Convenient Synthesis of Water Soluble, Isomerically Pure Ruthenium Phthalocyanine Complexes

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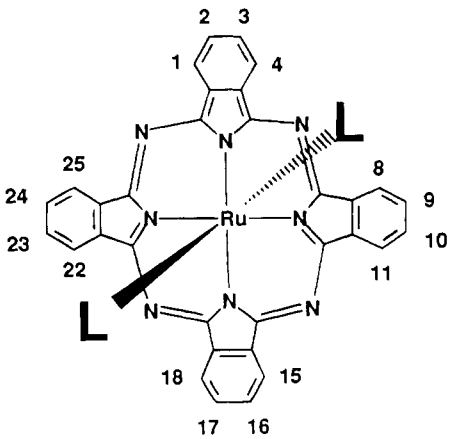
A simple high-yielding synthesis of water soluble ruthenium phthalocyanine complexes, (Pc)RuL_2, is reported. Use of an unsubstituted or symmetrically substituted phthalocyanine ring and solubilizing ligands axially coordinated to the central ruthenium allowed pure compounds, without positional isomers, to be made. Key to the success of the synthesis is the use of a soluble (Pc)RuL_2 intermediate with labile nitrile axial ligands that could be easily and completely substituted. A range of axial ligands was introduced into the (Pc)Ru moiety including pyridines, alkyl amines, amino acids, and phosphines.

Introduction

Phthalocyanines are of interest as potential sensitizers for photodynamic therapy, PDT, a promising therapy for neoplastic and other disease.[1] Phthalocyanines have high absorbitivity in the deep-red spectral region, where absorption by hemoglobin or scattering in various tissue is minimal. There are problems associated with these compounds such as a limited solubility and a tendency to aggregate (which negates their sensitizing properties), especially in aqueous solution.[1] Attempts to increase the water solubility of phthalocyanines have generally involved adding substituents, such as sulfonate groups, to the periphery of the macrocycle.[2] While peripheral substitution greatly increases the solubility of phthalocyanines, it also produces positional isomers.[3] Because a sensitizer for PDT is a drug, a single compound without isomers and of high purity is quite desirable.



This paper reports a simple high-yielding preparation of a series of ruthenium phthalocyanines, RuPc, with many desirable characteristics. These compounds are water soluble, nonaggregating, and strongly absorbing in the 600−700 nm region, are formed in high purity, have no positional isomers, and show good PDT activity.[4] The preparative scheme given here is convenient, low cost, and easily performed on a multigram scale. A wide variety of compounds can be made allowing a systematic variation of their physical properties.

Experimental Section

Sodium triphenylphosphinemonosulfonate, Na[TPPMS],[5] and 3,6-dimethylphthalonitrile[6] were made by literature procedures. All other reagents and solvents were reagent grade and used as received. NMR spectra were recorded using Bruker 300 MHz NMR spectrometer; optical spectra were obtained with a Cary 219 spectrophotometer. ^{31}P NMR spectra were recorded using phosphoric acid as an internal standard. HPLC separations were performed using a modification of a literature method using a Phenomenex Spherex 5 μm ODS 250 × 4.6 mm column and the following conditions:[3]

Solvent A: 10 mM ammonium acetate pH 5.0

Solvent B: methanol

Gradient: 0 - 10 min. 0% B

10 - 65 min. 0–95% B

65 - 75 min. 95% B

75 - 90 min. 95–0% B

Flow = 1 mL/min

Elemental analyses were performed by Atlantic Microlab, Norcross, GA, and mass spectra were obtained from M-Scan, West Chester, PA.

The preparations of several specific compounds are given below, including the preparation of the key intermediates. A list of other compounds and their associated elemental analysis and Q-band absorbance characteristics is included in the supplementary material.

Diammineruthenium Phthalocyanine, (Pc)$Ru(NH_3)_2$. A 50 mL three neck flask with a gas inlet on neck one and an air condenser on neck two, topped with a gas inlet and connected to a bubbler filled with pentanol, was charged with 6.50 g, 50.7 mmol (5.2 equiv), of phthalonitrile, 0.54 g, 4.9 mmol, of hydroquinone, and 15 mL of pentanol. The reaction was set to reflux under a slow nitrogen purge.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1995.

