Ruthenium(II) complexes with tetra-15-crown-5-phthalocyanine: synthesis and spectroscopic investigation

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The ruthenium complexes with tetra-15-crown-5-phthalocyanine and various axial ligands were synthesized and characterized by spectroscopy. A method for the synthesis of bisaxially coordinated ruthenium(II) tetra-15-crown-5-phthalocyaninates with the N-donor ligands $(R_4Pc)Ru(L_2)$ (R_4Pc^{2-} = [4,5,4′,5′,4″,5″,4‴,5‴-tetrakis(1,4,7,10,13-pentaoxotridecamethylene)phthalocyaninate-ion], L is trimethylamine (Me_3N), pyridine (py), isoquinoline (iqnl), triethylamine (Et_3N), pyrazine (pyz)) was developed. The preparation technique involves selective decarbonylation of $(R_4Pc)Ru(CO)(MeOH)$ on treatment with Me_3NO in excess N-donor solvent.

Key words: crown-ether-substituted phthalocyanines, ruthenium(II) complexes, N-donor ligand, supramolecular aggregation, electronic absorption spectra, ^1H NMR.

Platinum metals are characterized by the highest complexing ability throughout the Periodic Table.[1] In the series of platinum metals, ruthenium attracts attention as being able to have different oxidation states and different coordination numbers in the complexes. Therefore, its complexation with macrocyclic tetrapyrrole ligands may give coordination compounds of diverse structures, including complexes with macrocyclic ligands and different extra ligands, dimers with Ru—Ru bonds, and oligomers with bridging ligands.

Ruthenium phthalocyaninates are of practical interest as models of biological systems[2—4] and effective catalysts for oxidation of hydrocarbons.[5—7]

Metal crown-phthalocyaninates attract attention of researchers as building blocks for the design of supramolecular systems of different architectures surpassing in electrophysical characteristics similar types of compounds with other substituents.[8—11]

The purpose of this work was to synthesize and study the structure and spectroscopic properties of ruthenium(II) complexes with tetra-15-crown-5-phthalocyanine.

Results and Discussion

Previously,[12] we prepared the complex of ruthenium(II) tetra-15-crown-5-phthalocyaninate with CO and MeOH molecules as axial ligands, $(R_4Pc)Ru(MeOH)(CO)$ (**1**). The methanol molecule enters the complex during chromatography in which a chloroform—methanol mixture is used as the eluent.

The presence of the carbonyl ligand firmly attached to the Ru atom in complex **1** restricts the potential for further synthesis of monomeric and oligomeric ruthenium phthalocyaninates with other axial ligands. Variation of axial ligands could reveal new interesting properties of this type of compound or result in the synthesis of complexes with Ru—Ru bonds from these precursors. Thus, it appears pertinent to develop efficient methods for removal of the carbonyl ligand from complex **1** to replace it by labile axial ligands.

A method for decarbonylation of ruthenium complexes with porphyrin[13—15] or unsubstituted phthalocyanine[2,16] has been reported. A solution of PcRu(CO)X is subjected to long-term (20—50 h) photolysis by a mercury lamp with UV radiation. However, intense UV irradiation induces partial destruction of the tetrapyrrole macrocycles, which markedly decreases the yield of the complex (to 20—25%).

We showed that refluxing complex **1** in pyridine for 8 h does not induce decarbonylation. The IR spectrum of the resulting complex exhibits a strong band at 1945 cm^{-1} for the ν(CO) stretching mode. A similar reaction with pyrazine for 5 h does not result in decarbonylation either. It was also shown by IR spectroscopy that the methanol molecule present in complex **1**, unlike the CO molecule, is readily displaced by an N-donor ligand on dissolution of the complex in an appropriate solvent.

In the chemistry of heterometallic complexes, Me_3NO is used as a mild selective decarbonylating agent.[17,18]

We found that refluxing of a solution of complex **1** in chloroform with a fourfold excess of Me_3NO for 3 h fur-

