Synthesis of bridged soluble phthalocyaninatoruthenium complexes

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The synthesis and characterization of hitherto unknown soluble octasubstituted ruthenium phthalocyanines R_8PcRu ($R = C_5H_{11}O$) by vacuum thermolysis of their bisaxial adducts with 3-chloropyridine is described. R_8PcRu ($R = C_5H_{11}O$, 2-Et-hexO) was reacted with 1,4-diisocyano-2,3,5,6-tetramethylbenzene (me_4dib) and 1,4-diisocyanobenzene (dib) to afford the oligomers $[R_8PcRu(me_4dib)]_n$ ($R = C_5H_{11}O$, 2-Et-hexO) and $[R_8PcRu(dib)]_n$ ($R = C_5H_{11}O$), which were characterized by spectroscopic methods.

Stacked transition metal phthalocyanines (MPc) have been synthesized by us to study their electrical and nonlinear optical properties.[1] In the so-called shish-kebab approach, stacking is achieved by linking transition metal macrocycles together with bidendate bridging ligands (L) to form compounds of the type $[PcM(L)]_n$. In this context, bridged macrocyclic transition metal complexes $[PcM(L)]_n$ with Ru as the central transition metal and tetrazine (tz), for example, as the bridging ligand have been investigated in great detail, since these compounds exhibit conductivities of $\sigma_{RT} = 0.01$–0.1 S cm^{-1} without external oxidative doping. These phthalocyaninatoruthenium bridged systems are more stable than the well-studied iron derivatives toward chemical and electrochemical oxidation of the central metal atom.[1,2] In addition, these compounds show a higher stability for complexation with ligands due to the larger radius of the metal ion in comparison with the corresponding iron derivatives.[1]

The synthesis of pure unsubstituted PcRu had been carried out by us for the first time by thermal decomposition of the complex $[PcRu(DMSO)_2] \cdot 2DMSO$,[3] however this method has some disadvantages, such as the rather complicated reaction path for its preparation. Hence, we developed an easier method for its preparation *via* the corresponding bis-isoquinoline complex, $PcRu(iqnl)_2$,[4] which can be thermally decomposed at 250 °C with formation of analytically pure PcRu. This synthetic route provided the basis for the preparation of novel bridged PcRu oligomers, $[PcRu(L)]_n$, with L = pyz, dib, tz and others, forming a new class of intrinsic semiconductors.[5]

A serious disadvantage of these PcRu oligomers is their insolubility in common organic solvents. Generally the solubility of metal phthalocyanines (PcM) can be increased by introducing substituents onto the periphery of the macrocycle,[1] leading to a larger distance between the inclined stacked PcMs and enabling their solvation. Introducing bulky groups like *tert*-butyl was an early approach used to obtain soluble compounds, *e.g.*, $Bu^t_4PcSi(OH)_2$.[6]

To prepare a soluble phthalocyaninatoruthenium with *tert*-butyl groups as peripheral substituents, the bis-pyridine or bis-isoquinoline complex $Bu^t_4PcRu(L)_2$ (L = py, iqnl) has to be synthesized first. Attempts to obtain Bu^t_4PcRu from $Bu^t_4PcRu(L)_2$ by careful removal of the ligands L by thermogravimetric methods afforded only an impure Bu^t_4PcRu.[7] However, this was reacted with bidendate ligands L such as dib or tz to give the corresponding phthalocyaninatoruthenium oligomers $[Bu^t_4PcRu(L)]_n$, which are found to be soluble in common organic solvents such as chloroform or toluene.[7,8] The oligomeric structures were proved by the usual methods and a chain length of about 30 units was determined by a detailed analysis of the ^1H NMR spectra.[8] The $[(Bu^t_4PcRu(dib)]_n$ oligomer prepared shows interesting optical properties.[9,10]

These interesting results obtained with the bridged phthalocyaninatoruthenium compounds prompted us to concentrate our efforts on the synthesis of other soluble phthalocyaninatoruthenium oligomers with a well-defined structure. $[Bu^t_4PcRu(dib)]_n$ contains a tetrasubstituted phthalocyaninatoruthenium subunit, which always leads to a mixture of four different isomers,[11] with D_{2h}, C_{4h}, C_s and C_{2v} symmetries. An octasubstituted system is symmetric, so there is no problem with isomer separation. We report here for the first time a general synthetic approach for these compounds.