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Simultaneously ruthenium trichloride hydrate ($RuCl_3 \cdot xH_2O$), 2.32 g, 9.72 mmol, was boiled in 20 mL of pentanol until the solution turned completely blue and all the water had distilled out. The ruthenium was added over 5 min through the third neck of the flask and washed in with more pentanol. The flask was purged with ammonia gas and the third neck stoppered. The resulting brown suspension was gently refluxed (to reduce the loss of pentanol) under a slow flow of ammonia gas for 3 days. After cooling to room temperature the product was washed out and diluted to 200 mL with methanol. The purple solid was filtered off using a medium frit and washed alternately with methanol and dichloromethane until the washings were nearly colorless. The solid was air dried, yielding 6.58 g of crude $(Pc)Ru(NH_3)_2$, which was used without further purification.

$(Pc)Ru(NH_3)_2 \cdot {}^1/_2$pentanol. Into 25 mL of an ammonia-saturated solution of pentanol was dissolved 0.28 g, 0.34 mmol, of $(Pc)Ru(PhNH_2)_2$. The ammonia purged solution was slowly heated to 80 °C at which point a solid began to precipitate. The temperature was maintained at 80 °C for 1 h and then cooled to room temperature. Filtration and washing with methanol and dichloromethane gave 0.23 g, 0.33 mmol, 98% of a purple powder. Anal. Calcd for $C_{34.5}H_{28}N_{10}O_{0.5}Ru$: C, 59.90; H, 4.08; N, 20.25. Found: C, 59.82; H, 3.76; N, 20.27.

$RuCl_2$(phthalonitrile)$_4$. This compound was isolated from a reaction set up as for $(Pc)Ru(NH_3)_2$ but stopped after the "ruthenium blue" addition. After cooling under nitrogen, the orange solid was filtered off, washed thoroughly with methanol and dichloromethane, and air dried. The yield was 5.97 g, 90%. Anal. Calcd for $C_{32}H_{16}N_8Cl_2Ru$: C, 56.15; H, 2.36; N, 16.37; Cl, 10.36. Found: C, 55.84; H, 2.61; N, 16.09; Cl, 10.27. IR (cm^{-1}, CsI): 2244 (ν(CN)), 279 (ν(RuCl)).

$(Pc)Ru(PhCN)_2 \cdot H_2O$. $(Pc)Ru(NH_3)_2$, 6.58 g, was refluxed in 75 mL of benzonitrile for 1 day under nitrogen. The mixture was diluted to 1 L with hot chloroform and stirred at reflux for 1 h. The solution was filtered hot, and 3 L of methanol was added to the filtrate. A first crop of product, 5.39 g, was filtered off after 16 h, washed with methanol, and air dried. A second crop (1.48 g) was isolated by reducing the filtrate to 2.5 L by boiling, giving a total yield of 6.87 g, 84%, of $(Pc)Ru(PhCN)_2.H_2O$ as purple crystals. Anal. Calcd for $C_{46}H_{28}N_{10}ORu$: C, 65.94; H, 3.37; N, 16.72. Found: C, 65.55; H, 3.34; N, 16.73. IR (cm^{-1}, CsI): 2239 (ν(CN)). ^1H NMR (DMF-d_7; δ): 9.31 (8H, m), 7.98 (8H, m), 6.83 (2H, t), 6.51 (4H, t), 5.52 (4H, d). FAB MS [*m/z* (assignment)]: 820 $(M)^+$, 614 $(PcRu)^+$.

$(PcMe_8)Ru(PhCN)_2$. 1,4,8,11,15,18,22,25-Octamethylphthalocyaninato)diammineruthenium(II) was made by an equivalent reaction to that for $(Pc)Ru(NH_3)_2$. Substituting 7.50 g, 48.0 mmol, of 3,6-dimethylphthalonitrile for the phthalonitrile and using only methanol washes yielded 6.73 g, 91%, of crude $(PcMe_8)Ru(NH_3)_2$.