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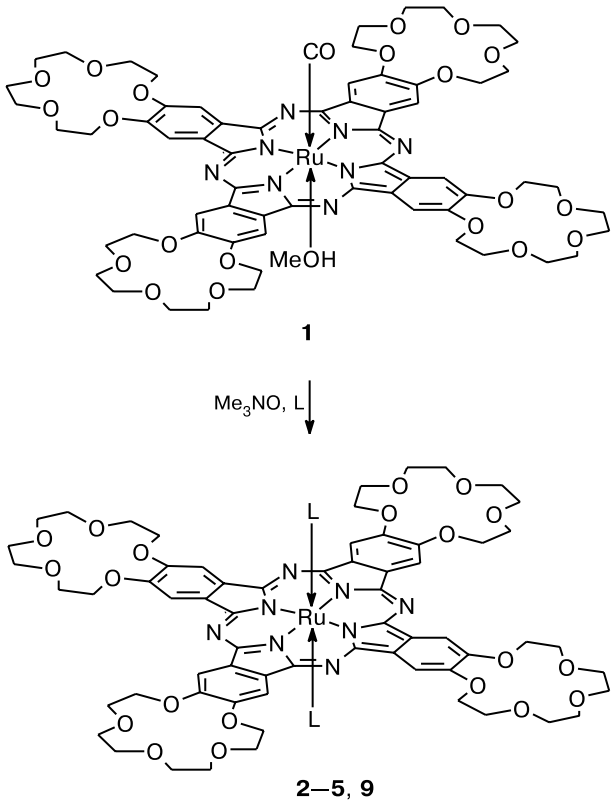
nishes the complex $(R_4Pc)Ru(Me_3N)_2$ (**2**) (Scheme 1). The degree of transformation was monitored by electronic absorption spectroscopy. In the spectra of the reaction mixture, a band at 625 nm appears during the synthesis in addition to the Q-band of the initial complex **1** at 655 nm. After separation and chromatographic purification of the reaction mixture, complex **2** was isolated in 14% yield.

Scheme 1



L is MeN, pyridine (py), isoquinoline (iqnl), Et_3N, or pyrazine (pyz)

To remove the carbonyl ligand from complex **1** with simultaneous replacement by labile axial ligands, we carried out the above-described reaction in N-donor solvents (pyridine, quinoline, triethylamine, and pyrazine), which substantially increased the yield of the complex compared to the synthesis in chloroform.

The reaction of a pyridine solution of **1** with Me_3NO (molar ratio **1** : Me_3NO = 1 : 4) at room temperature results in a new complex already after 10 min. A new band appears in the electronic absorption spectrum of the reaction mixture, in addition to the Q-band of complex **1** at 655 nm. The relative intensity of the new band increases with time. After 3 h, the electronic spectrum exhibits an intense band at 625 nm and no Q-band of complex **1**, indicating complete transformation of the starting complex. The separation and chromatographic purification of the reaction mixture gave complex $(R_4Pc)Ru(py)_2$ (**3**) in a yield of 38%.

We also carried out a similar decarbonylation of complex **1** in quinoline. Unlike the reaction in pyridine, this reaction did not proceed at room temperature. However, after heating of the reactants (**1** : Me_3NO = 1 : 4) for 15 min at 150 °C, the electronic spectrum of the reaction mixture did not show the absorption band for the starting complex **1**. After recrystallization and chromatography, the complex $(R_4Pc)Ru(iqnl)_2$ (**4**) was isolated in 42% yield (see ^1H NMR data).

To prepare the complex of ruthenium crown-phthalocyaninate with bulky aliphatic ligands, which markedly increase the solubility of the complex, we carried out the reaction of compound **1** with Me_3NO in triethylamine. As in the reaction with quinoline, no changes were observed at room temperature. The reaction took place on refluxing of the reaction mixture for 1 h. After recrystallization and chromatography, the complex $Ru(R_4Pc)(Et_3N)_2$ (**5**) was isolated in 40% yield.

Apart from complexes **3**—**5**, the three last-mentioned syntheses gave by-products $(R_4Pc)Ru(Me_3N)(L)$, where L is py (**6**), isoquinoline (**7**), and Et_3N (**8**) in ~20% yields (see ^1H NMR data). These complexes are formed upon decarbonylation induced by trimethylamine oxide.

With the view of preparing oligomeric ruthenium complexes with tetra-15-crown-5-phthalocyanine, complex **1** was made to react with Me_3NO in pyrazine, which is a bidentate N-donor ligand. Refluxing of a fourfold excess of Me_3NO with complex **1** in molten pyrazine for 20 min afforded complex $(R_4Pc)Ru(pyz)_2$ (**9**) in 48% yield. No oligomeric complexes were obtained (see ^1H NMR spectra). Probably, such complexes could be prepared under more drastic conditions. An oligomeric complex with bridging pyrazine molecules has been prepared[19] from the ruthenium complex with octaphenyltetraazaporphyrin (OPTAP)[19] by refluxing a solution of monomeric $(OPTAP)Ru(pyz)_2$ in chloroform for 5 days in a nitrogen flow. In the synthesis of complex **9**, the complex $(R_4Pc)Ru(Me_3N)(pyz)$ (**10**) was also isolated in 7% yield.

