmol) and 2 mg (0.003 mmol/1.33 equiv.) $Ru(bpy)_2C1_2 \cdot 2H_2O$ were dissolved in 5 ml ethylene glycol after the addition of two drops of water and heated for 4×2 min in a modified microwave oven (530 W). The brownish solution was treated as mentioned before but without purification on preparative plate. Green brown crystals (4 mg, 0.002 mmol, 88%) were obtained which showed only one spot on the TLC.

R_f (SiO_2, $CH_3CN/CH_3OH/H_2O/KNO_3$: 40:10:10:1 v/v): 0.31; ^{1}H-NMR (300 MHz, CD_3CN): very complicated due to the loss of symmetry. However, a splitting of the signal of the protons of the C–C double bond can be easily seen in the region between 6.8 and 7.0 ppm; MS (FAB): *m/z* 1966 [$M^+ - PF_6$], 1823 [$M^+ - 2PF_6$], 1678 [$M^+ - 3PF_6$].

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