Results and Discussion

Our first attempt to synthesize the pure, uncoordinated 2,3,9,10,16,17,23,24-octakis(pentyloxy)phthalocyaninatoruthenium(II), $(C_5H_{11}O)_8PcRu$ (**1**), was to react the metal-free $(C_5H_{11}O)_8PcH_2$ with $RuCl_3 \cdot 3H_2O$. We expected insertion of the metal ion into the metal-free phthalocyanine macrocycle; however, only an impure product was obtained with the metal-exchange technique.[12–14]

Alternatively, $(C_5H_{11}O)_8PcLi_2$ was prepared first by the cyclotetramerization of the corresponding dinitrile with lithium in pentanol and attempts were made to insert the ruthenium ion directly into the macrocycle by reacting $(C_5H_{11}O)_8PcLi_2$ with $RuCl_3 \cdot 3H_2O$ in 2-ethoxyethanol. The IR spectrum of the reaction product showed that this synthetic route leads also to an impure product, $(C_5H_{11}O)_8PcRuL_x$; the axially coordinated impurities show absorptions around 1900 cm^{-1}. Combined with a signal in the ^{13}C NMR spectra at 181.06 ppm the axial impurity L was identified as a carbonyl group. The $(C_5H_{11}O)_8PcRu(CO)$ complex (**2a**) appears to have been formed, although no carbonyl source was used along the synthetic pathway.[15] This result was proven by an analoguous synthesis with another substituent R = 2-ethylhexyloxy (2-Et-hexO) in the phthalocyanine ring. Again the carbonyl complex $(2\text{-Et-hexO})_8PcRu(CO)$ (**2b**) was obtained (Scheme 1).

However, we succeeded in using the complexes **2a**,**b** obtained by this method, without further purification, for the preparation of the bisaxially coordinated complexes $(C_5H_{11}O)_8PcRu(Bu^tNC)_2$ (**3a**) and $(2\text{-Et-hexO})_8PcRu(Bu^tNC)_2$ (**3b**) by reaction with an excess of *tert*-butyl isocyanide at 50 °C for 3 days. The purity of these products is proved by

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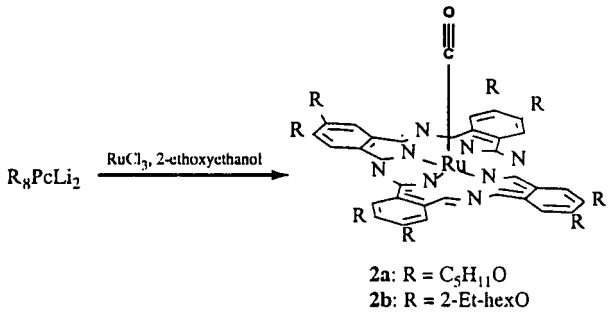
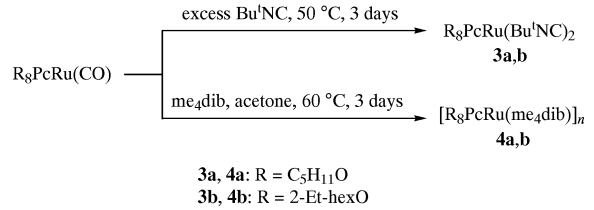


Scheme 1 Synthesis of $R_8PcRu(CO)$

spectroscopic data. The $[(C_5H_{11}O)_8PcRu\text{-}(me_4dib)]_n$ oligomer **4a** and the $[(2\text{-Et-hexO})_8PcRu(me_4dib)]_n$ oligomer **4b** can be synthesized by stirring **2a**,**b** with me_4dib in acetone for 3 days at 60 °C (Scheme 2). This pathway was used for the first time to synthesize oligomers based on octaalkoxy-substituted phthalocyaninatoruthenium.