Direct template synthesis of crown-substituted ruthenium phthalocyaninates with various axial ligands from dicyanobenzo-15-crown-5 and ruthenium compounds in an appropriate N-donor solvent appears equally interesting. We started by using pyridine as such a solvent. However, the reaction did not proceed, apparently, as the pyridine boiling point is not high enough (b.p. 115 °C) for template condensation. Therefore, quinoline whose boiling point is much higher (b.p. 237 °C) was further chosen as the solvent. A mixture of $RuCl_3 \cdot 3H_2O$ and dicyanobenzo-15-crown-5 (molar ratio 1 : 8) was refluxed in quinoline for 4 h in an argon flow. Recrystallization and chromatography gave complex **4** in 24% yield. Complex **1** was also obtained in this synthesis.

Table 1. Parameters of the electronic absorption spectra of solutions of ruthenium(II) complexes with phthalocyanines

Compound	Solvent	λ_{max}/nm (logε)				Ref.
		Q	V	CT	B	
$Ru(R_4Pc)(CO)(MeOH)$ (**1**)	$CHCl_3$	655 (4.97)	593 (4.30)		313 (4.81)	*
$Ru(R_4Pc)(py)_2$ (**3**)	$CHCl_3$	625 (4.84)	573 sh	368 (4.57)	323 (5.13)	*
$Ru(Et_4Pc)(py)_2$	C_6H_5Me	630	571 sh	380 sh	338	20
$Ru(R_4Pc)(Me_3N)_2$ (**2**)	$CHCl_3$	625 (4.56)	573 sh	375 (4.26)	322 (4.80)	*
$Ru(R_4Pc)(Et_3N)_2$ (**5**)	$CHCl_3$	625 (4.88)	573 sh	368 (4.59)	324 (5.15)	*
$Ru(R_4Pc)(iqnl)_2$ (**4**)	$CHCl_3$	625 (4.42)	573 sh	368 (4.26)	324 (4.73)	*
$RuPc(iqnl)_2$	$CHCl_3$	628	576 sh	371 sh	314	21
$Ru(R_4Pc)(pyz)_2$ (**9**)	$CHCl_3$	631 (4.79)	576 sh	362 (4.54)	322 (5.15)	*
$RuPc(pyz)_2$	C_6H_5Cl	641	587	376 sh	314	19

* This work.

The crown-ether substituents in the complexes under study tend to retain solvent molecules; therefore, obtaining of elemental analysis data is faced with considerable difficulties.

Complexes **2**—**10** were described by electronic absorption, IR, and ^{1}H NMR spectroscopy and mass spectrometry.

The electronic absorption spectra of solutions of the complexes consist of intense bands for the $\pi\rightarrow\pi^*$ transitions of the tetra-15-crown-5-phthalocyanine ring, namely, the Q and B (Soret) bands (Table 1). The nature of the axial ligands affects appreciably the positions of bands in the electronic spectra of complexes. The Q-band of complex **1** is shifted bathochromically with respect to that in the spectra of complexes **2**—**10**, whereas the Soret band undergoes a hypsochromic shift (Fig. 1). The introduction of crown substituents into the macrocycle does not change much the electronic spectra of the complex as compared to the spectra of unsubstituted analogs. In addition, the electronic absorption spectra of complexes **2**—**10** exhibit a medium-intensity band CT at 368 nm. The absorption in this region observed in the spectra of low-spin phthalocyanine complexes of d^6-metals (M = Fe, Ru, Os) is usually assigned to charge transfer from the axial ligand to the macrocyclic ligand through the metal.[19] The position of this band depends on the nature of the axial ligand. In the series of Me_3N, Et_3N, pyridine, isoquinoline, and pyrazine, the band shifts bathochromically due to enhancement of the back dative π-bond with the corresponding ligands. The electronic absorption spectra of the complexes $(R_4Pc)Ru(L)_2$ and $(R_4Pc)Ru(Me_3N)L$ containing the same axial ligand L, where L is pyridine, isoquinoline, Et_3N, or pyrazine, virtually do not differ.

