APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 649–660 (1996)

Synthesis of Oligomeric Axially Bridged Ruthenium Phthalocyanines and 2,3-Naphthalocyanines

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Bridged 2,3-naphthalocyaninatoruthenium oligomers {[MacRu(L)]$_n$} were synthesized and characterized using solid-state methods. For comparison, soluble t-butyl substituted phthalocyaninatoruthenium oligomers were prepared and their chain length examined by ^{1}H NMR spectroscopy. The powder conductivities of all bridged compounds ([MacRu(L)]$_n$) were measured and the dependence of the conductivities on the bridging ligands is discussed.

Keywords: naphthalocyanine; ruthenium; bridged; oligomers; solid state; NMR; conductivity

INTRODUCTION

Macrocyclic transition-metal complexes MacM [Mac=phthalocyaninato (Pc), tetrabenzoporphyrinato (TBP), 1,2- and 2,3-naphthalocyaninato (1,2-Nc and 2,3-Nc)] can be linked axially by bidentate bridging ligands (L) [e.g. L=1,4-diisocyanobenzene (dib), pyrazine (pyz), tetrazine (tz)] to form linear stacked systems [MacM(L)]$_n$ (e.g. M=Fe, Ru, Os) which show good semiconducting properties with and without doping.[1] Use of 2,3-naphthalocyanines as the macrocycle instead of phthalocyanines leads to oligomers which exhibit even better conductivities on account of their lower HOMO–LUMO gap.[2] Recently we reported for the first time on the synthesis of 2,3-naphthalocyaninatoruthenium and the axially bridged oligomers [2,3-NcRu(L)]$_n$ (L=pyz, tz).[3] Ruthenium complexes of the type MacRu(L)$_2$ and [MacRu(L)]$_n$ are more stable towards oxidation of the central metal atom[4] and they show a stronger complex stability due to the larger radius of the central metal atom than the well-studied iron derivatives.[1] Furthermore, materials with higher conductivities are obtained.[3]

In this paper we describe the synthesis and characterization of the monomeric complexes 2,3-NcRu(L)$_2$ [L=benzylisonitrile (BzNC) (**1**), 4,4′-bipyridine (bpy) (**2**)] and of the oligomers [2,3-NcRu(L)]$_n$ [L=1,4-di-isocyanobenzene (dib) (**3**), 1,4-di-isocyano-2,3,5,6-tetramethylbenzene (Me$_4$dib) (**4**), 9,10-di-isocyanoanthracene (dia) (**5**), 4-isocyano-3,5-dimethylpyridine (Me$_2$pyNC) (**6**), 4,4′-bipyridine (bpy) (**7**) and 1,4-diazabicyclo[2.2.2]octane (dabco) (**8**)] and the influence of bridging ligands (L) on their conductivities.

The bridged complexes [PcM(L)]$_n$ and [2,3-NcM(L)]$_n$, prepared by us, are hardly soluble in noncoordinating organic solvents.[1] Thus, to characterize these compounds, spectral methods specially applicable to solid-state materials were used. However, phthalocyanines and related macrocycles can be made soluble in common organic solvents by introducing bulky or long-chain substituents in the peripheral positions of the macrocycle,[1,5] e.g. t-butyl,[6] trimethylsilyl,[7] n-alkyl,[8] branched alkyl,[9] alkoxy[10] and alkoxymethylene[11] groups. The appropriate bridged oligomers of the type [(R)$_4$PcM(L)]$_n$ or [(R)$_8$PcM(L)]$_n$ also show a higher solubility in most organic solvents. Some time ago we reported on the first soluble oligomeric phthalocyaninatoruthenium complexes [(t-Bu)$_4$PcRu(dib)]$_n$ and [(t-Bu)$_4$PcRu(Me$_4$dib)]$_n$, which have been completely characterized by ^{1}H NMR spectroscopy,[12] including the chain length n, and which were further investigated with respect to their nonlinear[13] and photophysical properties.[14] These oligomers were prepared by reacting crude (t-Bu)$_4$PcRu(X)$_2$ with the appropriate ligand. Since no pure and ligand-free (t-Bu)$_4$PcRu was

CCC 0268–2605/96/080649–12

Received 27 April 1995
Accepted 11 May 1995

available, the synthesis of the more interesting pyrazine and tetrazine bridged complexes was not possible.

Recently we reported for the first time on an easy procedure for the preparation of pure (t-Bu)$_4$PcRu and (t-Bu)$_4$NcRu.[15] In continuation of our work we present herein the synthesis of the oligomeric t-butyl-substituted complexes [(t-Bu)$_4$PcRu(L)]$_n$ [L=pyz (**9**), dabco (**10**), bpy (**11**), tz (**12**), diaminotetrazine (datz) (**13**), Me$_2$pyNC (**14**) and dia (**15**)] and [(t-Bu)$_4$-2,3-NcRu(bpy)]$_n$ (**16**) respectively. For comparison, the monomers (t-Bu)$_4$PcRu(L)$_2$ [L=pyz (**17**), dabco (**18**), bpy (**19**)] and (t-Bu)$_4$-2,3-NcRu(L)$_2$ [L=isoquinoline (iqnl) (**20**), pyz (**21**)] were also prepared. The monomeric and axially bridged compounds were characterized by spectroscopic methods (mostly in solution) and their powder conductivities are discussed.

The monomeric complexes 2,3-NcRu(L)$_2$ [L=BzNC (**1**), bpy (**2**)] were prepared by treating 2,3-NcRu[3] with an excess of the appropriate ligand in chloroform. (t-Bu)$_4$ PcRu(L)$_2$ [L=pyz (**17**), dabco (**18**), bpy (**19**)] were synthesized by reacting stoichiometric amounts of 1,3-di-imino-5-t-butyl-1,3-dihydroisoindole[16] with $RuCl_3 \cdot H_2O$ in presence of excess of ligand. In the cases of **17** and **18**, the reaction was carried out in a solution of 2-ethoxyethanol, and in the case of **19** in a melt of bipyridine. The t-butyl-substituted 2,3-naphthalocyaninatoruthenium derivatives were prepared analogously to the phthalocyaninatometal complexes: (t-Bu)$_4$-2,3-NcRu(iqnl)$_2$ (**20**) was synthesized by reacting 2,3-dicyano-6-t-butylnaphthalene[17] with $RuCl_3 \cdot H_2O$ in quinoline which contained a small amount of isoquinoline,[18] and (t-Bu)$_4$-2,3-NcRu(pyz)$_2$ (**21**) was prepared starting from (t-Bu)$_4$-2,3-NcRu(II)[15] by treating it with an excess of pyrazine in chloroform. The monomeric complexes 2,3-NcRu(BzNC)$_2$ (**1**), 2,3-NcRu(bpy)$_2$ (**2**) and (t-Bu)$_4$MacRu(L)$_2$ (**17–21**) were purified by column chromatography.

The axially bridged oligomers [2,3-NcRu(L)]$_n$ (**3–8**) and [(t-Bu)$_4$PcRu(L)]$_n$ (**9–15**) were prepared by the reaction of stoichiometric amounts of the appropriate macrocycle with the bidentate ligands in acetone or chloroform at 60 °C. The solid products were filtered and washed with solvents (acetone or chloroform, respectively; see the Experimental section) and dried. In the case of [(t-Bu)$_4$PcRu(pyz)]$_n$ (**9**) the yield obtained by this method was low (35%) while considerable amounts of the monomeric complex (t-Bu)$_4$PcRu(pyz)$_2$ (**17**) were formed. The thermogravimetric data show that the thermal scission of the ligands in **17** takes place in two separate steps. At first, starting from 170 °C the oligomer [(t-Bu)$_4$PcRu(pyz)]$_n$ (**9**) is formed (T_{max}=240 °C), which decomposes completely in the second step. A similar procedure has been found to occur in the case of PcRu(pyz)$_2$[19] and 2,3-NcRu(pyz)$_2$,[3] respectively. Thus (t-Bu)$_4$ PcRu(pyz)$_2$ (**17**) was decomposed in a nitrogen stream at 200 °C to form [(t-Bu)$_4$PcRu(pyz)]$_n$ (**9**). The solid obtained was washed thoroughly with acetone and dried. The acetone-soluble fraction consists of the monomeric complex **17** and shorter chains, as shown by ^{1}H NMR spectroscopy (see below).

