Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2012, **22**, 196–198

Mendeleev
Communications

One-pot synthesis of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin complexes with rhenium and iridium in various oxidation states

Tatyana N. Lomova,* Elena G. Mozhzhukhina, Elena Yu. Tyulyaeva and Natalia G. Bichan

G. A. Krestov Institute of Solution Chemistry, Russian Academy of Sciences, 153045 Ivanovo, Russian Federation. Fax: +7 4932 33 6237; e-mail: tnl@isc-ras.ru

DOI: 10.1016/j.mencom.2012.06.008

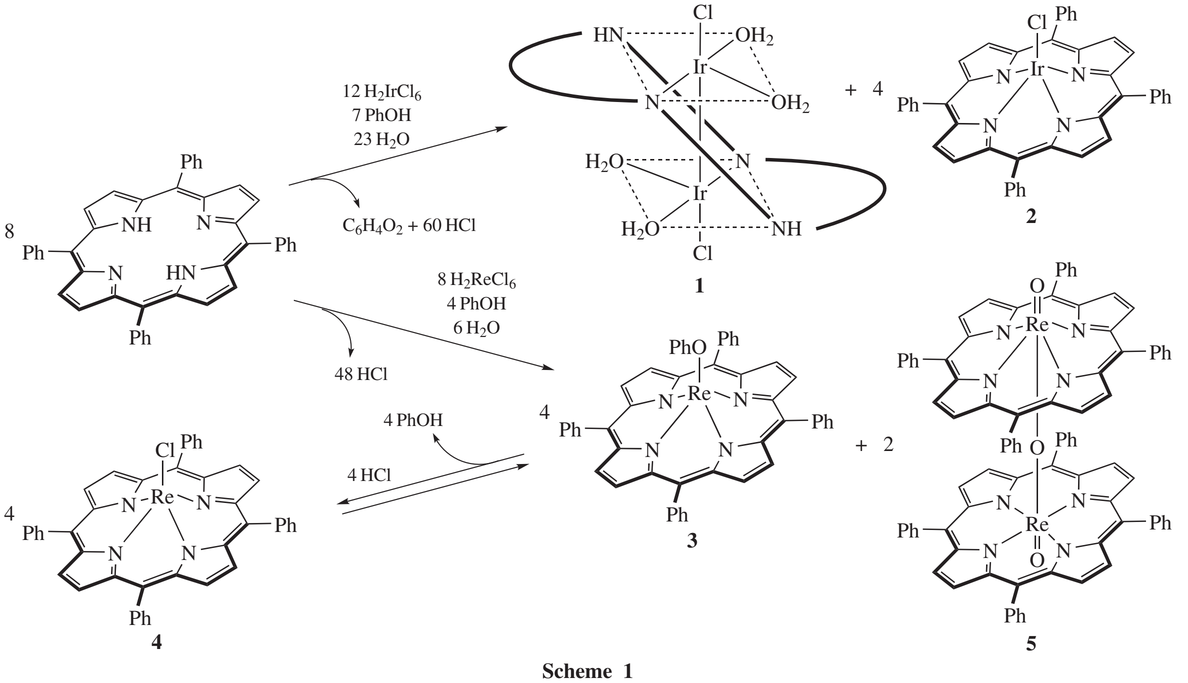
The complexes of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin with $\mathrm{Ir^I/Ir^{III}}$ or $\mathrm{Re^{III}/Re^V}$ have been obtained in one-pot synthesis due to redox properties of the solvent or metal ion.

Porphyrin metal complexes are of considerable interest for catalysis[1,2] as a simple model of biocatalysts[3,4] and because of a wide range of potential industrial-scale applications.[5] Porphyrin complexes of platinum group metals demonstrate catalytic activity in reactions with oxygen.[6,7] The Pd and Pt complexes, as well as the metals, catalyze the reactions of hydrogen.[8] Rhenium and its compounds catalytic activity is like what is observed in platinum group porphyrin complexes.[9] Recent progress in rhenium and iridium porphyrin chemistry extends to the corresponding complexes of porphyrin analogues such as porphycene,[10] N-confused porphyrins and N-fused porphyrins[11] and expanded porphyrins.[12] Reactive metal carbonyls with the low oxidation states of metals were used for the porphyrin complexing in most cases.[7,10,13–15] The metal porphyrin complexes produced in such syntheses retain the carbon monoxide ligand in their coordination sphere. The CO ligand decreasing coordination nonsaturation of a complex can change its properties sharply.[16] The use of metal carbonyls was developed due to difficulty in an incorporation of the Group 7–9 metals and high resistance to reduction of start compounds of metal in high degrees of oxidation.