The $\tilde{\nu}_{NC}$ frequencies of the oligomers **4a**,**b** are lower than those of the monomers **3a**,**b** (Table 1) due to the strong π-acceptor ability of the aromatic isocyanide ligand in me_4dib, leading to a stronger π backbonding compared with *tert*-butyl isocyanide.[16,17] In comparison to iron, ruthenium has a better ability to form π back bonds and hence the $\tilde{\nu}_{NC}$ frequencies of the ruthenium oligomers are around 10 cm^{-1} lower. The high electron density in octaalkoxy-substituted phthalocyanines causes a more intensive π backbonding to the axial ligand; consequently the $\tilde{\nu}_{NC}$ values of **3a**,**b** are lower than the free ligand values.

Further searching for a general route to synthesize soluble ruthenium phthalocyanines of the type R_8PcRu (*e.g.*, R = $C_5H_{11}O$) led to the synthesis of the model compound $Bu^t{}_4PcRu$ in a "pure" form by thermal decomposition of a suitable axial ligand from a bisaxially coordinated monomeric complex, $Bu^t{}_4PcRuL_2$. We have recently reported[18] on the synthesis of pure $Bu^t{}_4PcRu$ and $Bu^t{}_4NcRu$ (Nc = naphthalocyanine) by thermal decomposition of $Bu^t{}_4PcRu(3\text{-Clpy})_2$ and $Bu^t{}_4NcRu(3\text{-Clpy})_2$, respectively. 3-Chloropyridine (3-Clpy) was chosen as the axial ligand due to its low coordination strength, leading to a lower decomposition temperature. This has also the advantage that only the axial ligands and not the peripheral *tert*-butyl substituents are split off. 3-Chloropyridine as an axial ligand seemed to be suitable also for the preparation of octasubstituted alkoxyruthenium phthalocyanines for the thermolysis reaction. The monomeric complex $(C_5H_{11}O)_8PcRu(3\text{-Clpy})_2$ (**5**) was prepared by the reaction of stoichiometric amounts of 1,2-dicyano-4,5-bis(pentyloxy)benzene with $RuCl_3 \cdot 3H_2O$ in 2-ethoxyethanol in the presence of an excess of 3-chloropyridine and catalytic amounts of DBU (Scheme 3).



Scheme 2 Synthesis of $R_8PcRu(Bu^tNC)_2$ and $[R_8PcRu(me_4dib)]_n$

Table 1 $\tilde{\nu}_{NC}$ stretching frequencies of selected isocyanide complexes

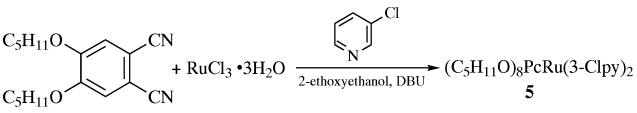
Compound	$\tilde{\nu}_{NC}/cm^{-1}$
Bu^tNC	2138
$(C_5H_{11}O)_8PcRu(Bu^tNC)_2$ (**3a**)	2129
$(2\text{-Et-hexO})_8PcRu(Bu^tNC)_2$ (**3b**)	2129
$(2\text{-Et-hexO})_8PcFe(Bu^tNC)_2$	2139
me_4dib	2113
$[(C_5H_{11}O)_8PcRu(me_4dib)]_n$ (**4a**)	2077
$[(C_5H_{11}O)_8PcRu(dib)]_n$ (**6**)	2079
$[(C_5H_{11}O)_8PcFe(me_4dib)]_n$	2079
$[(2\text{-Et-hexO})_8PcRu(me_4dib)]_n$ (**4b**)	2081
$[(2\text{-Et-hexO})_8PcFe(me_4dib)]_n$	2096

The ^1H NMR spectra of phthalocyanines are known to show large diamagnetic ring current shifts[19] and the ^1H NMR spectrum of **5** is found to be in agreement with the proposed structure. The signal of the macrocyclic protons appears at low field, 8.55 ppm, while the axial ligands are considerably shielded (see Experimental). The shorter the distance between the protons of the axial ligands and the centre of the macrocycle, the larger the shift of the ^1H NMR resonances to higher field.