The monomeric complexes 2,3-NcRu(L)$_2$ (**1**, **2**) and (t-Bu)$_4$MacRu(L)$_2$ (**17–21**) are sufficiently soluble in chloroform to measure ^{1}H NMR spectra. The ^{1}H NMR spectra of phthalocyanines[20] and 2,3-naphthalocyanines[3,21] are known to show large ring current shifts. The resonances of the aromatic macrocyclic protons appear at low field, while the axial ligands are considerably shielded by the heteroaromatic ring system. The shorter the distance between the protons of a ligand and the centre of the metallomacrocycle, the larger is the shift of the resonances to higher field. The ^{1}H NMR data of **17–19** are given in Table 1 (for assignments, see Fig. 1).

Tetrasubstituted phthalocyanines and 2,3-naphthalocyanines are known to form mixtures of four constitutional isomers. Recently we reported on a successful separation of all four isomers of tetraethylhexyloxyphthalocyaninato =nickel (II) [(ethexO)$_4$PcNi] which were characterized by NMR spectroscopic methods.[22] The four constitutional isomers of (t-Bu)$_4$PcRu and

Table 1 ^{1}H NMR data of (t-Bu)$_4$Pc(pyz)$_2$ (**17**), (t-Bu)$_4$Pc-(dabco)$_2$ (**18**) and (t-Bu)$_4$Pc(bpy)$_2$ (**19**) (assignments: see Fig. 1)

Compound	H^a	H^b	H^c	H^d
pyz	8.63	8.63	—	—
(t-Bu)$_4$PcRu(pyz)$_2$ (**17**)	2.36	6.40	—	—
dabco	2.65	2.65	—	—
(t-Bu)$_4$PcRu(dabco)$_2$ (**18**)	−2.52	0.7	—	—
bpy	8.68	7.51	7.51	8.68
(t-Bu)$_4$PcRu(bpy)$_2$ (**19**)	2.55	5.42	6.36	7.96

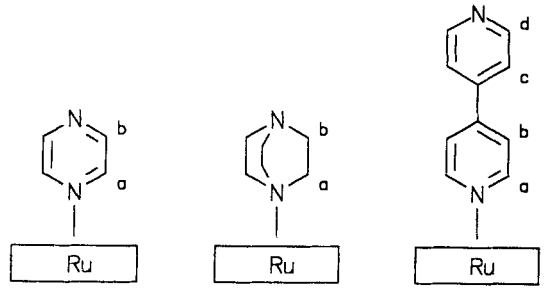

Figure 1 Assignment of (t-Bu)$_4$Pc(pyz)$_2$ (**17**), (t-Bu)$_4$Pc-(dabco)$_2$ (**18**) and (t-Bu)$_4$Pc(bpy)$_2$ (**19**) in Table 1.

(t-Bu)$_4$-2,3-NcRu are statistically distributed in the monomeric complexes **17–21**. Thereby eight isoindole units that are nonequivalent with regard to their neighbours are formed (C_{4h}: 1, D_{2h}: 1, C_{2v}: 2, C_s: 4), having protons which are expected to exhibit only slightly different chemical shifts. The oligomeric tetra-t-butylphthalocyaninatoruthenium complexes with dabco, bpy, me$_2$pyNC and dia as the bridging ligands are soluble enough to measure ^{1}H NMR spectra. The protons of the bridging ligands are influenced from the heteroaromatic π-systems and hence their resonances are more shifted to higher field than the proton resonances of the end groups. The integral ratio of the resonances due to the end groups to those of the inner protons serves to determine the chain length of the oligomers, which is about 20 for [(t-Bu)$_4$PcRu-(dabco)]$_n$ (**10**) and between 25 and 30 for [(t-Bu)$_4$PcRu(dia)]$_n$ (**15**). The solubility of the oligomeric complexes [(t-Bu)$_4$PcRu(pyz)]$_n$ (**9**) and [(t-Bu)$_4$PcRu(tz)]$_n$ (**12**) is insufficient to characterize them by NMR spectroscopic methods in solution, because their short inter-ring distances (*ca* 680 pm) hinder the solvation. As mentioned above, the acetone-soluble fraction of **9** consists of short chains (n = 1–4). The ^{1}H NMR data are given in Table 2 (for assignments, see Fig. 2). The diaminotetrazine-bridged complex **13** is not stable enough in solution to record an NMR spectrum (decomplexation occurs). Due to their enhanced solubility, ^{13}C NMR spectra of the monomeric (t-Bu)$_4$PcRu(L)$_2$ [L=pyz (**17**), dabco (**18**), bpy (**19**)] could be obtained. The oligomers [(t-Bu)$_4$PcRu(bpy)]$_n$ (**11**) and [(t-Bu)$_4$PcRu (Me$_2$pyNC)]$_n$ (**14**) are also highly soluble in chloroform, so that the ^{13}C-NMR data, the first for such species, were obtained. Spin–echo experiments were carried out to discriminate between tertiary (−) and quaternary C-atoms (+) (see the experimental section). For the oligomeric complexes, which are not soluble—or in the case of [(t-Bu)$_4$PcRu(datz)]$_n$ (**13**) not soluble enough to measure NMR spectra in solution—^{13}C-CP/MAS–NMR measurements were carried out. The ^{13}C-CP/MAS–NMR spectrum of [(t-Bu)$_4$PcRu(dia)]$_n$ (**15**) is shown in Fig. 3. The assignment was done by comparison with spectra measured in solution and by the NQS-technique (non-quaternary suppression). All ^{13}C NMR data are given in the Experimental section.

The IR spectrum of (t-Bu)$_4$PcRu(pyz)$_2$ (**17**) shows an intensive absorption at 1583 cm^{-1}, but a negligible absorption at this wavenumber in the corresponding oligometric [(t-Bu)$_4$PcRu(pyz)]$_n$ (**9**). This absorption is assigned to the centrosymmetric ring-stretching vibration, which is IR- and Raman-allowed for monocomplexed pyrazine and Raman-allowed for bidentate and free pyrazine.[23] This is due to the higher local symmetry in the bidentate (bridging) or free pyrazine (D_{2h}) compared with monocomplexed (terminal) pyrazine (C_{2v}), which has only one nitrogen bond to a metal atom. Similar explanations can be used for the interpretation of the IR spectra of (t-Bu)$_4$PcRu(bpy)$_2$ (**19**) and [(t-Bu)$_4$PcRu(bpy)]$_n$ (**11**). In the IR spectrum of **19**, the strong absorption due to the centrosymmetric ring-stretching vibration is observed at 1593 cm^{-1}, while in **11** this band appears with much lower intensity. These results were also observed for

Table 2 ^{1}H NMR data of ((t-Bu)$_4$PcRu)$_n$(pyz)$_{n+1}$; n = 1–4 (assignments: see Fig. 2)

Compound	H$^{2'}$	H^2	H^1	H^a	H^b	H^c	H^d	H^e
17	9.25	9.17	8.10	6.40	2.36			
9a	8.86	8.74	7.79	6.10	1.99	0.14		
9b	8.72	8.59	7.68	5.98	*	−0.13	−0.46	
9c	8.34	8.22	7.59	5.94	*	−0.24	−0.66	−0.76

* Signals under the signals of the t-Bu groups.

