$Ru(bpy\text{-}pyr)_3^{2+}$ films exhibit reversible metal-centered redox behavior at about +1.4V.

Scheme II

$$Ru^{II}(bpy\text{-}pyr)_3^{2+} \xrightarrow{h\nu} Ru^{III}(bpy\text{-}pyr)_2(bpy^{\bullet-}\text{-}pyr)^{2+*} \quad (5)$$

$$Ru^{III}(bpy\text{-}pyr)_2(bpy^{\bullet-}\text{-}pyr)^{2+*} + MV^{2+} \rightarrow Ru^{III}(bpy\text{-}pyr)_3^{3+} + MV^{+} \quad (6)$$

$$Ru^{III}(bpy\text{-}pyr)_3^{3+} \rightarrow Ru^{II}(bpy\text{-}pyr)_2(bpy\text{-}pyr^{+})^{3+} \quad (7)$$

$$n\,Ru^{II}(bpy\text{-}pyr)_2(bpy\text{-}pyr^{+})^{3+} \rightarrow \text{poly-}Ru^{II}(bpy\text{-}pyr)_3^{m+} + n\,H^{+} \quad (8)$$

$$Ru^{III}(bpy\text{-}pyr)_3^{3+} + MV^{+} \rightarrow Ru^{II}(bpy\text{-}pyr)_3^{2+} + MV^{2+} \quad (9a)$$

$$Ru^{II}(bpy\text{-}pyr)_2(bpy\text{-}pyr^{+})^{3+} + MV^{+} \rightarrow Ru^{II}(bpy\text{-}pyr)_3^{2+} + MV^{2+} \quad (9b)$$

As noted above, thicker films (vbpy-derived) are not fully electroactive in a direct electrochemical sense. If that problem cannot be overcome, then clearly many of the hoped for electrochromic applications will be largely circumscribed. Even so, the photoassembled films should be useful for analytical (fluorescence) applications—especially when prepared on nonconductive (nonquenching) glass or quartz surfaces. Our current interests are directed, in part, toward the design and assembly of chemically functionalized films and film-precursor complexes suitable for binding and detection of specific ions and molecules. With appropriate modifications, the photoredox approach might also provide an interesting entry into *soluble* metallopolymers and copolymers.

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Synthesis and Semiconducting Properties of Bridged (Phthalocyaninato)osmium Compounds with Bidentate N-Donor Ligands

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Monomeric and bridged bisaxially coordinated transition-metal complexes $MacML_2$ and $[MacML]_n$ with phthalocyanine (Pc), tetrabenzoporphyrine (TBP), 1,2- or 2,3-naphthalocyanine (1,2- or 2,3-Nc), and phenanthrenocyanine (Phc) as the macrocycles (Mac), transition metals, e.g. iron or ruthenium, as the central metal atom (M), and bidentate ligands (L), e.g. pyrazine (pyz), tetrazine (tz), and 1,4-diisocyanobenzene (dib), have been systematically investigated by us regarding their semiconducting properties.[1] Doping of the bridged systems $[MacML]_n$, e.g. with iodine leads to comparatively thermally stable compounds $[MacMLI_y]_n$ with good semiconducting properties (σ_{RT} = ~0.1 S/cm).[2]

We have shown that PcFe, PcRu, and some of their peripherally substituted derivatives and 2,3-NcFe, depending upon the conditions, react with tetrazine and 3,6-dimethyl-*s*-tetrazine (Me_2tz) to form the corresponding monomers $MacM(tz)_2$ and bridged compounds $[MacM(tz)]_n$, respectively.[3] In contrast to other bridged systems $[PcML]_n$ (M = e.g. Fe, Ru; L = e.g. pyz, dib) the tetrazine-bridged systems $[MacML]_n$ (L = tz, Me_2tz) already exhibit conductivities σ_{RT} = 0.01–0.1 S/cm without additional external oxidative doping.[3]

One of the factors responsible for the electrical conductivity in bridged macrocyclic transition-metal complexes is the band gap, which is determined by the energy difference between the LUMO of the bridging ligand and the HOMO of the transition metallomacrocycle.[4] Therefore, to achieve semiconducting properties in such systems, the metallomacrocycle should contain a high-lying HOMO; in addition, a bridging ligand which has a low-lying LUMO such as tz or Me_2tz should be used.[5] More detailed investigations about this intrinsic effect[5,6] have shown that these special semiconducting properties without doping were only observed with tetrazine-bridged systems $[MacM(tz)]_n$ in which the group VIII elements Fe and Ru were used as the central metal atom of the macrocycle. Therefore it is of interest to investigate whether or not the corresponding osmium compound $[PcOs(tz)]_n$ would also exhibit comparable intrinsic semiconducting properties like the corresponding iron and ruthenium systems $[PcM(tz)]_n$ (M = Fe, Ru).