Previously,[17] we reported the syntheses of porphyrin complexes with metals in various degrees of oxidation based on the complex formation reaction between porphyrin and the stable inorganic compound of the corresponding metal, being in high degrees of oxidation as a rule, in boiling phenol. The fact of providing of more easy complex formation between metal cation and porphyrin due to phenol was already known.[18] However, there are only a few reports where the role of phenol in a complex formation process was under discussion.[19] We synthesized metal porphyrins taking for an introduction of metal into a porphryrin cavity metal cations with both low and high redox potential and different solvents including phenol. In our opinion, the possibility of incorporating phenol as an acido ligand into the coordination sphere of an initial salt is not the main factor. Complex formation takes place due to preceded redox processes in a reaction mixture on the phenol basis. We observed complex formation reactions in the redox processes with both phenol–metal cation and phenol–porphyrin participations.[20] The reaction between 5,10,15,20-tetraphenyl-21*H*,23*H*-pophyrin and $\mathrm{Pb(AcO)_2}$ in pyridine as a solvent is accompanied by the porphyrin reduction and the $\mathrm{Pb^{2+}}$ oxidation due to atmospheric oxygen.[20(*h*)]

Here, we describe the synthesis and spectral properties of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin complexes with $\mathrm{Ir^I/Ir^{III}}$ and $\mathrm{Re^{III}/Re^V}$.

The complexes μ-(5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)-bis(chloro)iridium(I), $\mathrm{[IrCl(H_2O)_2]_2H_2TPP}$ **1** and (5,10,15,20-



Scheme 1

tetraphenyl-21*H*,23*H*-porphinato)chloroiridium(III), (Cl)IrTPP **2** were synthesized by the reaction of H_2TPP with chloroiridic acid $[(H_3O)_2IrCl_6]$[†] (Scheme 1), which was prepared by the treatment of IrO_2 with concentrated HCl (343 K, 8 h). The purify of compounds **1** and **2** was confirmed by TLC on Silufol plates using chloroform (R_f = 0.94 and 0.30). The total yield of the Ir^I and Ir^{III} complexes was 52%, the relative yields were 25 and 75%, respectively.

The complexes (5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato)-(phenoxo)rhenium(III), (PhO)ReTPP **3**, (5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato)chlororhenium(III), (Cl)ReTPP **4** and μ-oxo-bis[(oxo)(5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato)]-rhenium(V), $[O{=}ReTPP]_2O$ **5** were synthesized in 7, 0.5 and 75% yields, respectively, [‡] by the reaction of H_2TPP with chlororhenic acid H_2ReCl_6 in a molar ratio of 1:2 in boiling phenol for 2 h.

The chemical structures of iridium and rhenium complexes were determined by a detailed comparative analysis of their spectral properties[§,¶] with those of other iridium porphyrin complexes,[21] isostructural Rh complexes[22] and μ-oxo-bridge porphyrin complexes.[23–26] The Ir compounds are the 1:2 donor–acceptor complexes of the molecular ligand H_2TPP with iridium(I) containing chloride anion and water molecules in the coordination spheres of both Ir^I atoms $[IrCl(H_2O)_2]_2H_2$TPP and the chelate salt (Cl)IrTPP, which is typical of metal porphyrins. The coordination compounds obtained by the reaction of H_2TPP with chlororhenic acid are classic porphyrin complexes of rhenium(III) with the dianion

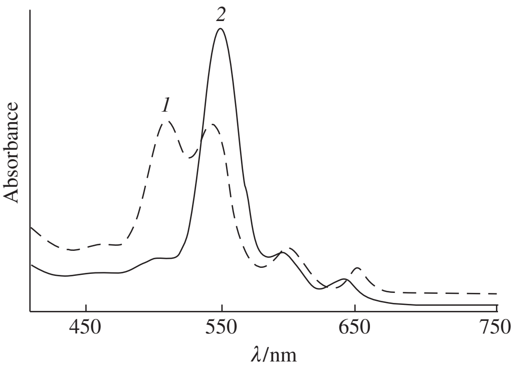


Figure 1 UV-VIS spectra of (*1*) **1** in benzene and (*2*) **2** in $CHCl_3$.

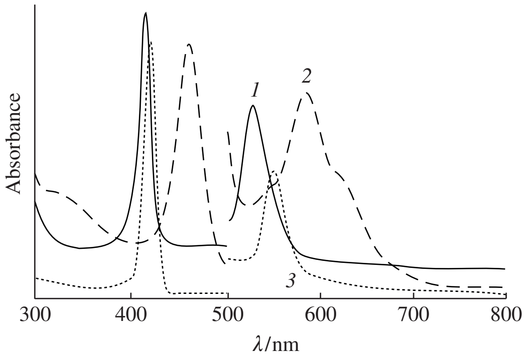


Figure 2 UV-VIS spectra of (*1*) **4**, (*2*) **5** and (*3*) **3** in $CHCl_3$.