The benzonitrile complex was formed by refluxing 5.62 g of the crude ammine complex in 30 mL of benzonitrile for 1 day under nitrogen. Cooling and adding methanol precipitated the product which was filtered off, washed with methanol, and air dried. The yield was 4.29 g, 61% (56% from $RuCl_3$). Anal. Calcd for $C_{54}H_{42}N_{10}Ru$: C, 69.59; H, 4.54; N, 15.03. Found: C, 69.46; H, 4.55; N, 15.04. IR (cm^{-1}, CsI): 2239 (ν(CN)). ^1H NMR ($CDCl_3$; δ): 7.60 (8H, s), 6.83 (2H, t), 6.53 (4H, t), 5.61 (4H, d), 3.94 (24H, s).

Water Soluble Ruthenium Phthalocyanines. K_2[(Pc)Ru(TPPMS)$_2$]·4H$_2$O (JM 2929). Tetrabutylammonium triphenylphosphinemonosulfonate, TBA[TPPMS], was made by dissolving 5.50 g, 15.10 mmol, of Na[TPPMS] and TBA[HSO_4], 5.30 g, 15.61 mmol, into basic (pH >10) aqueous solution and extracting with dichloromethane three times. Drying the organic solution with $MgSO_4$, adding a small quantity of ethanol, and removing the solvent gave an oil which was used directly.

To the TBA[TPPMS] in 20 mL of ethanol was added $(Pc)Ru(PhCN)_2.H_2O$, 4.50 g, 5.37 mmol, in 50 mL of toluene. The mixture was degassed and the solution refluxed under nitrogen for 1.5 days. The solvents were removed, and the residue was dissolved in a minimum volume of methanol. The solution was filtered and 2.2 g of potassium acetate in 25 mL of methanol was filtered into the filtrate. The product was allowed to crystallize over 2 days before being filtered off, washed with ethanol and ether, and dried *in vacuo*. The yield of purple crystals was 6.91 g, 4.78 mmol, 89.0%. Anal. Calcd for $C_{68}H_{52}N_8K_2O_{10}P_2RuS_2$: C, 56.46; H, 3.62; N, 7.75. Found: C, 56.52; H, 3.74; N, 7.59. HPLC: 2 major peaks, retention time 59.3 min (81%), 51.0 min (8%), detector at 280 nm. ^{31}P NMR (DMF-d_7; δ): −6.7 (TPPMS), 23.8 (TPPMS oxide), 38.1 (PcRu(TPPMS)). FAB MS [*m/z* (assignment)]: 1375 $(M + 2K)^+$, 1337 $(M + HK)^+$, 1299 $(M + 2H)^+$, 957 $([PcRu(TPPMS)] + H)^+$, 614 $(PcRu)^+$. UV−vis (H_2O) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 650 (8.71×10^4).

K[(Pc)Ru(TPPMS)]·2H$_2$O·0.6methanol·0.6KI. A 0.200 g amount of $K_2[(Pc)Ru(TPPMS)_2]$ was dissolved in 15 mL of methanol. Carbon tetrachloride (0.2 mL) was added, and the reaction mixture was stirred for 24 h at room temperature in ambient light. Sufficient potassium iodide was added to saturate the reaction mixture (approximately 1.9 g). After 2 h the reaction mixture was filtered to remove any undissolved KI. Water (15 mL) was added to the filtrate. A microcrystalline solid formed overnight, which was collected and dried *in vacuo*. Yield = 0.098 g, 68%. Anal. Calcd for $C_{50.6}H_{36.4}N_8K_{1.6}I_{0.6}SO_{5.6}PRu$: C, 52.90; H, 3.19; N, 9.75; S, 2.79; I, 6.63. Found: C, 52.80; H, 3.50; N, 9.76; S, 2.45; I, 6.34. ^1H NMR (DMF-d_7; δ): 9.08 (8H, m), 8.01 (8H, m), 7.39−4.00 (14H, coordinated TPPMS), 3.35 (1.8H, s, methanol). ^{31}P NMR (DMF-d_7; δ): 38.1. HPLC: 1 peak, retention time = 59.3 min (detector at 280 nm). FAB MS [*m/z* (assignment)]: 957 $(M + 2H)^+$, 614 $(PcRu)^+$. UV−vis (H_2O): 647 (7.76×10^4).