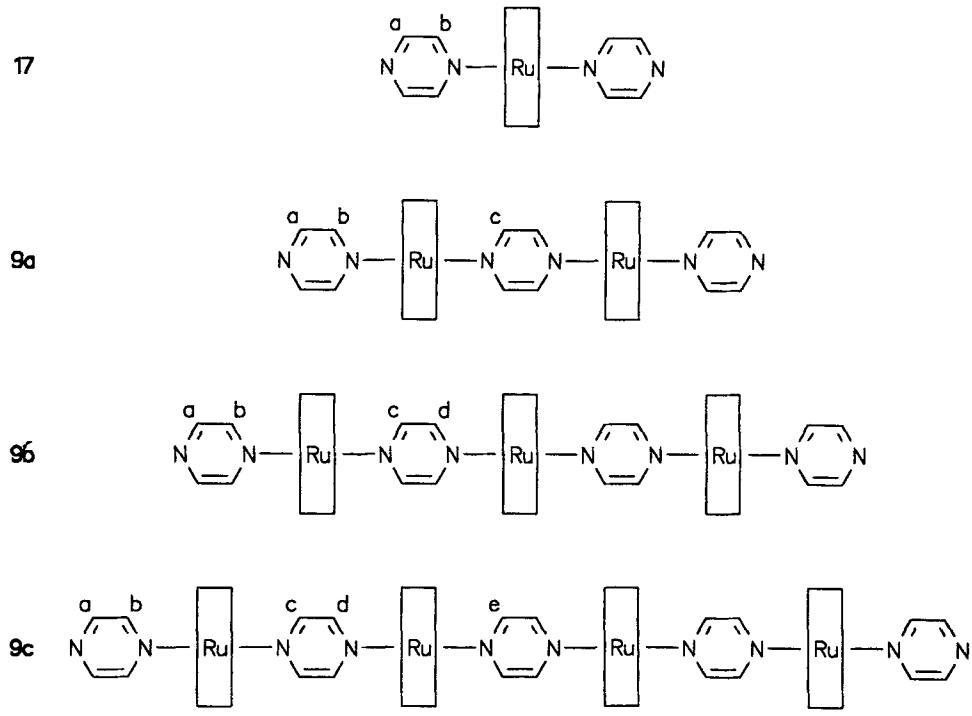

Figure 2 Assignment of $(t\text{-Bu})_4PcRu_n(pyz)_{n+1}$; $n = 1-4$ (**17**, **9a–9c**) in Table 2.

unsubstituted iron- and ruthenium-phthalocyaninato pyrazine and bipyridine complexes.[19,23] IR spectroscopy is also a useful tool for the analysis of isocyanide complexes because of the strong absorption of the NC groups. The different absorptions of the NC stretching frequency arising from changing from a free to a metal-coordinated ligand is dependent on the σ-donor and π-acceptor abilities of the metal–ligand bond.[24,25] For the formation of the σ-donor bond to the metal, a weakly antibonding MO is used, whereas the π-backbonding transfers electron density in a strongly antibonding MO of the isocyanide. While the coordination of an aliphatic isocyanide [e.g. BzNC in 2,3-NcRu(BzNC)$_2$ (**1**)] leads to a shift to higher frequencies, the NC absorptions of aromatic isocyanides complexes appear at lower frequencies. The reinforced π-acceptor ability of aromatic isocyanides can be explained by the possibility of delocalizing electron density into antibonding MOs. The charge transfer to π^*-orbitals of the NC group leads to a decrease of the bond order and hence to a decrease of the NC valence frequency. The strength of the π-acceptor bond depends on the bridging ligand, on the central metal and on the electronic properties of the equatorial macrocycle. The NC stretching frequencies of the oligomers prepared are given in Table 3, together with some other data for comparison.

In general, the isocyanophthalocyaninatoiron complexes show higher NC valence frequencies in comparison with the corresponding isocyano-2,3-naphthalocyaninatoiron compounds. In comparison with the dib-bridged oligomers, a decrease of the NC absorption is observed by using the annulated derivative 9,10-di-isocyanoanthracene (dia). In di-isocyanoanthracene, the antibonding MOs are lowered, and hence the π-acceptor ability is increased.

The UV/Vis spectra of phthalocyanines and 2,3-naphthalocyanines are mainly determined by $\pi-\pi^*$ transitions within the heteroaromatic π-system. The data of the complexes **1–21** are given in Table 4. In general, the 2,3-naphthalocyaninatoruthenium complexes show a bathochromically shifted Q-band in comparison to the appropriate phthalocyaninato derivatives. In the cases of $[(t\text{-Bu})_4PcRu(tz)]_n$ (**12**) and $[(t\text{-Bu})_4PcRu(datz)]_n$ (**13**) a broad absorption at 1315 nm and 1180 nm, respectively, was observed, which is typical for tetrazine-bridged coordination oligomers.[33] This near-IR absorp-

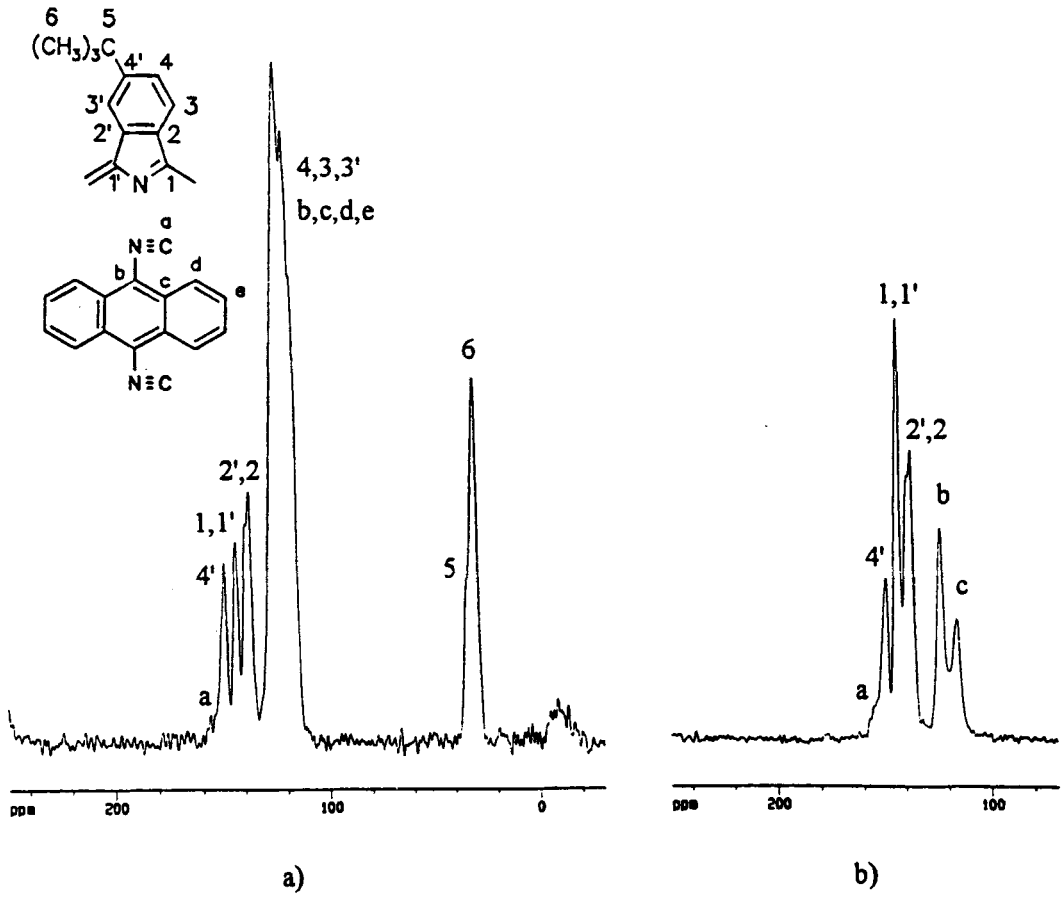

Figure 3 ^{13}C-CP/MAS–NMR spectrum of $[(t\text{-Bu})_4Pc(9,10\text{-dia})]_n$ (**15**).

tion is a metal-to-ligand charge-transfer band caused by a transfer of charge density from the central metal to the axially coordinated tetrazine. As shown by ultraviolet photoelectron spectroscopy (UPS), the energy of this transition can be correlated with the HOMO–LUMO gap. Accordingly, compound **12** has a band gap of 0.94 eV while for **13** a band gap of 1.05 eV was obtained. For $[(t\text{-Bu})_4PcFe(tz)]_n$, a band gap of only 0.82 eV was found. These different HOMO–LUMO gaps explain the different powder conductivities of the axially bridged oligomers **3–16**, which were measured by the two-probe or four-probe technique. The data are given in Table 5.