The UV/VIS spectrum of **5** shows the typical pattern of a phthalocyanine, mainly the π-π* transition within the heteroaromatic π system. Substitution by electron-donating groups like alkyl or alkoxy chains on the macrocycle gives rise to a weak bathochromic shift of the Q band in comparison to the corresponding unsubstituted compounds. The absorption maxima reached in chloroform are given in Table 2.

The suitability of **5** to form pure $(C_5H_{11}O)_8PcRu$ (**1**) after thermal decomposition under vacuum was tested by thermogravimetric (TG) measurements under nitrogen, which is an easy procedure from which to obtain information on the thermal stability of the complexes $MacM(L)_2$.[7] The measurement shows the splitting off of the axial ligands at about 220 °C with a mass loss of 14.2% (calculated 14.9%). The alkoxy groups start to split off at about 330 °C. In comparison in the compound $Bu^t{}_4PcRu(3\text{-Clpy})_2$ the scission of the alkyl groups at about 400 °C proves its higher stability than the alkoxy-substituted Pcs.

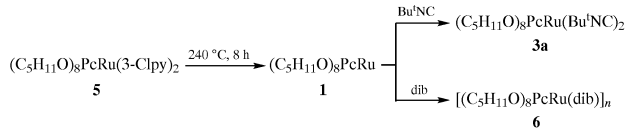
To ensure that only the axial ligands and none of the pentyloxy groups are removed during the thermal decomposition of the monomer **5**, the obtained $(C_5H_{11}O)_8PcRu$ **1** was treated with *tert*-butyl isocyanide to afford **3a** (Scheme 4). Integration of the resonances in the ^1H NMR spectrum of **3a** confirmed that none of the eight pentyloxy substituents is



Scheme 3 Synthesis of $(C_5H_{11}O)_8PcRu(3\text{-Clpy})_2$

Table 2 UV/VIS spectra of R_xPcRuL_2 in $CHCl_3$

R_xPcRuL_2	Q band/nm	B band/nm
$PcRu(3\text{-Clpy})_2$	626, 573 sh	402, 363, 321
$Bu^t{}_4PcRu(3\text{-Clpy})_2$	633, 585 sh	410, 364, 313
$(C_5H_{11}O)_8PcRu(3\text{-Clpy})_2$ (**5**)	626	366, 323
$Bu^t{}_4PcRu(Bu^tNC)_2$	648, 586 sh	314
$(C_5H_{11}O)_8PcRu(Bu^tNC)_2$ (**3a**)	647, 587 sh	325
$[(C_5H_{11}O)_8PcRu(me_4dib)]_n$ (**4a**)	658, 600	400, 325, 300
$[(2\text{-Et-hexO})_8PcRu(me_4dib)]_n$ (**4b**)	655, 600	410, 330, 310
$[(C_5H_{11}O)_8PcRu(dib)]_n$ (**6**)	652, 597 sh	320 sh, 297



Scheme 4 Synthesis of $(C_5H_{11}O)_8PcRu(Bu^tNC)_2$ (**3a**) and $[(C_5H_{11}O)_8PcRu(dib)]_n$ (**6**)

removed during decomposition of $(C_5H_{11}O)_8PcRu(3\text{-}Clpy)_2$ (**5**) under the experimental conditions used.

$(C_5H_{11}O)_8PcRu$ (**1**) is an air-stable black powder that is soluble in common organic solvents like chloroform and toluene. The ^1H NMR spectrum of **1** in $CDCl_3$ shows broad signals because of the expected paramagnetism of non coordinated square planar ruthenium(II) complexes.[20]

The axially bridged oligomer μ-(1,4-diisocyanobenzene)-2,3,9,10,16,17,23,24-octakis(pentyloxy)phthalocyaninatoruthenium(II), $[(C_5H_{11}O)_8PcRu(dib)]_n$ (**6**), was prepared by reaction of stoichiometric amounts of **1** with 1,4-diisocyanobenzene in acetone at 60 °C for 3 days (Scheme 4). In the IR spectrum a lower $\tilde{\nu}_{NC}$ stretching frequency at 2079 cm^{-1} is observed, which is comparable to that of **4a**. The higher value at 2087 cm^{-1} of the $[Bu^t{}_4PcRu(dib)]_n$ oligomer[8] is due to the lower electron density in the macrocycle and a consequence of the weak π backbonding abilities (Table 1). The Q band in the UV/VIS spectrum of **6** at 652 nm is bathochromically-shifted as compared to **5** (Table 2).