K_2[(Pc)Ru(3-pyridinesulfonate]·2H$_2$O. This complex was prepared similarly to $K_2[(Pc)Ru(TPPMS)_2]$ from the tetrabutylammonium salt of 3-pyridinesulfonic acid and $[(Pc)Ru(PhCN)_2]$ in 96% yield. Anal. Calcd for $C_{42}H_{28}N_{10}K_2O_8RuS_2$: C, 48.31; H, 2.70; N, 13.41; S, 6.14. Found: C, 48.47; H, 2.85; N, 13.46; S, 6.02. ^1H NMR (DMF-d_7; δ): 9.13 (8H, m), 7.92 (8H, m), 6.48 (2H, m), 5.52 (2H, m), 3.16 (2H, s), 2.37 (2H, d). HPLC: 1 peak, retention time = 45.8 min (detector at 280 nm). FAB MS [*m/z* (assignment)]: 1009 $(M + 2K)^+$, 970 $(M + HK)^+$, 932 $(M + 2H)^+$, 614 $(PcRu)^+$. UV−vis (H_2O): 630, (7.59×10^4).

K_2[(PcMe$_8$)Ru(3-pyridinesulfonate)$_2$]·1.5H$_2$O. The complex was prepared in a similar manner in 87% yield starting with $[(PcMe_8)Ru(PhCN)_2]$. Anal. Calcd for $C_{50}H_{43}N_{10}K_2O_{7.5}RuS_2$: C, 52.34; H, 3.78; N, 12.21; S, 5.59. Found: C, 52.31; H, 3.76; N, 12.30; S, 5.20. ^1H NMR (DMF-d_7; δ): 8.02 (8H, s), 6.45 (2H, m), 5.44 (2H, m), 3.81 (24H, s), 3.14 (2H, s), 2.39 (2H, d). HPLC: 1 peak, retention time = 51.1 min (detector at 280 nm). FAB MS [*m/z* (assignment)]: 1120 $(M + 2K)^+$, 1083 $(M + K + 2H)^+$, 1045 $(M + 3H)^+$, 726 $(PcMe_8Ru)^+$. UV−vis (H_2O): 682 (1.35×10^5).

Results

Ruthenium-templated phthalocyanine formation occurred in pentanol in the presence of a base. Under these conditions but without a metal, phthalocyanine did not form. Using $RuCl_3 \cdot xH_2O$ directly as the metal template gave low yields of highly contaminated products. When an anhydrous "ruthenium blue" solution (made by boiling "$RuCl_3 \cdot xH_2O$" in pentanol until it was completely blue and no water remained) was used as the ruthenium source, the phthalocyanine formation reactions were essentially quantitative.

The base used in these reactions was often coordinated to the ruthenium in the final product. With ammonia this gave the previously unreported diammine complex, $(Pc)Ru(NH_3)_2$, as an insoluble blue solid. This compound was characterized by infrared absorbances at 3310, 3250, 3150, and 3055 cm^{-1} ($\nu_{a\&s}$) and one at 1617 cm^{-1} (δ_a), a split band at 1329 and 1323 cm^{-1}, and a unique absorbance at 1254 cm^{-1} (δ_s).[7a]

Insoluble $RuCl_2$(phthalonitrile)$_4$ was formed initially when the "ruthenium blue" solution was treated with phthalonitrile and could be isolated in good yield. This was converted to $(Pc)Ru(NH_3)_2$ over a 3 day period. Yields were identical using either ruthenium blue or $RuCl_2$(phthalonitrile)$_4$ as the ruthenium source. Use of 3,6-dimethylphthalonitrile gave the corresponding octamethylphthalocyanine in good yield.

Substitution of the benzonitrile ligands with ligands containing water solubilizing groups, such as sulfonic acids, gave com-

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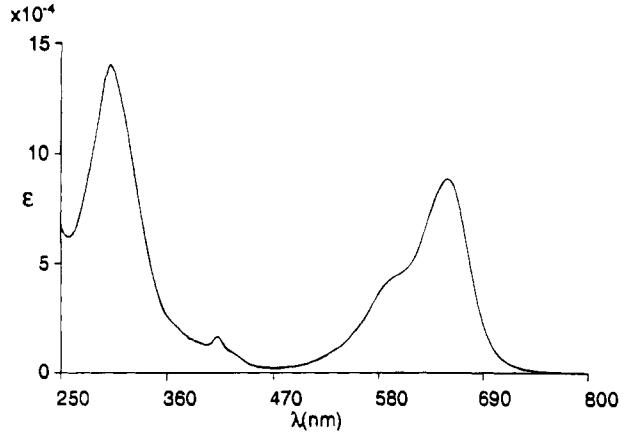