Comparing the powder conductivities of $[MacM(L)]_n$, some general trends can be observed. Using 2,3-naphthalocyanine instead of

Table 3 ν_{NC} stretching frequencies of selected isocyanide bridged complexes $[MacM(L)]_n$

L	PcFe	$(t\text{-Bu})_4$PcFe	2,3-NcFe	PcRu	$(t\text{-Bu})_4$PcRu	2,3-NcRu	free L
dib	2100[a]	2099[e]	2110[f]	2087[g]	2087[i]	2077	2130
Me_4dib	2109[b]	2096[e]	—	2084[h]	2084[i]	2081	2113
dia	2083[c]	—	2073[c]	—	2064	2054	2116
Me_2pyNC	2099[d]	2088[e]	—	—	2079	2021	2120

[a] Ref. 26. [b] Ref. 27. [c] Ref. 28. [d] Ref. 29. [e] Ref. 30. [f] Ref. 31. [g] Ref. 19. [h] Ref. 32. [i] Ref. 12.

Table 4 UV/Vis data of Q-bands of $MacRu(L)_2$ and $[MacRu(L)]_n$

Compound	Q-band (nm)
2,3-NcRu(BzNC)$_2$ (**1**)	715
2,3-NcRu(bpy)$_2$ (**2**)	718
(t-Bu)$_4$-2,3-NcRu(iqnl)$_2$ (**20**)	718
(t-Bu)$_4$-2,3-NcRu(pyz)$_2$ (**21**)	723
(t-Bu)$_4$PcRu(pyz)$_2$ (**17**)	648
(t-Bu)$_4$PcRu(dabco)$_2$ (**18**)	630
(t-Bu)$_4$PcRu(bpy)$_2$ (**19**)	632
[2,3-NcRu(dib)]$_n$ (**3**)	734
[2,3-NcRu(Me$_4$dib)]$_n$ (**4**)	734
[2,3-NcRu(dia)]$_n$ (**5**)	746
[2,3-NcRu(Me$_2$pyNC)]$_n$ (**6**)	756
[2,3-NcRu(bpy)]$_n$ (**7**)	726
[2,3-NcRu(dabco)]$_n$ (**8**)	737
[(t-Bu)$_4$-2,3-NcRu(bpy)]$_n$ (**16**)	724
[(t-Bu)$_4$-PcRu(pyz)]$_n$ (**9**)	645
[t-Bu)$_4$PcRu(dabco)]$_n$ (**10**)	622
[(t-Bu)$_4$PcRu(bpy)]$_n$ (**11**)	631
[(t-Bu)$_4$PcRu(tz)]$_n$ (**12**)	640
[(t-Bu)$_4$PcRu(datz)]$_n$ (**13**)	644
[(t-Bu)$_4$PcRu(Me$_2$pyNC)]$_n$ (**14**)	645
[(t-Bu)$_4$-PcRu(dia)]$_n$ (**15**)	647

phthalocyanine as the macrocycle in $[MacM(L)]_n$ leads to an increase in conductivity. This fact can be explained by the lowered HOMO–LUMO gap of 2,3-Nc in comparison with Pc.[2] Substitution with bulky groups, such as t-butyl, leads to a decrease of the powder conductivities. This decrease is stronger in the case of phthalocyanines than in 2,3-naphthalocyanines. The decrease of conductivity is caused by the substituents on the periphery of the macrocycle, which hinder the charge transfer from one chain to the other. In the case of the 2,3-naphthalocyanines, the influence of the substituents is lower. According to previous calculations,[35] the powder conductivities of $[PcM(L)]_n$ (L=pyz, tz) increase going from pyrazine to *s*-tetrazine as the bridging ligand, due to the lower HOMO–LUMO gap in the latter. An increase of the inter-ring distance in the bridged Pc and Nc oligomers leads to a decrease of the conductivities, which is shown using (for example) the pair pyrazine and bipyridine. 4-Isocyano-3,5-dimethylpyridine causes an inter-ring distance which lies between those of a pyrazine- and a tetramethyldi-isocyano-bridged oligomer, and hence the powder conductivity of $[(t\text{-}Bu)_4PcRu(Me_2pyNC)]_n$ (**14**) is found between $[(t\text{-}Bu)_4PcRu(pyz)]_n$ (**9**) and $[(t\text{-}Bu)_4PcRu(Me_4dib)]_n$.[12] Using 9,10-diisocyanoanthracene (dia) instead of dib leads to a decrease in conductivity. However, 9,10-dia is an interesting bridging ligand, because it is easy to dope due to its enlarged π-system, which was shown for $[PcFe(dia)]_n$.[28] Use of 1,4-diazabicyclo[2.2.2]octane (dabco) as a bridging ligand instead of pyrazine in $[(t\text{-}Bu)_4PcRu(L)]_n$ leads to an insulator. Dabco has no π-electrons; hence no charge transfer along the axis which links the metallomacrocycles together is possible. In the case of 2,3-naphthalocyaninatoruthenium as the macrocycle, the dabco-bridged oligomer shows a comparable high conductivity of 1.3×10^{-4} S cm^{-1}, which is due to partial oxygen doping of the macrocycle, which has been shown by us previously with other bridged 2,3-Nc oligomers.[1] Oxygen doping of the macrocycle

Table 5 Powder conductivities of $[MaCM(L)]_n$

Compound	σ_{RT} (S/cm^{-1})
$[PcFe(pyz)]_n$[a]	1×10^{-6}
$[PcRu(pyz)]_n$[b]	1×10^{-7}
$[(t\text{-}Bu)_4\text{-}PcFe(pyz)]_n$[c]	5×10^{-11}
$[(t\text{-}Bu)_4\text{-}PcRu(pyz)]_n$ (**9**)	7×10^{-8}
$[2,3\text{-}NcFe(pyz)]_n$[d]	1×10^{-5}
$[2,3\text{-}NcRu(pyz)]_n$[e]	7×10^{-3}
$[PcRu(dabco)]_n$[d]	1×10^{-9}
$[(t\text{-}Bu)_4PcRu(dabco)]_n$ (**10**)	$<10^{-12}$
$[2,3\text{-}NcRu(dabco)]_n$ (**8**)	1×10^{-4}
$[PcRu(bpy)]_n$[b]	2×10^{-8}
$[(t\text{-}Bu)_4PcRu(bpy)]_n$ (**11**)	1×10^{-10}
$[2,3\text{-}NcRu(bpy)]_n$ (**7**)	3×10^{-5}
$[(PcFe(tz)_n$[d]	2×10^{-2}
$[(PcRu(tz)]_n$[d]	1×10^{-2}
$[(t\text{-}Bu)_4PcFe(tz)]_n$[d]	9×10^{-9}
$[(t\text{-}Bu)_4PcRu(tz)]_n$ (**12**)	1×10^{-6}
$[2,3\text{-}NcFe(tz)]_n$[d]	4×10^{-2}
$[2,3\text{-}NcRu(tz)]_n$[e]	4×10^{-2}
$[PcRu(datz)]_n$[d]	1×10^{-3}
$[(t\text{-}Bu)_4PcRu(datz)]_n$ (**13**)	3×10^{-8}
$[(t\text{-}Bu)_4PcFe(Me_2pyNC)]_n$[c]	5×10^{-10}
$[(t\text{-}Bu)_4PcRu(Me_2pyNC)]_n$ (**14**)	2×10^{-10}
$[2,3\text{-}NcRu(Me_2pyNC)]_n$ (**6**)	1×10^{-5}
$[PcRu(dib)]_n$[d]	2×10^{-7}
$[(t\text{-}Bu)_4PcRu(dib)]_n$[f]	1×10^{-8}
$[2,3\text{-}NcRu(dib)]_n$ (**3**)	3×10^{-3}
$[PcRu(Me_4dib)]_n$[g]	1×10^{-7}
$[(t\text{-}Bu)_4PcRu(Me_4dib)]_n$[f]	1×10^{-11}
$[2,3\text{-}NcRu(Me_4dib)]_n$ (**4**)	1×10^{-4}
$[PcFe(dia)]_n$[h]	3×10^{-7}
$[(t\text{-}Bu)_4PcFe(dia)]_n$	2×10^{-10}
$[2,3\text{-}NcFe(dia)]_n$[h]	2×10^{-4}
$[2,3\text{-}NcRu(dia)]_n$ (**5**)	2×10^{-4}

[a] Ref. 34. [b] Ref. 19. [c] Ref. 30. [d] Ref. 1. [e] Ref. 3. [f] Ref. 12. [g] Ref. 32. [h] Ref. 28.

leads also to an increase in conductivity of all the bridged transition-metal 2,3-naphthalocyaninato oligomers reported in this paper, in comparison with the corresponding bridged phthalocyaninato transition-metal systems (Table 5).