Only recently have we been able to prepare pure osmium phthalocyanine, PcOs, and some of its monomeric bisaxially substituted complexes, e.g. $PcOs(py)_2$ and $PcOs(pyz)_2$.[7] We now report here on the first examples of the bridged oligomeric systems $[PcOsL]_n$ with the bidentate N-donor ligands pyz and tz.

Results and Discussion

PcOs was prepared essentially following our earlier method;[7] however, the yield could be improved by a slight change in the experimental procedure: *o*-cyanobenzamide is reacted with $OsCl_3 \cdot H_2O$ in molten naphthalene, and the crude reaction product is directly extracted with pyridine. As a result, all the $PcOsL_x$ derivatives described before[7] are converted into soluble $PcOs(py)_2$ which is isolated by chromatography. From the pure $PcOs(py)_2$ two pyridine molecules are split off at 400 °C, as indicated by an endothermic differential thermal analysis (DTA) maximum at 360 °C (mass loss 17.5%, calc 18.5%).[7] The remaining blue-black residue is pure PcOs(II) with an overall yield of 38%.

In order to obtain $PcOs(pyz)_2$, PcOs is reacted with an excess of pyrazine (1:10) at 80 °C. Extraction of the crude reaction product with chloroform yields $PcOs(pyz)_2$ in about 60% yield.

Among the routes developed by us for the preparation of $[PcFe(pyz)]_n$[8] and $[PcRu(pyz)]_n$,[9] respectively, only the method in which one pyrazine molecule is split off thermally from the monomer $PcRu(pyz)_2$ appeared to be promising for obtaining a homogeneous bridged $[PcOs(pyz)]_n$. The thermogravimetry (TG)/DTA analyses show that the splitting off of the pyrazine molecules from $PcOs(pyz)_2$ does not take place in two distinct steps as found in the case of $PcRu(pyz)_2$.[9] The first pyrazine

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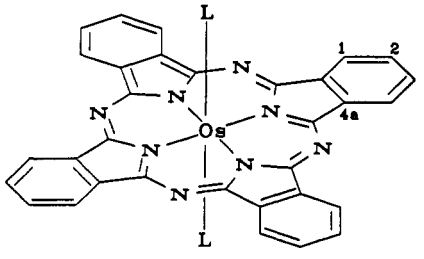
Table I. Powder Conductivities of Pyrazine- and Tetrazine-Bridged Phthalocyaninato Group VIII Metal Compounds $[PcML]_n$ (L = pyz, tz; M = Fe, Ru, Os) and the Corresponding Monomers $PcM(tz)_2$ (M = Fe, Ru, Os)

compd	σ_{RT}, S/cm[a]	ref
$[PcOs(pyz)]_n$	1×10^{-6}	this work
$PcOs(tz)_2$	4×10^{-8}	this work
$[PcOs(tz)]_n$	9×10^{-3} [b]	this work
$[PcFe(pyz)]_n$	2×10^{-6}	1
$PcFe(tz)_2$	$<10^{-9}$	1
$[PcFe(tz)]_n$	1×10^{-1} [b]	3
$[PcRu(pyz)]_n$	1×10^{-7}	9
$PcRu(tz)_2$	10^{-11}	3
$[PcRu(tz)]_n$	1×10^{-2} [b]	3

[a] All conductivities were measured at ambient temperature under aerobic conditions. [b] Four-probe method.

molecule in $PcOs(pyz)_2$ is split off below 320 °C (with an endothermic maximum at 312 °C) and the second pyrazine molecule gradually afterward. The product obtained below 320 °C is insoluble in common organic solvents and exhibits a ratio of PcOs:pyz = 1:1 as shown by TG. A pentacoordinated PcOs(pyz) can be ruled out by the diamagnetism of the product, indicating the hexacoordinated structure $[PcOs(pyz)]_n$ for a d^6 metal ion. Comparison of the IR spectra of $PcOs(pyz)_2$ and the product left from TG/DTA analyses also confirms the oligomerization and formation of the bridged $[PcOs(pyz)]_n$: The characteristic absorption of the monodentate pyrazine molecule around ν = 1580 cm^{-1} in $PcOs(pyz)_2$ appears only as a very weak band after oligomerization.[10] The weak absorption is attributed to the end groups of the oligomer $[PcOs(pyz)]_n$. The IR spectra of $[PcOs(pyz)]_n$ and $[PcRu(pyz)]_n$[9] are almost identical.