Figure 1. UV−visible spectrum of $K_2[(Pc)Ru(TPPMS)_2]$ in water.

pounds with sufficient water solubility (~10^{-3} M solubility in H_2O) for *in vitro* and *in vivo* biological studies. Reaction of $[PcRu(PhCN)_2]$ with TPPMS resulted in the isolation of a six-coordinate species, $K_2[(Pc)Ru(TPPMS)_2]$, as determined by elemental analysis and mass spectroscopy. This complex gave a typical metallophthalocyanine optical spectrum in aqueous solution as shown in Figure 1. The spectrum shows intense Q (650 nm) and B (315 nm) absorptions of the phthalocyanine moiety. Investigation of this compound by HPLC showed one peak using 650 nm detection and two peaks using 280 nm detection. The ^{31}P NMR spectrum of this compound showed three peaks, two of which are due to free TPPMS and TPPMS oxide. These results are consistent with the dissociation of one TPPMS ligand in solution.

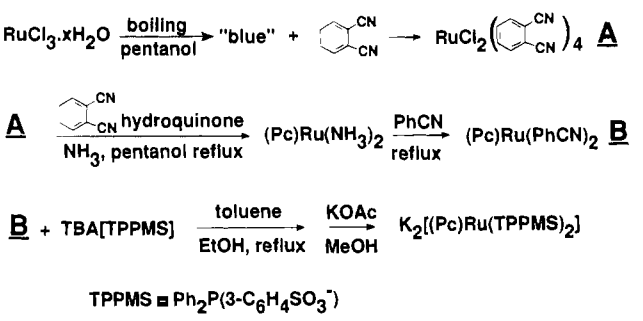
^{31}P NMR studies indicated that addition of carbon tetrachloride to methanolic solutions of $K_2[(Pc)Ru(TPPMS)_2]$ facilitated the formation of TPPMS oxide. This observation was used in the preparation of the monophosphine complex, K[(Pc)Ru-(TPPMS)]. This material was isolated from a 50/50 v/v methanol/water solution containing KI and was characterized by elemental analysis, HPLC, ^{31}P and ^1H NMR spectroscopy, and mass spectroscopy.

In contrast to the phosphine complexes, 3-pyridinesulfonate gave stable six-coordinate complexes with (Pc)Ru and $(PcMe_8)$-Ru as determined by elemental analysis, UV−vis, mass and ^1H NMR spectroscopies, and HPLC analysis. The ^1H NMR spectra of these molecules gave results similar to other $(Pc)RuL_2$ (where L = heterocyclic nitrogen ligand).[8] A variety of other axial ligands may be used including alkylamines and amino acids. A list of these complexes is included in the supplementary material.

Discussion

Previous syntheses of pure ruthenium phthalocyanine complexes have been difficult, tedious, and suffered from low yields.[9] Many reactions involving high temperatures give not only multiple products but also incorporation of chlorine into the phthalocyanine.[10,11] A chromatography step is also required for purification. In addition, many preparations involve the use of expensive *o*-cyanobenzamide rather than the readily available and inexpensive phthalonitrile. Even the synthesis recently reported by Hanack,[12] which is a considerable improvement over other procedures, has these problems.

Scheme 1



Ruthenium(III) is known to catalyze the rates of base hydrolysis of free and coordinated nitriles;[13] in the case of $[Ru(NH_3)_5NCR]^{3+}$ the hydrolysis of the coordinated nitrile is accelerated by a factor of 10^8-10^9. At low tempertatures under the basic conditions used for the formation of ruthenium phthalocyanines $RuCl_3{\cdot}xH_2O$ can provide both the Ru(III) and water needed to hydrolyze phthalonitrile. This results in low yields of the desired RuPc. In high temperature reactions employing $RuCl_3{\cdot}xH_2O$ hydrolyzed products are not observed because they are dehydrated back to nitriles. Our use of anhydrous "ruthenium blue" minimizes hydrolysis of the starting nitrile by removing water and reducing the ruthenium.