In summary, we have prepared a number of axially bridged oligomers $[MacRu(L)]_n$ using $(t\text{-}Bu)_4Pc$, 2,3-Nc and $(t\text{-}Bu)_4$-2,3-Nc as macrocycles. While most of the oligomeric $(t\text{-}Bu)_4PcRu$ complexes are readily soluble in common organic solvents, the axially bridged 2,3-NcRu- and $(t\text{-}Bu)_4$-2,3-NcRu complexes are hardly soluble and their characterization was limited to solid-state methods. The powder conductivities of $[MacRu(L)]_n$ were measured and the dependence of the conductivity on the bridging ligands was discussed.

EXPERIMENTAL

The following instruments were used for characterization of the compounds.

IR	Bruker IFS 48
UV/VIS	Shimadzu UV-365, Shimadzu UV-3102 PC
MS	Varian MAT 711
^{1}H NMR	Bruker AC 250
Elemental analyses	Carlo Erba Elemental Analyzer 1104, 1106
CV	EG&G/PAR, Potentiostat/ Galvanostat Model 273
SEC	Jaissle Potentiostat model 1001 T-NC/Shimadzu UV-365

Tetra(t - butyl)phthalocyaninatoruthenium,[15] tetra(t - butyl) - 2,3 - naphthalocyaninatoruthenium,[15] 2,3 - naphthalocyaninatoruthenium,[3] di - isocyanobenzene,[36] tetramethyldi - isocyanobenzene,[32] 9,10 - di - isocyanoanthracene,[28] tetrazine,[29] 3,5 - dimethyl - 4 - isocyanopyridine[29] and 2,3 - dicyano - 6 - t - butylnaphthalene[17] were prepared according to literature methods.

Bis(benzylisocyano)-2,3-naphthalocyaninatoruthenium(II) (1) and bis(4,4'-bipyridyl)-2,3-naphthalocyaninatoruthenium(II) (2)

General method (Method a)
2,3-Naphthalocyaninatoruthenium(II) (163 mg; 0.2 mmol) and 10 mmol of the respective ligand were stirred in 5 ml $CHCl_3$ for 24 h at 60 °C. The solvent was evaporated and the excess of ligand was distilled in vacuum or removed by washing the reaction mixture with n-hexane. Further purification was carried out by column chromatography (silica gel/$CHCl_3$ for **1** or deactivated $Al_2O_3/CHCl_3$ for **2**).

2,3-NcRu(BzNC)$_2$ (1) (Method a)
Yield: 155 mg (74%), green powder. $C_{64}H_{38}N_{10}Ru$ calcd: C, 73.62; H, 3.28; N, 13.41. Found: C, 72.39; H, 3.50; N, 11.57%. IR (KBr), ν (cm^{-1}): 3051vw, 2920vw, 2152vs, 1493m, 1371s, 1354s, 1339s, 1199w, 1161m, 1128s, 1105vs, 1036w, 1016w, 885w, 758w. UV/Vis ($CHCl_3$), λ_{max} (nm): 715, 686, 641, 323. ^{1}H NMR (250 MHz), $CDCl_3$, δ (ppm): 9.78 (s, 8H), 8.51 (m, 8H), 7.78 (m, 8H), 6.66 (m, 2H), 6.45 (m, 4H), 5.19 (d, J=7.8 Hz, 4H), 2.60 (s, 4H). MS (FAB), m/z (%): 1048 (M^+), 931 ($M^+ - BzNC$), 814 ($M^+ - 2\times BzNC$).

2,3-NcRu(bpy)$_2$ (2) (Method a)
Yield: 170 mg (76%), green powder. $C_{68}H_{40}N_{12}Ru$ calcd: C, 72.52; H, 3.58; N, 14.92. Found: C, 71.04; H, 2.68; N, 14.70. IR (KBr), ν (cm^{-1}): 3049w, 1593m, 1504m, 1493m, 1406w, 1371s, 1354s, 1339m, 1261w, 1215w, 1200w, 1163s, 1130s, 1107vs, 1036w, 1016w, 950w, 887m, 872w, 806m, 760m, 739w, 714w, 623vw. UV/Vis ($CHCl_3$), λ_{max} (nm): 718, 688sh, 644, 423, 318. ^{1}H NMR (250 MHz), $CDCl_3$, δ (ppm): 9.72 (s, 8H), 8.48 (m, 8H), 8.16 (d, J=6.3 Hz, 4H), 7.76 (m, 8H), 6.36 (d, J=6.3 Hz, 4H), 5.53 (d, J=6.9 Hz, 4H), 2.89 (d, J=6.9 Hz, 4H). MS (FD), m/z (%): 1627 [$2\times(M^+ - 2\times bpy)$].

$[2,3\text{-}NcRu(L)]_n$

General method (Method b)
2,3-Naphthalocyaninatoruthenium(II) (81 mg; 0.1 mmol) and 0.11 mmol of the respective bidentate ligand were stirred in 5 ml $CHCl_3$ for 3 days at 60 °C. The precipitate was centrifuged and washed with $CHCl_3$. The residue was dried (0.01 Torr, 80 °C).

$[2,3\text{-}NcRu(Me_2pyNC)]_n$ (6)
Yield: 110 mg (86%), green powder. $C_{64}H_{32}N_{10}Ru$ calcd: C, 71.10; H, 3.41; N, 14.81. Found: C, 73.68; H, 3.17; N, 14.57%. IR (KBr), ν (cm^{-1}): 3049w, 2021s, 1493m, 1371s, 1354s, 1339s, 1261w, 1200w, 1161m, 1130s, 1105vs, 1036m, 1016m, 885m, 758s, 735m, 714m. UV/

Vis (fluorolube), λ_{max} (nm): 756, 680sh, 335. ^{13}C-CP/MAS–NMR (ref. glycine δ_{COOH}=176.03 ppm), δ (ppm): flip 143.9, 127.7, 13.3; NQS 144.0, 133.6, 13.12. MS (FAB), *m/z* (%): 946 (M^+), 814 ($M^+ - Me_2pyNC$).

[2,3-NcRu(dib)]$_n$ (3)
Yield: 89 g (94%), green powder. $C_{56}H_{28}N_{10}Ru$ calcd: C, 71.40; H, 3.00; N, 14.87. Found: C, 70.59; H, 2.99; N, 14.67%. IR (KBr), ν (cm^{-1}): 3049w, 2077s, 1495m, 1369s, 1354s, 1339s, 1261w, 1200w, 1159m, 1128s, 1103vs, 1033m, 1015w, 947w, 885w, 872w, 837w, 756m, 735m. UV/Vis (fluorolube), λ_{max} (nm): 734, 665sh, 346, 271. ^{13}C-CP/MAS–NMR (ref. glycine δ_{COOH}=176.03 ppm), δ (ppm): flip 144.4, 127.2, NQS 144.5, 133.1, 124.0. MS (FAB), *m/z* (%): 814 ($M^+ -$ dib).