Reaction of (phthalocyaninato)osmium(II) (PcOs) with tetrazine (tz) in a ratio of 1:15 in chloroform at 70 °C for 48 h afforded both the monomer $PcOs(tz)_2$ and the oligomer $[PcOs(tz)]_n$. In contrast to the insoluble $[PcOs(tz)]_n$, the monomer $PcOs(tz)_2$ is very soluble in $CHCl_3$ and is easily separated from the oligomer. From the ^1H and ^{13}C NMR spectra of the soluble $PcOs(tz)_2$, the coordination of only one nitrogen atom of tetrazine with the metal ion could be demonstrated. The IR spectra of $PcOs(tz)_2$ and $[PcOs(tz)]_n$ compare very well with the IR spectra of the corresponding ruthenium compounds $PcRu(tz)_2$ and $[PcRu(tz)]_n$,[3] respectively, and thereby prove also the bridged structure of $[PcOs(tz)]_n$.



L = pyridine, pyrazine, tetrazine

The UV/vis spectrum of $[PcOs(tz)]_n$ shows, besides the typical Pc absorption at λ = 325 (B-band) and 670 nm (Q-band), a strong absorption between 1000 and 1700 nm, which we assign to a CT-band. This absorption is not present in $[PcOs(pyz)]_n$. Similar CT-bands were also observed in the tetrazine-bridged systems $[MacML]_n$ (Mac = Pc, 2,3-Nc; M = Fe, Ru; L = tz, Me_2tz).[5,11] These bands arise due to an internal charge transfer from the central group VIII metal atom to the bridging ligands tz and Me_2tz, which is one of the reasons for the intrinsic semiconducting properties of this type of compounds.[11]

The powder conductivities of the phthalocyaninatoosmium compounds prepared are listed in Table I together with the (phthalocyaninato)iron and -ruthenium monomers $PcM(tz)_2$ (M = Fe, Ru) and the bridged systems $[PcML]_n$ (M = Fe, Ru; L = tz, pyz).

As can be seen from the data listed in Table I, $[PcOs(pyz)]_n$, like the iron and ruthenium compounds $[PcM(pyz)]_n$ (M = Fe, Ru), is a weak semiconductor, whereas $[PcOs(tz)]_n$ exhibits good semiconducting properties without oxidative doping. This effect is also found in the tetrazine-bridged iron and ruthenium compounds $[MacM(tz)]_n$ (Table I). As we have described earlier for the corresponding (phthalocyaninato)iron and -ruthenium monomers $PcM(tz)_2$ (M = Fe, Ru), $PcOs(tz)_2$ exhibits almost insulating properties. After oligomerization to form $[PcOs(tz)]_n$ the conductivity increases also here by 5 powers of 10.

Experimental Section

$PcOs(py)_2$. A mixture of *o*-cyanobenzamide (15 g, 0.1 mol), $OsCl_3 \cdot H_2O$ (1.0 g, 2.94 mmol), and naphthalene (10 g, 78 mmol) was heated up to 290 °C under N_2 and kept at this temperature for 1 h. After cooling, the product was ground and washed with ethanol (50 mL). Then it was extracted with pyridine until the extract became completely colorless (~8 h), and this pyridine solution was further refluxed for 24 h. Pyridine was completely evaporated under reduced pressure, the residue was dissolved in $CHCl_3$ (150 mL), and then the solution was filtered. The volume of the filtrate was reduced by evaporation, and then the filtrate chromatographed (activated neutral $Al_2O_3/CHCl_3$). Yield: 950 mg (37.5%). IR (Nujol): 1605, 1522, 1417, 1377, 1325, 1291, 1216, 1171, 1125, 1067, 1007, 945, 915, 773, 763, 755, 735, 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.18 (d, 4 H, py—H^a), 5.22 (t, 4 H, py—H^b), 6.16 (t, 2 H, py—H^c), 7.67 (m, 8 H, Pc—H^2), 8.78 (m, 8 H, Pc—H^1). ^{13}C NMR ($CDCl_3$): δ 121.9 (C_1), 123.6 (py—C_b), 128.3 (C_2), 132.5 (py—C_c), 139.8 (C_{4a}), 148.4 (N=C—N), 150.9 (py—C_a). MS (FD): *m/e* = 858, 859, 860, 862, 863 (M^+). UV/vis ($CHCl_3$): λ = 620, 580 (sh), 465, 440, 423, 375, 310 nm. Anal. Calc for $C_{42}H_{26}N_{10}Os$ (860.9): C, 58.59; H, 3.04; N, 16.27. Found: C, 58.73; H, 3.33; N, 14.97.