Conclusion

We have presented a method for the preparation of octaalkoxy-substituted phthalocyaninatoruthenium compounds R_8PcRu, *e.g.*, $R = C_5H_{11}O$ (**1**), by thermal scission of the axial ligands from the corresponding monomer $(C_5H_{11}O)_8PcRu(3\text{-}Clpy)_2$ (**5**). The purity of **1** was proven by IR, UV/VIS and ^1H NMR spectra and derivatization with Bu^tNC to obtain pure **3a**. R_8PcRu ($R = C_5H_{11}O$, 2-Et-hexO) was reacted with me_4dib and dib to afford the oligomers **4a**,**b** and **6**, which were characterized by spectroscopic methods.

Experimental

[Bis(3-chloropyridine)-2,3,9,10,16,17,23,24-octakis-(pentyloxy)phthalocyaninato]ruthenium(II) (5)

A mixture of $RuCl_3 \cdot 3H_2O$ (2.78 g, 9.27 mmol), 1,2-dicyano-4,5-bis(pentyloxy)benzene (0.61 mg, 2.32 mmol), 3 mL of 3-chloropyridine, 1.5 mL of DBU and 40 mL of 2-ethoxyethanol was refluxed for 3 days. The cooled solution was poured into MeOH–H_2O (1:1) and the precipitate was centrifuged and dried. After purification by column chromatography (silica gel; chloroform) the compound was dried at 60 °C *in vacuo*; (yield: 442 mg; 3.7%); anal. calcd (%) for $C_{82}H_{104}N_{10}O_8Cl_2Ru$: C 64.38; H 6.85; N 9.16; Cl 4.64; found: C 65.89; H 6.85; N 8.43; Cl 4.69; FT-IR (KBr, cm^{-1}): 2955 s, 2934 s, 2868 m, 1607 m, 1497 vs, 1458 vs, 1412 m, 1384 vs, 1340 m, 1273 vs, 1198 s, 1159 m, 1115 vs, 1055 s, 849 w, 833 w; UV/VIS ($CHCl_3$, nm): 625, 576 sh, 366, 323; ^1H NMR: δ = 8.55 (s, 8H); 6.00 (m, 2H, Ha); 5.15 (m, 2H, Hd); 4.51 (t, 16H); 2.42 (m, 2H, Hb); 2.38 (m, 2H, Hc); 2.08 (m, 16H); 1.61 (m, 32H); 1.02 (t, 24H).

2,3,9,10,16,17,23,24-Octakis(pentyloxy)phthalocyaninato-ruthenium(II), $(C_5H_{11}O)_8PcRu$ (1)

$(C_5H_{11}O)_8PcRu(3\text{-}Clpy)_2$ (**5**) (250 mg, 0.16 mmol) was heated slowly (5 °C min^{-1}) *in vacuo* (0.01 Torr) to a final temperature of 240 °C, which was maintained for 8 h to afford pure $(C_5H_{11}O)_8PcRu$ (**1**) as a black powder in quantitative yield (213 mg, 100%); anal. calcd (%) for $C_{72}H_{96}N_8O_8Ru \cdot 2H_2O$; C 64.60; H 7.53; N 8.37; Cl 0.00; found: C 62.80; H 7.41; N 8.02; Cl 0.00; UV/VIS ($CHCl_3$, nm): 700 sh, 632.5, 587 sh, 420 sh, 318; MS (FD, CH_2Cl_2): $m/z = 2604$ $[(C_5H_{11}O)_8PcRu]^+ \cdot 2$; MS (FAB, CH_2Cl_2): $m/z = 1302$ $[(C_5H_{11}O)_8PcRu]^+$.