[2,3-NcRu(Me$_4$dib)]$_n$ (4)
Yield: 91 mg (91%), green powder. $C_{60}H_{36}N_{10}Ru$ calcd: C, 72.20; H, 3.64; N, 14.03]. Found: C, 71.36; H, 3.67; N, 14.35%. IR (KBr), ν (cm^{-1}): 3049w, 2081s, 1491m, 1371s, 1354s, 1339s, 1261w, 1200w, 1161s, 1128s, 1105vs, 1036m, 1016w, 949w, 885m, 758m, 737w, 714m. UV/Vis (fluorolube), λ_{max} (nm): 734, 652sh, 351. ^{13}C-CP/MAS–NMR (ref. glycine δ_{COOH}=176.03 ppm), δ (ppm): flip 153.3, 144.3, 131.1, 12.4; NQS 144.2, 135.9, 131.6, 13.4. MS (FAB), *m/z* (%): 813 ($M^+ -$ Me$_4$dib).

[2,3-NcRu(dia)]$_n$ (5)
Yield: 100 mg (96%), green powder. $C_{64}H_{32}N_{10}Ru$ calcd: C, 73.77; H, 3.10; N, 13.44. Found: C, 72.74; H, 3.03; N, 12.86%. IR (KBr), ν (cm^{-1}): 3049w, 2054s, 1489m, 1369s, 1354s, 1339s, 1285w, 1261w, 1200w, 1159m, 1128s, 1103vs, 1034m, 1015m, 949w, 885m, 871w, 806w, 758s, 735m, 714m. UV/Vis (fluorolube), λ_{max} (nm): 746, 670sh, 356, 264. ^{13}C-CP/MAS–NMR (ref. glycine δ_{COOH}=176.03 ppm), δ (ppm): flip 157.3, 144.7, 135.5, 125.4, 119.7, NQS 156.9, 144.5, 135.7, 132.4, 125.1, 117.9. MS (FAB), *m/z* (%): 813 ($M^+ -$ dia).

[2,3-NcRu(bpy)]$_n$ (7)
Yield: 86 mg (89%), green powder. $C_{58}H_{32}N_{10}Ru$ calcd: C, 71.82; H, 3.33; N, 14.44. Found: C, 68.19; H, 3.41; N, 13.31%. IR (KBr), ν (cm^{-1}): 3047w, 1591m, 1485m, 1369s, 1354s, 1339s, 1261w, 1200w, 1163m, 1130s, 1105vs, 1036w, 1016w, 885m, 872w, 806m, 758s, 737w, 714m. UV/Vis (fluorolube), λ_{max} (nm): 726, 657, 429, 369, 318, 245. ^{13}C-CP/MAS–NMR (ref. glycine δ_{COOH}=176.03 ppm), δ (ppm): flip 150.6, 143.8, 137.2, 132.8, 128.0, 120.1; NQS 150.5, 143.9, 137.2, 133.1, 119.9. MS (FAB), *m/z* (%): 814 ($M^+ -$ bpy).

[2,3-NcRu(dabco)]$_n$ (8)
Yield: 74 g (79%), green powder. $C_{54}H_{36}N_{10}Ru$ calcd: C, 70.04; H, 3.92; N, 15.13. Found: C, 66.66; H, 3.92; N, 14.07%. IR (KBr), ν (cm^{-1}): 3047w, 1493w, 1466w, 1369s, 1329s, 1261w, 1198w, 1159s, 1130s, 1105vs, 1036w, 1015w, 883m, 804w, 758s, 729w, 714w. UV/Vis (fluorolube), λ_{max} (nm): 737, 666, 440, 373, 315. ^{13}C-CP/NAS–NMR (ref. glycine δ_{COOH}=176.03 ppm), δ (ppm): flip 143.5, 131.6, 126.4, 44.7; NQS 143.5, 135.9, 44.8. MS (FAB), *m/z* (%): 925 (M^+), 814 ($M^+ -$ dabco).

(t-Bu)$_4$NcRu(L)$_2$

Method c
6-t-Butyl-2,3-dicyanonaphthalene (2.34 g; 10 mmol) and $RuCl_3 \cdot 3H_2O$ (600 mg; 2.3 mmol) were heated in 20 ml quinoline (containing about 1% isoquinoline) for 20 h under reflux. The excess of solvent was distilled off. The black–green residue was purified by column chromatography (silica gel/$CHCl_3$) and dried in vacuum (0.01 Torr) at 80 °C.

(t-Bu)$_4$-2,3-NcRu(iqnl)$_2$ (20) (Method c)
Yield: 1.4 g (48%), green powder. $C_{82}H_{70}N_{10}Ru$ calcd: C, 75.96; H, 5.44; N, 10.80. Found: C, 76.06; H, 5.66; N, 10.44%. IR (KBr), ν (cm^{-1}): 3055 vw, 2953s, 2905w, 2866vw, 1499s, 1462m, 1369s, 1356vs, 1317w, 1271m, 1258m, 1188w, 1163m, 1144s, 1113vs, 1092w, 1042m, 949w, 901m, 822w, 808w, 746w, 721m, 642w. ^{1}H NMR (250 MHz), $CDCl_3$, δ (ppm): 9.68 (s, 4H), 9.64 (s, 4H), 8.41 (d, 4H), 8.38 (s, 4H), 7.84 (d, J=8.6 Hz, 4H), 6.90 (m, 2H), 6.73 (m, 2H), 6.64 (d, J=8.2 Hz, 2H), 6.42 (d, J=8.2 Hz, 2H), 5.62 (d, J=6.6 Hz, 2H), 3.42 (s, 2H), 2.69 (d, J=6.6 Hz, 2H), 1.60 (s, 36H). UV/Vis ($CHCl_3$), λ_{max} (nm): 718, 689sh, 640, 325. MS (FAB), *m/z* (%): 1296 (M^+, 20), 1167 ($M^+ -$ iqnl, 10), 1038 ($M^+ - 2\times$iqnl, 100).

(t-Bu)$_4$-2,3-NcRu(pyz)$_2$ (21) (Method a)
The preparation was as for 2,3-NcRu(BzNC)$_2$ (**1**) and 2,3-NcRu(bpy)$_2$ (**2**) starting from 100 mg (t-Bu)$_4$-2,3-NcRu(II). Yield: 85 mg (74%), green powder. $C_{72}H_{64}N_{12}Ru$ calcd: C, 72.16; H, 5.38; N, 14.02. Found: C, 72.23; H, 6.06; N, 13.24%. IR

(KBr), ν (cm^{-1}): 3051vw, 2953s, 2905w, 2866w, 1616w, 1582m, 1501m, 1481m, 1462m, 1416m, 1367s, 1356vs, 1317w, 1271m, 1259m, 1163w, 1144s, 1112vs, 1042w, 949w, 901m, 891m, 808m, 721m. ^{1}H NMR (250 MHz), $CDCl_3$, δ (ppm): 9.71 (s, 4H), 9.67 (s, 4H), 8.43 (d, 4H), 8.41 (s, 4H), 7.89 (d, J=8.7 Hz, 4H), 6.52 (d, J=4.5 Hz, 4H), 2.78 (d, J=4.5 Hz, 4H), 1.62 (s, 36H). UV/Vis ($CHCl_3$), λ_{max} (nm): 723, 690sh, 648, 322. MS (FAB), m/z (%): 1198 (M^+, 10), 1038 ($M^+ - 2\times$pyz, 60).

(μ-4,4′-Bipyridyl)-tetra(t-butyl) 2,3-naphthalocyaninatoruthenium(II) (16)

Method d

Compound **16** was prepared as for $[2,3\text{-NcRu(L)}]_n$ (**3–8**) starting from 100 mg $(t\text{-Bu})_4$-2,3-NcRu(II).

$[(t\text{-Bu})_4\text{-}2,3\text{-NcRu(bpy)}]_n$ (26)

Yield: 30 mg (26%), green powder. $C_{74}H_{64}N_{10}Ru$ calcd: C, 74.41; H, 5.40; N, 11.73. Found: C, 72.14; H, 6.73; N, 11.08%. IR (KBr), ν (cm^{-1}): 3053w, 2957s, 2905m, 2868w, 1612m, 1595m, 1502m, 1483m, 1462m, 1247m, 1367s, 1358vs, 1271m, 1259m, 1146s, 1113vs, 1042w, 1024vw, 949vw, 903m, 810m, 723w. UV/Vis (fluorolube$_3$), λ_{max} (nm): 724, 653, 426, 370, 320, 249. MS (FAB), m/z (%): 1038 (M^+ − bpy).