PcOs. $PcOs(py)_2$ (140 mg, 0.165 mmol) was heated slowly (2 °C/min) to 400 °C under nitrogen and then cooled to room temperature. The yield of the blue-black powder was 115 mg (quantitative). IR (Nujol): 1605, 1417, 1377, 1325, 1291, 1171, 1125, 1099, 1067, 768, 755, 735 cm^{-1}. Anal. Calcd for $C_{32}H_{16}N_8Os$ (702.7): C, 54.70; H, 2.30; H, 15.95. Found: C, 54.57; H, 2.20; N, 15.75.

$PcOs(pyz)_2$. A mixture of PcOs (100 mg, 0.142 mmol) and pyrazine (1.0 g, 12.5 mmol, excess) was stirred in a small vial stoppered with a septum for 24 h at 80 °C. After cooling, the pulverized melt was washed thoroughly with methanol. The residue was extracted with chloroform and evaporated to give the violet product. Yield: 73 mg (58.7%). IR (Nujol): 1583, 1418, 1327, 1291, 1170, 1125, 1067, 1014, 776, 755, 735, 631 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.02 (d, 4 H, pyz—H^a), 6.48 (d, 4 H, pyz—H^b), 7.83 (m, 8 H, Pc—H^2), 8.95 (m, 8 H, Pc—H^1). ^{13}C NMR ($CDCl_3$): δ = 122.3 (C_1), 128.9 (C_2), 139.4 (C_{4a}), 146.1 (N=C—N), 146.6 (pyz—H^b), 147.5 (pyz—H^a). UV/vis ($CHCl_3$): λ = 625, 570 (sh), 420, 365 (sh), 310 nm. Anal. Calc for $C_{40}H_{24}N_{12}Os$ (862): C, 55.68; H, 2.80; N, 19.48. Found: C, 54.99; H, 2.68; N, 16.65.

$[PcOs(pyz)]_n$. $PcOs(pyz)_2$ (201 mg, 0.223 mmol) was heated (2 °C/min) to 320 °C under nitrogen and then cooled to room temperature. Yield: 181 mg (quantitative). IR (Nujol): 1582 (w), 1415, 1378, 1323, 1168, 1123, 1097, 1064, 770, 755, 722, 635 (w) cm^{-1}. ^{13}C NMR-CP-MAS (50, 325 MHz): δ = 122.6 (C_1), 128.5 (C_2), 138.1 (C_{4a}), 145.6 (N=C—N). NQS:[11] δ = 137.5 (C_{4a}), 145.0 (N=C—N). UV/vis (chlorobenzene): λ = 632, 580 (sh), 420 (sh) nm. Anal. Calc for $(C_{36}H_{20}N_{10}Os)_n$ (782): C, 55.24; H, 2.55; N, 17.90. Found: C, 55.96; H, 3.13; N, 17.20.

$PcOs(tz)_2$ and $[PcOs(tz)]_n$. A 200-mg sample of PcOs (0.284 mmol) was added to a solution of tetrazine (400 mg, 5 mmol, excess) in 60 mL of chloroform (the solvent was purified by passing through a column of neutral Al_2O_3). The mixture was stirred under nitrogen at 70 °C for 48 h. After cooling to room temperature, it was filtered and then washed with chloroform until the filtrate became colorless. The violet residue was dried in vacuo at 50 °C. Yield of $[PcOs(tz)]_n$: 118 mg (53%). IR (Nujol): 1517, 1490, 1326, 1288, 1166, 1121, 1100, 1064, 995, 934, 900, 773, 735, 724 cm^{-1}. UV/vis (fluoro mull): λ = 325, 670 nm. Anal. Calc for $(C_{34}H_{18}N_{12}Os)_n$ (784): C, 52.04; H, 2.30; N, 21.43. Found: C, 49.83; H, 2.11; N, 20.10.