The formation of insoluble $(Pc)Ru(NH_3)_2$ was an essential ingredient to the success of the reaction shown in Scheme 1. It allowed the bulk of the impurities to be easily washed away after RuPc formation. The relatively pure $(Pc)Ru(NH_3)_2$ permitted a simple preparation of $(Pc)Ru(PhCN)_2$. Other bases such as *N,N*-dimethylethanolamine (used as the solvent) also facilitated RuPc formation. However, this base gave multiple soluble products that could not be easily purified.

The properties of $(Pc)Ru(PhCN)_2$ (high solubility, high purity, relative lability of the axial ligands) made it particularly suitable as a starting material for the synthesis of $(Pc)RuL_2$ complexes. Interestingly, ν_{CN} of $(Pc)Ru(PhCN)_2$ is 2239 cm^{-1}, which is at higher energy than that of free benzonitrile (2231 cm^{-1}). While this is normal for most metal−nitrile complexes, those of Ru-(II), such as $(NH_3)_5Ru(PhCN)^{2+}$ (ν_{CN} = 2188 cm^{-1}), are at lower energy. This indicates that RuPc may be a weaker π-back-bonder than some other Ru(II) complexes.[7b]

Our use of $(Pc)Ru(L)_2$ starting materials with axial nitrile ligands allowed substitution reactions to occur under the gentle conditions of refluxing at 80 °C for several hours. This contrasted with other starting materials, such as $(Pc)Ru(py)_2$, which required temperatures over 100 °C and several days and still gave no or only partial substitution with many ligands.

Reactions of both TPPMS and 3-pyridinesulfonate with (Pc)-$Ru(PhCN)_2$ result in the isolation of $(Pc)RuL_2$ complexes, but the solution properties of these compounds are different. K_2-$[(Pc)RuL_2]$ (where L = TPPMS) dissociates in solution to a five-coordinate complex. When L = 3-pyridinesulfonate, stable six-coordinate solution species are obtained. This is probably due to the greater trans-effect of tertiary phosphine vs pyridine ligands.

Phthalocyanines have been extensively studied as potential photosensitizing agents for the photodynamic therapy (PDT) of cancer and other conditions. Many phthalocyanines or metallophthalocyanines have been prepared by the addition of sulfonic acid or carboxylate moieties to the periphery of the macrocyclic ring. This approach can result in mixtures of

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isomers that are difficult to resolve.[3] An alternative approach is to confer improved solubility to the metallophthalocyanine via axial coordination of solubilizing groups to the central metal atom. Lipid soluble main group naphthalocyanines have been prepared in this manner.[14] Since six-coordinate Ru(II) phthalocyanines were well established in the literature, we synthesized the water soluble derivatives described in this paper with the goal of evaluating their activity as PDT agents. Many of these Ru(II) phthalocyanines are potent photosensitizers both *in vitro* and *in vivo*.[4] This result is contrary to reports in the literature claiming the inactivity of transition metal derivatives of phthalocyanines.[15] The photosensitizer activity of metallophthalocyanines has been attributed in the literature to the light-induced generation of singlet oxygen ($^1O_2$), a highly reactive cytotoxic species.[15] Recent work by Charlesworth et al. has shown that $K_2[(Pc)Ru(TPPMS)_2]$ does not produce $^1O_2$ in aqueous solution.[16] The photosensitizer activity of this and related species is therefore due to a type I mechanism.[17] Work by Nyokong et al. has demonstrated the formation of ruthenium phthalocyanine π-cation radical species by the Q-band irradiation of $(Pc)RuL_2$ complexes in the presence of an electron acceptor.[18] Formation of radical cations in the biological millieu may be responsible for the light-induced cytotoxicity of water soluble ruthenium phthalocyanines.

Conclusion

This paper describes a convenient high-yielding synthesis of pure $(Pc)RuL_2$ complexes without the need of a chromatography purification step. The procedure is versatile allowing a variety of axial ligands to be coordinated to several different ruthenium phthalocyanine ring systems. In particular, when L = TPPMS or 3-pyridinesulfonate, isomerically pure ruthenium phthalocyanines with water solubility can be prepared.

Supplementary Material Available: Tables of spectral and analytical data for 10 compounds (2 pages). Ordering information is given on any current masthead page.

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