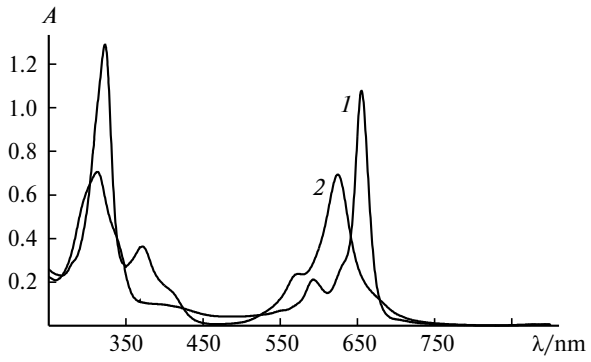


Fig. 1. Electronic absorption spectra for complexes **1** (*1*) and **4** (*2*).

The ^{1}H NMR spectra of the synthesized compounds, unlike the electronic absorption spectra, proved to be very useful for determination of the composition of complexes and the nature of axial ligands (Table 2). The spectra of the complexes exhibit, in the aromatic region, one narrow singlet with a chemical shift of about δ 8.5—8.9, which attests to the equivalence of all aromatic protons in the phthalocyanine macrocycle. The region of δ 3.90—4.82 contains a signal for the protons of the crown-ether CH_2 groups, $C(1)H_2$, $C(2)H_2$, $C(3)H_2$, and $C(4)H_2$. The ratio of the integral intensities of the signals corresponding to different protons in the phthalocyanine ligand is as follows: $I_{Ar} : I_{C(1)H_2} : I_{C(2)H_2} : I_{C(3)H_2,C(4)H_2} = 1 : 2 : 2 : 4$. In addition to the proton signals of the phthalocyanine ring and the crown ether fragments, the ^{1}H NMR spectra of the complexes also show the proton signals for the axially coordinated ligands. Owing to the pronounced influence of the ring current of the phthalocyanine macrocycle, the proton signals of the axial ligands are markedly shifted upfield with respect to those in free molecules. In the spectrum of a solution of complex **1** in $CDCl_3$, the high-field signal with δ −1.23 can be assigned to the protons of the Me group in MeOH; in the spectrum of complex **2**, the signal with δ −2.25 is attributable to the Me-group protons in Me_3N. In the spectrum of complex **3**, the signals with δ 2.49, 5.26, and 6.06 refer to the protons of the coordinated pyridine molecule. In conformity with published data,[21] the axially coordinated quinoline molecules are expected to be responsible for a doublet at

Table 2. Parameters of the ^{1}H NMR spectra of solutions of $Ru(R_4Pc)(L)(L')$ in $CDCl_3$

Complex	δ				
	H_{Ar}	$H_{C(1)H_2,C(8)H_2}$	$H_{C(2)H_2,C(7)H_2}$	$H_{C(3)H_2,C(4)H_2,C(5)H_2,C(6)H_2}$	$H_{axial\ ligands}$
$Ru(R_4Pc)(CO)(MeOH)$ (**1**)	8.90	4.82	4.26	3.97	−1.23
$Ru(R_4Pc)(Me_3N)_2$ (**2**)	8.53	4.67	4.17	3.91	−2.25
$Ru(R_4Pc)(py)_2$ (**3**)	8.50	4.62	4.15	3.90	6.06, 5.26, 2.49
$Ru(R_4Pc)(iqnl)_2$ (**4**)	8.54	4.64	4.15	3.90	6.98, 6.82, 6.66, 6.45, 5.58, 3.16, 2.39
$Ru(R_4Pc)(Et_3N)_2$ (**5**)	8.53	4.66	4.17	3.91	−0.15, −0.37
$Ru(R_4Pc)(pyz)_2$ (**9**)	8.58	4.66	4.17	3.90	6.44, 2.35

δ ~2.3 (α-proton), a triplet at δ ~3 (β-proton), and a doublet at δ ~5.5 (γ-proton).[21] However, the spectrum of complex **4** exhibits a doublet at δ 2.41, a singlet at δ 3.18, and a doublet at δ 5.62 with equal integral intensities. By analogy with published data,[22] these signals can be assigned to the protons of the coordinated isoquinoline molecule. The researchers cited[22] faced a similar problem during the synthesis of bis-quinoline adducts of the ruthenium complex with unsubstituted phthalocyanine. They performed a GC/MS study and found that commercially available quinoline always contains some isoquinoline. This reaction does not proceed in quinoline from which the isomer impurity has been removed. Apparently, this is due to the fact that coordination of a quinoline molecule is hampered by steric restrictions, which results in coordination of the isoquinoline ligand (Fig. 2). Since we use a 2000-fold excess of quinoline in the synthesis, the presence of even a 0.1% isoquinoline impurity in the initial commercial chemical is sufficient for the formation of a complex containing two isoquinoline molecules.