$PcOs(tz)_2$. The combined filtrates were evaporated to dryness and washed with methanol to dissolve excess tz. The residue was dried in vacuo at 50 °C. The yield of $PcOs(tz)_2$ was 110 mg (44%). IR (Nujol):

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1605, 1416, 1376, 1355, 1326, 1290, 1171, 1125, 1107, 1091, 1067, 1007, 978, 930, 913, 778, 756, 740, 729 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.53 (d, 2 H, tz—H^a), 7.34 (d, 2 H, tz—H^b), 7.93 (m, 8 H, Pc—H^2), 9.15 (m, 8 H, Pc—H^1). ^{13}C NMR ($CDCl_3$): δ = 122.7 (C_1), 129.9 (C_2), 139.0 (C_{4a}), 145.6 (N=C—N), 157.3 (tz—C_a), 160.3 (tz—C_b). UV/vis ($CHCl_3$): λ = 618, 570 (sh), 365, 305 nm. Anal. Calc for $C_{36}H_{20}N_{16}Os$ (866): C, 49.88; H, 2.31; N, 25.87. Found: C, 50.28; H, 2.63; N, 20.43.

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Additions and Corrections

1988, Volume 27

Janet R. Morrow and William C. Trogler*: Hydrolysis of Phosphate Diesters with Copper(II) Catalysts.

Page 3390. Table III of the original paper suffered from an erroneous data entry in the program used to calculate the species present at equilibrium. The equilibrium constants used and the corrected table follow. The new values suggest $Cu(OH)(bpy)^+$ is the major species in solution with a 1:1 Cu:bpy ratio, not the dimer. This removes the inconsistency between the kinetics data, which showed a simple first-order dependence in $[Cu^{2+}]_{tot}$, and the previous calculation of equilibrium species, which predicted significant dimer formation. This change strengthens the conclusions in the paper.

$$[Hbpy^+]/[bpy][H^+] = 1.13 \times 10^4$$

$$[Cu(bpy)^{2+}]/[Cu^{2+}][bpy] = 6.47 \times 10^6$$

$$[Cu(bpy)_2{}^{2+}]/[Cu^{2+}][bpy]^2 = 5.15 \times 10^{11}$$

$$[Cu(bpy)(OH)^+]/[Cu(bpy)(OH)_2][H^+] = 4.06 \times 10^{10}$$

$$[Cu(bpy)^{2+}]/[H^+][Cu(bpy)(OH)^+] = 1.15 \times 10^7$$

$$[(Cu(bpy)(OH))_2{}^{2+}]/[Cu(bpy)(OH)^+]^2 = 8.65 \times 10^3$$

Table III. Effect of the Concentration (M) of 2,2′-Bipyridine on the Concentrations (M) of Copper(II) Complexes in Water at 75 °C[a]

[bpy]	$[Cu^{2+}]$	$[Cu(bpy)^{2+}]$	$[Cu(bpy)_2{}^{2+}]$	$[Cu(bpy)(OH)^+]$	$[(Cu(bpy)(OH))_2{}^{2+}]$
2.5×10^{-5}	2.5×10^{-5}	2.8×10^{-6}	3.8×10^{-9}	1.7×10^{-5}	2.5×10^{-6}
5.0×10^{-5}	1.0×10^{-6}	4.7×10^{-6}	2.7×10^{-7}	2.9×10^{-5}	7.4×10^{-6}
1.0×10^{-4}	1.6×10^{-8}	3.9×10^{-6}	1.2×10^{-5}	2.4×10^{-5}	5.0×10^{-6}
2.0×10^{-4}	3.3×10^{-9}	2.6×10^{-6}	2.6×10^{-5}	1.6×10^{-5}	2.3×10^{-6}

[a] bpy = 2,2′-bipyridine; pH 7.85; $[Cu^{2+}] = 5.0 \times 10^{-5}$ M. The $[Cu(bpy)(OH)_2]$ calculated was below 10^{-7} M in all cases.

—William C. Trogler