Carbonyl[2,3,9,10,16,17,23,24-octakis(alkyloxy)phthalocyaninato]ruthenium(II), alkoxy = pentyloxy (2a) and 2-ethylhexyloxy (2b)

1,2-Dicyano-4,5-bis(alkyloxy)benzene (**2a** 1.5 g, 4.99 mmol; **2b** 1 g, 2.60 mmol) was added to a solution of Li metal (**2a** 350 mg, 50.72 mmol; **2b** 180 mg, 26.09 mmol) in pentan-1-ol (20 mL) and the mixture was refluxed for 2 h. The solvent was removed under reduced pressure and the residue was dried (80 °C, 0.01 Torr). The crude alkyloxyphthalocyaninatolithium formed was used without further purification in the next step. To a solution of alkyloxyphthalocyaninatolithium in refluxing 2-ethoxyethanol (20 mL) was added a solution of $RuCl_3 \cdot 3H_2O$ (**2a** 490 mg, 1.88 mmol; **2b** 260 mg, 0.99 mmol) in the same solvent (20 mL). The mixture was refluxed until the visible spectrum showed that all the metal had been exchanged (*ca.* 6 h) [Q band ($CHCl_3$): λ = 682 nm]. The cooled solution was poured into MeOH–H_2O (3:1) and the precipitate was centrifuged and dried. After purification by column chromatography (neutral alumina, $CHCl_3$) and drying (80 °C, 0.01 Torr), compounds **2a** and **2b** were obtained as blue powders [yield: **2a** 500 mg (30%), **2b** 270 mg (25%)]. **2a**: Anal. calcd (%) for $C_{73}H_{96}N_8O_9Ru$: C 65.89; H 7.27; N 8.42; found: C 66.01; H 7.37; N 7.55; FT-IR (KBr, cm^{-1}): 2955 vs, 2932 vs, 2870 vs, 1940 vs, 1607 m, 1497 vs, 1458 vs, 1412 m, 1383 s, 1277 vs, 1200 s, 1111 s, 1074 m, 1055 s, 989 w, 916 w, 887 w, 858 w; UV/VIS ($CHCl_3$, nm): 658, 634, 594, 410, 320, 300. **2b**: Anal. calcd (%) for $C_{97}H_{144}N_8O_9Ru$: C 69.88; H 8.71; N 6.72; found: C 68.75; H 9.04; N 6.37; FT-IR (KBr, cm^{-1}): 3078 vw, 2959 vs, 2928 vs, 2872 s, 2858 s, 1942 vs, 1607 w, 1497 vs, 1456 vs, 1410 m, 1381 s, 1348 w, 1277 s, 1200 m, 1157 w, 1109 s, 1055 vs, 901 w, 858 w, 731 w; UV/VIS ($CHCl_3$, nm): 658, 634, 594, 410, 320, 300 sh; MS (FD, CH_2Cl_2): $m/z = 3278.4$ $[(2\text{-Et-hexO})_8PcRu]^+ \cdot 2$.

[Bis(*tert*-butyl isocyanide)-2,3,9,10,16,17,23,24-octakis(2-ethylhexyloxy)phthalocyaninato]ruthenium(II), $(2\text{-Et-hexO})_8PcRu(Bu^tNC)_2$ (3b)

Compound **2b** (100 mg, 0.06 mmol) was stirred in an excess of *tert*-butyl isocyanide (1 mL) for 3 d at 50 °C. MeOH (5 mL) was added to the cooled solution and the precipitate was filtered and washed with MeOH until the solution was colorless. The residue was dried at 80°C in vacuum; yield 57 mg (53%). Anal. calcd (%) for $C_{106}H_{162}N_{10}O_8Ru$: C 70.52; H 9.04; N 7.76; found C: 69.98; H 8.97; N 7.69; FT-IR (KBr, cm^{-1}): 3069 vw, 2959 s, 2928 vs, 2872 m, 2858 m, 2129 vs, 1607 w, 1495 vs, 1456 vs, 1412 s, 1342 w, 1277 s, 1234 vs, 1198 s, 1155 m, 1113 vs, 1053 vs, 899 w, 860 w, 843 w; UV/VIS ($CHCl_3$, nm): 651, 595 sh, 330; ^1H NMR: δ 8.69 (s, 8H); 4.45 (d, 16 H, $J = 5.6$ Hz); 2.06 (m, 8H); 1.42–1.81 (m, 64H); 1.11 (t, 24H, $J = 7.4$ Hz); 0.98 (t, 24H, $J = 7.0$ Hz); −0.47 (s, 18H); MS (FD, CH_2Cl_2): $m/z = 1805.1$ $[(2\text{-Et-hexO})_8PcRu(Bu^tNC)_2]^+$, 3442.9 $[(2\text{-Et-hexO})_8PcRu(Bu^tNC)_2]^+ \cdot 2$.