The high-field signals (δ −0.15, −0.37) in the spectrum of complex **5** are attributable to the protons of the coordinated triethylamine molecule.

The ^{1}H NMR spectrum of complex **9** exhibits, in addition to the signals for aromatic and crown-ether protons, two doublets at δ 6.44 and 2.35, which correspond to the protons of the pyrazine molecule. These data indicate that no bridging pyrazine molecule is present in the complex, because the signals of the pyrazine protons are magnetically inequivalent. Owing to the ring current of the phthalocyanine macrocycle, the signals of the pyrazine protons located closer to phthalocyanine are shifted upfield (δ 2.35) relative to the signals of the second group of protons (δ 6.44). The integral intensity of the signal for aromatic protons of the macrocycle is related to the sum of integral intensities of the δ 6.44 and 2.35 signals as 1 : 1, indicating the presence of two pyrazine molecules.

We also recorded the ^{1}H NMR spectra of the chromatographic fractions of compounds **6**—**8** and **10**, eluted after complexes **3**—**5** and **9**. In addition to the signals of the coordinated ligands, the spectra contained a high-field singlet at about 2 ppm. This signal was assigned to the protons of the coordinated trimethylamine molecule. The ratio of the integral intensities of the ^{1}H NMR signals of these complexes indicates that the composition of the complexes is $(R_4Pc)Ru(Me_3N)(L)$ (L = py, iqnl, Et_3N, pyz).

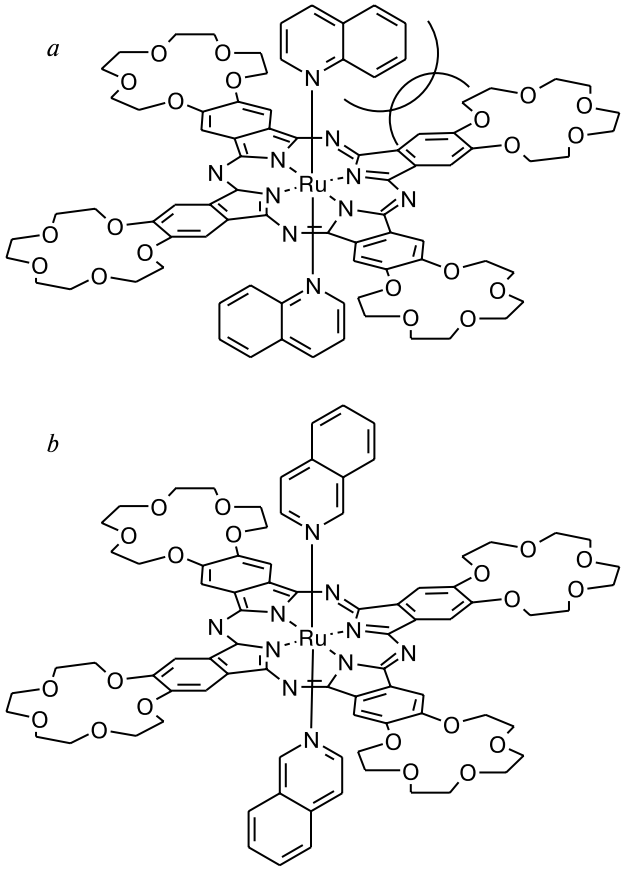


Fig. 2. Structure of the ruthenium complex and tetra-15-crown-5-phthalocyanine with axial ligands: quinoline (*a*) and isoquinoline (*b*).

The IR spectra of complexes 1—10 are typical of metal crown-phthalocyaninates. The strongest bands (900—1300 cm^{-1}) can be mainly assigned to vibrations of the crown-ether substituents in the macroring. The IR spectrum of complex **1** contains an intense band at

1934 cm^{-1}, which corresponds to the ν(CO) stretching mode. The fact that this band is missing from the IR spectra of complexes **2**—**10** attests to complete decarbonylation of complex **1** in these syntheses.