$(t\text{-Bu})_4PcRu(L)_2$

Bis(pyrazine)tetra (t-butyl)phthalocyaninatoruthenium(II) (17)

A mixture of 1.5 g (7.45 mmol) 1,3-di-imino-5-butyl-1,3-dihydroisoindole, 500 mg (1.9 mmol) $RuCl_3 \cdot 3H_2O$ and 1 g (12.49 mmol) pyrazine were heated under reflux in 40 ml 2-ethoxyethanol for two days. After cooling, the mixture was poured into 200 ml methanol/H_2O (3:1) and the crude product extracted with $CHCl_3$ and dried with $MgSO_4$. The solvent was evaporated and the product purified by column chromatography (silica gel/$CHCl_3$) and dried at 50 °C in vacuum. Yield: 682 mg (36%), violet powder. $C_{56}H_{56}N_{12}Ru$ calcd: C, 67.38; H, 5.66; N, 16.84. Found: C, 67.11; H, 5.73; N, 16.49%. IR (KBr), ν (cm^{-1}): 3071w, 2957vs, 2903s, 2858s, 1614w, 1583m, 1491s, 1416m, 1393m, 1364m, 1317m, 1281m, 1256m, 1225w, 1190w, 1152s, 1126s, 1115m, 1092m, 1051m, 1015w, 940w, 895w, 829w, 803w, 766w, 756w, 694w, 668w, 640w. UV/Vis ($CHCl_3$), λ_{max} (nm): 648, 591sh, 450, 315, 266sh. ^{1}H NMR ($CDCl_3$), δ (ppm): 9.25 (m, 4H), 9.17 (m, 4H), 8.10 (m, 4H), 6.40 (d, 4H), 2.36 (d, 4H), 1.68 (ns, 36H). ^{13}C NMR ($CDCl_3$), δ (ppm): 152.24, 144.92, 143.83, 143.65, 143.03, 140.45, 137.99, 126.10, 121.40, 118.23, 35.72, 32.06.

Bis(1,4-diazabicyclo[2.2.2]octan)tetra (t-butyl)phthalocyaninatoruthenium(II) (18)

A mixture of 1.5 g (7.45 mmol) of 1,3-di-imino-5 - t - butyl - ,3 - dihydroisoindole, 500 mg (1.9 mmol) $RuCl_3 \cdot 3H_2O$ and 2 g (17.83 mmol) 1,4-diazabicyclo[2.2.2]octane was heated in 60 ml 2-ethoxyethanol for two days under reflux. After cooling, the mixture was poured into 200 ml methanol/H_2O (3:1). The precipitate was centrifuged and dried. The crude product was purified by column chromatography (silica gel/$CHCl_3$ 98%, THF 2%) and dried at 50 °C in vacuum. Yield: 364 mg (18%), violet powder. $C_{60}H_{72}N_{12}Ru$ calcd: C, 67.83; H, 6.83; N, 15.82. Found: C, 66.87; H, 6.84; N 15.36%. IR (KBr), ν (cm^{-1}): 3065w, 2957vs, 2903s, 2876s, 1612m, 1491s, 1462s, 1394m, 1364m, 1317m, 1281m, 1256s, 1190m, 1150s, 1126s, 1115s, 1092m, 1063m, 1051m, 1012m, 981w, 948w, 919w, 899w, 829w, 807w, 779m, 766m, 758m, 735w, 692w, 669w. UV/Vis ($CHCl_3$), λ_{max} (nm): 630, 578sh, 380, 316. ^{1}H NMR ($CDCl_3$), δ (ppm): 9.14 (m, 4H), 9.07 (m, 4H), 7.97 (m, 4H), 1.74 (ns, 36H), 0.70 (t, 12H), −2.52 (t, 12H). ^{13}C NMR ($CDCl_3$), δ (ppm): 151.67, 143.94, 143.76, 141.12, 138.60, 125.64, 121.13, 118.05, 45.97, 44.61, 35.62, 32.02.

Bis(4,4′-bipyridine)tetra (t-butyl)phthalocyaninatoruthenium(II) (19)

1,3 - Di - imino - 5 - tert(butyl) - 1,3 - dihydroisoindole (**4**) (1.5 g, 7.45 mmol), 500 mg (1.9 mmol) $RuCl_3 \cdot 3H_2O$ and 20 g (128 mmol) 4,4′-bipyridine were heated at 160 °C for 36 h. After cooling, the excess of 4,4′-bipyridine was sublimed and the residue purified by column chromatography (silica gel/ethyl acetate). Yield: 743 mg (34%), violet powder. $C_{68}H_{64}N_{12}Ru$ calcd: C, 71.00; H, 5.61; N, 14.61. Found: C, 70.21; H, 6.02; N, 14.19%. IR (KBr), ν (cm^{-1}): 3071w, 2959vs, 2903m, 2866m, 1612m, 1593m, 1540w, 1491s, 1406s, 1394m, 1368m, 1317m, 1281m, 1258s, 1217w, 1193m, 1153s, 1128s, 1116m, 1092m, 1069m, 945w, 895w, 831w, 808m, 766m, 758w, 693w, 672w, 643w. UV/Vis ($CHCl_3$), λ_{max} (nm): 632, 584sh, 452, 365, 319. ^{1}H NMR ($CDCl_3$), δ (ppm): 9.20 (m, 4H), 9.08 (m, 4H), 8.19 (m, 4H), 7.96 (d, 4H), 6.36

(d, 4H), 5.42 (d, 4H), 2.55 (d, 4H), 1.72 (ns, 36H). ^{13}C NMR ($CDCl_3$), δ (ppm): 151.74, 150.62, 150.08, 143.83, 143.62, 142.82, 142.18, 140.60, 138.21, 125.65, 121.11, 120.06, 119.88, 117.93, 35.59, 32.00.

$[(t\text{-}Bu)_4PcRu(L)]_n$

μ-Pyrazine-tetra (t-butyl)phthalocyaninatoruthenium(II) (9)

$(t\text{-}Bu)_4PcRu(pyz)_2$ (**17**) (50 mg, 0.005 mmol) was heated under a nitrogen stream slowly to 200 °C. The temperature was maintained for 5 h. After cooling, the powder was extracted with acetone until the solvent was colourless. The residue was dried in vacuum at 50 °C. Yield: 46.5 mg (90%), violet powder. $[(t\text{-}Bu)_4PcRu(pyz)]_n \cdot 2$ acetone, $C_{58}H_{64}N_{10}O_2Ru$ calcd: C, 67.35; H, 6.24; N, 13.54. Found: C, 66.71; H, 6.23; N, 14.11%. IR (KBr), ν (cm^{-1}): 3076w, 2959vs, 2903s, 2868m, 1614m, 1583m, 1491s, 1416m, 1394m, 1364m, 1317m, 1281m, 1257m, 1191m, 1155s, 1126s, 1115m, 1092m, 1069w, 1051m, 1024w, 940w, 829w, 766w, 755w, 694w, 669w. UV/Vis ($CHCl_3$) λ max (nm): 645, 590, 305. ^{13}C-CP/MAS–NMR, δ (ppm): 151.05, 142.51, 136.00, 124.50, 120.97, 118.00, 35.00, 31.89.