μ-(1,4-Diisocyano-2,3,5,6-tetramethylbenzene)-2,3,9,10,16,17,23,24-octakis(alkyloxy)phthalocyaninato]ruthenium(II), alkoxy = pentyloxy (4a) and 2-ethylhexyloxy (4b)

Compound (**2a** 200 mg, 0.15 mmol; **2b** 200 mg, 0.12 mmol) was stirred with me_4dib in acetone (5 mL) for 3 days at 60 °C. MeOH (5 mL) was added to the cooled solution and the precipitate was filtered and washed with MeOH until the solution was colorless. The residue was dried at 80 °C in vacuum; (yield: **4a** 90 mg, 40%; **4b** 78 mg, 36%). **4a**: Anal. calcd (%) for $C_{84}H_{108}N_{10}O_8Ru$: C 67.85; H 7.32; N 9.42; found: C 67.44; H 7.15; N 9.28; FT-IR (KBr, cm^{-1}): 3080 vw, 2953 s, 2932 s, 2868 s, 2077 vs, 1607 m, 1495 vs, 1456 vs, 1412 s, 1385 vs, 1342 w, 1275 vs, 1198 s, 1155 m, 1111 vs, 1055 vs, 991 w, 914 w, 889 w, 851 w, 829 w, 752 w, 731 w; UV/VIS ($CHCl_3$, nm): 658, 600, 400, 325, 300; **4b**: Anal. calcd (%) for $C_{108}H_{156}N_{10}O_8Ru$: C 71.13; H 8.62; N 7.68; found: C 70.09;

H 8.16; N 7.11; FT-IR (KBr, cm^{-1}): 3078 vw, 2957 s, 2926 s, 2872 m, 2859 m, 2081 vs, 1607 w, 1495 vs, 1412 s, 1381 s, 1344 w, 1277 s, 1198 m, 1155 w, 1113 vs, 1053 vs, 899 w, 856 w, 729 w; UV/VIS ($CHCl_3$, nm): 655, 600, 410, 330, 310.

μ-(1,4-Diisocyanobenzene)-2,3,9,10,16,17,23,24-octakis-(pentyloxy)phthalocyaninato]ruthenium(II) (6)

Compound **1** (75 mg, 0.05 mmol) was stirred with dib (13 mg, 0.10 mmol) in acetone (5 mL) for 3 days at 60 °C. MeOH (5 mL) was added to the cooled solution and the precipitate was filtered and washed with MeOH until the solution was colorless. The residue was dried at 80 °C in vacuum; (yield: 83 mg, 94%). Anal. calcd (%) for $C_{80}H_{100}N_{10}O_8Ru$: C 67.16; H 7.04; N 9.79; found: C 62.41; H 6.39; N 10.08; FT-IR (KBr, cm^{-1}): 3082 w, 2953 s, 2932 s, 2079 vs, 1607 m, 1495 s, 1454 s, 1412 s, 1344 w, 1275 m, 1198 m, 1157 w, 111 s, 1055 s, 916 w, 887 w, 849 w, 752 w, 731 w, UV/VIS ($CHCl_3$, nm): 652, 597 sh, 320 sh, 297; ^{13}C NMR CP/MAS (Flip): δ 14.42, 22.75, 29.11, 68.82, 102.73, 122.56, 128.86, 132.89, 143.52, 149.44.

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