Previously, we have studied cation-induced supramolecular aggregation of $(R_4Pc)Ru(MeOH)(CO)$ by electronic absorption and FT IR spectroscopy.[23] It was found that the reactions of complex **1** with alkali metal thiocyanates afford "brickwork" supramolecular aggregates $n(R_4Pc)Ru(MeOH)(CO)\cdot 2nMNCS$ ($M^+ = K^+$, Rb^+, Cs^+). A specific feature of the aggregation processes induced by sodium thiocyanate is the participation of the central ruthenium(II) ion in the formation of supramolecular ensembles. The use of acetate or perchlorate substrate anions, instead of thiocyanate anions, was found to result in a different architecture of the supramolecular aggregate.

Experimental

The solvents (chloroform, pyridine, triethylamine) were dried and distilled prior to use. Methanol, quinoline, pyrazine, $Ru_3(CO)_{12}$, and Me_3NO (Aldrich) were used as received; $RuCl_3\cdot 3H_2O$ was prepared by solvent evaporation from a ruthenium(III) chloride solution in hydrochloric acid.

The UV-Vis electronic absorption spectra were recorded on a Varian Cary-100 spectrophotometer in quartz rectangular cells with an optical length of 1—10 mm.

^1H NMR spectra were recorded on a Bruker AC-200 instrument operating at 200 MHz. The samples were prepared as solutions in $CDCl_3$. Chemical shifts (δ) were measured at 303 K using signals of the residual protons in $CDCl_3$ (δ 7.25) as the internal standard.

The MALDI-TOF mass spectrum was obtained on a Bruker Daltonics, Reflex-III mass spectrometer with positive ion recording, using reflection mode with a target voltage of 20 mV. 2,5-Dihydroxybenzoic acid was used as the matrix. Electrospray ionization (ESI) mass spectra were obtained on a Finnigan MAT INCOS-50 mass spectrometer (EI, 70 eV, chemical ionization).

IR spectra were recorded on a Nicolet, Nexus FT IR spectrometer. The samples were prepared as films by evaporation of a chloroform solution of the complex on KRS-5 plates.

(Methanol)(tetra-15-crown-5-phthalocyaninato)carbonylruthenium(II) (1). The compound was synthesized by a previously reported procedure[12] from dicyanobenzo-15-crown-5 prepared by a known procedure[24] and $Ru_3(CO)_{12}$. Yield 80%. UV/Vis ($CHCl_3$) λ_{max}/nm (logε)): 655 (4.97), 593 (4.30), 313 (4.81). IR: ν(CO) = 1934 cm^{-1}. ^1H NMR (DMSO-d_6), 200 MHz, δ: 8.81 (s, 8 H, H_{Ar}); 4.68 (m, 16 H, $C(1)H_2$); 4.09 (m, 16 H, $C(2)H_2$); 3.80 (m, 32 H, $C(3)H_2$, $C(4)H_2$); –0.06 (s, 3 H, $C\underline{H}_3OH$). MALDI-TOF, *m/z*: found 1376.6 $[(R_4Pc)Ru]H^+$, 2750.0 $[(R_4Pc)Ru]_2H^+$, 4125.5 $[(R_4Pc)Ru]_3H^+$, 5496.8 $[(R_4Pc)Ru]_4H^+$. MS (ESI), *m/z*: found 1402.5 $[(R_4Pc)Ru(MeOH)]^+$.

Bis(trimethylamine)(tetra-15-crown-5-phthalocyaninato)ruthenium(II) (2). A mixture of $(R_4Pc)Ru(CO)(MeOH)$ (15 mg, 0.011 mmol) and Me_3NO (3.14 mg, 0.044 mmol), taken in 1 : 4 molar ratio, was dissolved in 4 mL of chloroform and the solution was refluxed for 3 h. The reaction mixture was diluted with chloroform, hexane was added, and the precipitate was filtered off. The precipitate was dissolved in chloroform and chromatographed on Al_2O_3 (neutral) using gradient elution with a $CHCl_3$—MeOH mixture. Elution with a $CHCl_3$—MeOH mixture (99.2 : 0.8, v/v) gave complex **2**. Yield 14%. MS (ESI), *m/z*: found 724.2 $[M - Me_3N]^{2+}$, calculated for $C_{67}H_{81}N_9O_{20}Ru$ 1430.4.