(μ-4,4′-Bipyridyl)-tetra (t-butyl)phthalocyaninatoruthenium(II) (11)

A mixture of 99 mg (0.118 mmol) of $(t\text{-}Bu)_4$-PcRu and 18.43 mg (0.118 mmol) 4,4′-bipyridine was heated in 25 ml acetone for three days under reflux. The precipitate was centrifuged and washed with acetone until the solvent was colourless. The residue was dried in vacuum at 50 °C. Yield: 108 mg (92%), violet powder. $C_{58}H_{56}N_{10}Ru$ calcd: C, 70.07; H, 5.68; N, 14.08. Found: C, 69.04; H, 5.87; N, 13.88%. IR (KBr), ν (cm^{-1}): 3074w, 2959vs, 2905s, 2866m, 1612m, 1593m, 1487s, 1404m, 1395s, 1364m, 1317m, 1281m, 1256s, 1192m, 1153s, 1126s, 1115m, 1092m, 1051m, 941w, 831m, 808w, 767m, 756w, 694w, 669w, 623w. UV/Vis ($CHCl_3$), λ max (nm): 631, 580sh, 492, 370, 315. ^1H NMR ($CDCl_3$), δ (ppm): 9.00–8.50 (m), 8.08 (m), 7.85–7.50 (m), 6.24 (m), 5.24 (m), 4.00 (m), 2.24 (m), 1.90 (m), 1.42 (ns). ^{13}C NMR ($CDCl_3$), δ (ppm): 151.31 (+), 149.86 (−), 143.21 (+), 140.03 (+), 139.28 (+), 137.60 (+), 125.01 (−), 120.66 (−), 118.29 (−), 117.50 (−), 35.28 (+), 31.72 (−).

μ-1,4-Diazabicyclo]2.2.2]octane-tetra-(t-butyl)phthalocyaninatoruthenium(II) (10)

The procedure was as described above, using 156.4 mg (0.187 mmol) $(t\text{-}Bu)_4PcRu$, 20.94 mg (0.187 mmol) dabco and 20 ml acetone. Yield: 171 mg (86%) violet powder. $[(t\text{-}Bu)_4PcRu(dabco)]_n \cdot 2$ acetone, $C_{60}H_{72}N_{10}O_2Ru$ calcd: C, 67.58; H, 6.81; N, 13.13. Found: C, 66.69; H, 6.08; N, 13.18%. IR (KBr), ν (cm^{-1}): 3063w, 2957s, 2903s, 2872s, 1612s, 1491s, 1466s, 1394s, 1364s, 1317s, 1283s, 1256s, 1190m, 1153s, 1126s, 1092m, 1051m, 1007m, 941m, 896w, 831w, 768m, 748m, 694w, 669w. UV/Vis ($CHCl_3$), λ_{max} (nm): 622, 578sh, 368, 310. ^1H NMR ($CDCl_3$), δ (ppm): 8.60–7.60 (m), 1.70–1.00 (ns), 0.23 (m), −3.20 (m), −5.04 (m), −5.34 (m), −5.60 to 6.20 (m).

μ-Tetrazine-tetra (t-butyl)phthalocyaninatoruthenium(II) (12)

The procedure as above was followed, using 50 mg (0.06 mmol) $(t\text{-}Bu)_4PcRu$, 5 mg (0.06 mmol) *s*-tetrazine and 20 ml acetone and refluxing for six days. Yield: 60 mg (96%), violet powder. $[(t\text{-}Bu)_4PcRu(tz)]_n \cdot 2$ acetone, $C_{56}H_{62}N_{12}O_2Ru$ calcd: C, 64.91; H, 6.03; N, 16.22. Found: C, 64.25; H, 5.77; N, 16.01%. IR (KBr), ν (cm^{-1}): 3076w, 2961vs, 2903m, 2868m, 1614m, 1497s, 1395s, 1364s, 1323s, 1283m, 1258s, 1215w, 1192m, 1155s, 1124s, 1115s, 1090s, 1053m, 989m, 957w, 939m, 897w, 829w, 766w, 756w, 738w, 694w, 671w. UV/Vis ($CHCl_3$), λ_{max} (nm): 1315, 640, 590, 302. ^{13}C-CP/MAS-NMR, δ (ppm): 160.00, 151.03, 142.57, 138.71, 136.78, 124.50, 121.00, 119.84, 34.54, 32.07.

(μ-Diaminotetrazine)tetra (t-butyl)phthalocyaninatoruthenium(II) (13)

The procedure was as above, using 158.4 mg (0.189 mmol) $(t\text{-}Bu)_4PcRu$, 21.2 mg (0.189 mmol) diaminotetrazine and 30 ml acetone. Yield: 118 mg (62%), dark blue powder. $[(t\text{-}Bu)_4PcRu(datz)]_n \cdot$ acetone, $C_{53}H_{58}N_{14}ORu$ calcd: C, 63.14; H, 5.80; N, 19.45. Found: C, 62.55; H, 5.24; N, 19.32%. IR (KBr), ν (cm^{-1}): 3493m, 3391m, 3074w, 2959vs, 2903m, 2868m, 1612s, 1597s, 1486s, 1394m, 1364s, 1318s, 1283m, 1256m, 1192m, 1155m, 1124m, 1091m, 1051m, 958m, 943m, 899w, 837w, 766w, 756w, 694w, 671w. UV/Vis ($CHCl_3$), λ_{max} (nm): 1180, 644, 589, 303. ^{13}C-CP/MAS − NMR, δ (ppm): 153.86, 151.04, 143.38, 139.04, 136.73, 125.34, 120.53, 119.37, 35.23, 31.86.

(μ-4-Isocyano-3,5-dimethylpyridine)tetra (t-butyl)phthalocyaninatoruthenium(II) (14) Using 150 mg (0.179 mmol) $(t\text{-}Bu)_4PcRu$, 23.65 mg (0.179 mmol) 4-isocyano-3,5-dimethylpyridine and 25 ml acetone, the procedure described above was followed. Yield: 162 mg (88%), violet powder. $[(t\text{-}Bu)_4PcRu(Me_2pyNC)]_n \cdot$ acetone, $C_{59}H_{62}N_{10}ORu$ calcd: C, 68.92; H, 6.08; N, 13.62. Found: C, 68.79; H, 5.44; N, 13.97%. IR (KBr), ν (cm^{-1}): 3065w, 2957vs, 2904s, 2866s, 2079s, 2029sh, 1614m, 1591m, 1491s, 1393m, 1364m, 1319m, 1281m, 1256m, 1190m, 1155s, 1126s, 1092m, 1051m, 939w, 890w, 831w, 766w, 756w, 739w, 694w, 671w. UV/Vis ($CHCl_3$), λ_{max} (nm): 645, 588sh, 465, 308. ^1H NMR ($CDCl_3$), δ (ppm): 9.10–8.30 (m), 7.90–7.40 (m), 7.30 (m), 1.43 (ns), 0.56 (m), 0.23 (m), −1.68 (m). ^{13}C NMR ($CDCl_3$), δ (ppm): 151.21 (+), 147.30 (−), 142.54 (+), 139.38 (+), 136.97 (+), 126.62 (+), 125.24 (−), 120.66 (−), 117.63 (−), 35.28 (+), 31.71 (−), 12.08 (−).

(μ-9,10-Di-isocyanoanthracene)tetra (t-butyl)phthalocyaninatoruthenium(II) (15) 150 mg (0.179 mmol) $(t\text{-}Bu)_4PcRu$, 40.86 mg (0.179 mmol) 9,10-di-isocyanoanthracene and 30 ml acetone. Yield: 183 mg (91%), violet powder. $[(t\text{-}Bu)_4PcRu(dia)]_n \cdot$ acetone, $C_{67}H_{62}N_{10}ORu$ calcd: C, 71.57; H, 5.56; N, 12.46. Found: C, 70.59; H, 4.83; N, 12.51%. IR (KBr), ν (cm^{-1}): 3065w, 2959s, 2903w, 2866w, 2064vs, 1614w, 1491s, 1393m, 1364s, 1319m, 1283m, 1256m, 1192w, 1155s, 1126s, 1115m, 1090w, 1051w, 939w, 827w, 764m, 694w, 671w, 627w. UV/Vis ($CHCl_3$), λ_{max} (nm): 647, 589, 549, 415, 310, 295. ^1H NMR ($CDCl_3$), δ (ppm): 8.90 (m), 7.81 (m), 6.55 (m), 5.87 (m), 4.93 (m), 4.18 (m), 1.54 (ns). ^{13}C CP/MAS-NMR, δ (ppm): flip 155.00, 149.52, 144.30, 139.64, 137.87, 130–110, 34.50, 30.98; NQS 155.00, 149.52, 144.30, 139.64, 137.87, 124.19, 116.47, 34.50, 30.98.

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