Bis(pyridine)(tetra-15-crown-5-phthalocyaninato)ruthenium(II) (3). A mixture of $(R_4Pc)Ru(CO)(MeOH)$ (20 mg, 0.014 mmol) and Me_3NO (4.14 mg, 0.056 mmol), taken in 1 : 4 molar ratio, was dissolved in 3 mL of a chloroform—pyridine mixture (1 : 2, v/v), and the mixture was kept for 3 h at room temperature. The reaction mixture was diluted with chloroform, hexane was added, and the precipitate was filtered off. The precipitate was dissolved in chloroform and chromatographed on Al_2O_3 (neutral) using gradient elution with a $CHCl_3$—MeOH mixture. Elution with a $CHCl_3$—MeOH mixture (99.5 : 0.5, v/v) gave complex **3**. Yield 38%. MALDI-TOF MS, *m/z*: found 1375.3 $[M - 2py + H]^+$; calculated for $C_{64}H_{72}N_8O_{20}Ru$ 1374.4. Elution with a $CHCl_3$—MeOH mixture (99 : 1, v/v) gave complex **6** in 20% yield.

Bis(isoquinoline)(tetra-15-crown-5-phthalocyaninato)ruthenium(II) (4). ***A.*** A mixture of $(R_4Pc)Ru(CO)(MeOH)$ (20 mg, 0.014 mmol) and Me_3NO (4.14 mg, 0.056 mmol) in 1 : 4 molar ratio was dissolved in 6 mL of a chloroform—quinoline mixture (1 : 1, v/v). The mixture was brought to boiling and kept for 15 min at 150 °C. Complex **4** was isolated and purified as described for the synthesis of complex **3**. Yield 42%. MS (ESI), *m/z*: found: 1375.4 $[M - 2qnl + H]^+$, 1627.8 $[M]^+$; calculated for $C_{64}H_{72}N_8O_{20}Ru$, 1374.4, for $C_{73}H_{79}N_9O_{20}Ru$, 1632.7.

By elution with a $CHCl_3$—MeOH mixture (99 : 1, v/v), complex **7** was isolated in 20% yield.

B. Dicyanobenzo-15-crown-5 (100 mg, 0.314 mmol) was dissolved in 5 mL of quinoline and $RuCl_3\cdot 3H_2O$ (10.3 mg, 0.039 mmol) was added. The reaction mixture was refluxed for 4 h under argon. After cooling, the mixture was diluted with chloroform and filtered. Hexane was added to give a dark-green crystalline precipitate. Column chromatography on Al_2O_3 (neutral) with gradient elution with a $CHCl_3$—MeOH mixture (99 : 0.5, v/v) gave complex **4** in 24% yield.

Bis(triethylamine)(tetra-15-crown-5-phthalocyaninato)ruthenium(II) (5). A mixture of $(R_4Pc)Ru(CO)(MeOH)$ (20 mg, 0.014 mmol) and Me_3NO (4.14 mg, 0.056 mmol), taken in 1 : 4 molar ratio, was dissolved in 6 mL of a chloroform—triethylamine mixture (1 : 1, v/v). The mixture was brought to boiling and refluxed for 1 h. Complex **5** was isolated and purified as described for the synthesis of complex **3**. Yield 40%. MS (ESI), *m/z*: found 727.2 $[M - Et_3N]^{2+}$; calculated for $C_{70}H_{87}N_9O_{20}Ru$, 1475.4.

Elution with a $CHCl_3$—MeOH mixture (99 : 1, v/v) gave complex **8** in 20% yield.

Bis(pyrazine)(tetra-15-crown-5-phthalocyaninato)ruthenium(II) (9). A mixture of $(R_4Pc)Ru(CO)(MeOH)$ (15 mg, 0.011 mmol) and Me_3NO (3.14 mg, 0.044 mmol), taken in 1 : 4 molar ratio, was dissolved in 3 mL of chloroform and put into 500 mg of molten pyrazine. The mixture was brought to boiling and refluxed for 20 min. Complex **9** was isolated and purified as described for the synthesis of complex **3**. Yield 48%. Elution with a $CHCl_3$/MeOH mixture (99 : 1, v/v) gave complex **10** in

7% yield. MS (ESI), *m/z*: found 727.1 $[M - pyz]^{2+}$; calculated for $C_{68}H_{76}N_{11}O_{20}Ru$, 1454.5.

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