[†] H_2TPP (0.01 g) and $(H_3O)_2IrCl_6$ (0.04 g) in a molar ratio of 1:5 were refluxed in phenol (4 g) for 3 h. The completion of the reaction was controlled by TLC (Silufol, chloroform). Then, the contents of a flask was cooled, dissolved in chloroform and washed with warm distilled water to remove phenol. The porphyrin complex mixture was chromatographed on alumina (Brockmann activity II) using chloroform. The chloroform solutions of **1** and **2** were put on a column with silica gel L 100/250 or alumina, respectively, for the second chromatography using chloroform. The individual areas of complexes **1** and **2** were washed out with a 1:1 (v/v) ethanol–chloroform mixture and ethanol, respectively.

[‡] H_2TPP (0.01 g) and H_2ReCl_6 (0.013 g) in a molar ratio of 1:2 were refluxed in phenol (5 g) for 2 h. The completion of the reaction was controlled by electron absorption spectra (EAS) [the bands of H_2TPP (λ_{max}/nm: 648.0, 592.0, 551.0, 516.0, 485.0, 420.0) disappeared]. The product was isolated from a cooled reaction mixture by diluting with water and extracting with chloroform. The chloroform solution was washed with warm distilled water to remove phenol; the solvent was partially evaporated, and the residue was chromatographed on alumina (Brockmann activity II) using chloroform. Two areas were obtained. The compounds of the first and the second areas were purified separately by chromatography on silica gel 40/100 Chemapol using benzene and then a 1:1 (v/v) ethanol–chloroform mixture. Both chromatographies resulted in two areas with two complexes: (Cl)ReTPP, $[O{=}ReTPP]_2O$ and (PhO)ReTPP, $[O{=}ReTPP]_2O$ for the compounds of the first and second initial areas, respectively. The individuality and purity of compounds **3**–**5** were confirmed by TLC on Silufol using $CHCl_3$–2% EtOH for $[O{=}ReTPP]_2O$ (R_f 0.42) and benzene for (Cl)ReTPP (R_f 0.80) and (PhO)ReTPP (R_f 0.83).

[§] The UV-VIS spectra were recorded with Agilent 8453 UV-VIS, Specord M40 and SF26 spectrophotometers; the IR and ^{1}H NMR spectra were measured with Avatar 360 FT-IR ESP (400–4000 cm^{-1}) and Bruker AVANCE-500 (500 MHz, TMS as an internal standard; 200 MHz, HMDS as an internal standard) spectrometers, respectively.

μ-(5,10,15,20-Tetraphenylporphine)-bis(chloro)iridium(I) **1**. UV-VIS [benzene, λ_{max}/nm (log ε)]: 420 (5.11), 482 (3.27), 518 (3.73), 544 (3.73), 594 (3.25), 652 (3.1). ^{1}H NMR (C_6D_6) δ: 8.92 (m, 8H, β-H, J_{HH} 17.6 Hz), 8.12, 8.09 (d, 8H, *o*-H, J_{HH} 1.61 and 2.44 Hz), 7.55, 7.47 (t, 8H, *m*-H, J_{HH} 16.32 Hz), 7.36 (s, 4H, *p*-H), –2.13 (s, 2H, NH). After the treatment of **1** by an acid: benzene–1 M AcOH, IR (chaotic layer obtained by the evaporation of the ethanol solution on the cell surface, ν/cm^{-1}): 423 and 446 ($\nu_{as\,Ir-N}$ and $\nu_{s\,Ir-N}$, skeletal vibrations of the macrocycle), 615 ($\nu_{s\,Ir-O}$), 750 (m, γ_{C-H} of the benzene ring), 799 (γ_{C-H} of the pyrrole ring, N–H), 968 (m, γ_{N-H}, bending, Ir–H), 1002 (s, δ_{C-H} of the pyrrole ring), 1046 and 1076 (m and s, δ_{C-H} of the benzene ring), 1262 (ν_{C-N}), 1378 (m, δ_{O-H}), 1464 (s, skeletal vibrations of the pyrrole ring), 1600 (m, $\nu_{C=C}$ of the benzene ring), 2852 and 2923 (m and s, ν_{C-H} of the pyrrole ring), 3036 (s), 3083 (ν_{C-H} of the benzene ring) (benzene, subtraction spectrum). ^{1}H NMR (C_6D_6, drops CF_3COOH) δ: 8.28 (t, 16H, β-H, *o*-H, J_{HH} 29.42 Hz), 7.63 and 7.56 (q and t, 8H, *m*-H, J_{HH} 9.42 Hz), 7.57 (d, 4H, *p*-H, J_{HH} 2.74 Hz), –1.06 (s, 2H, NH), –50.82 (m, 2H, Ir–H).

(5,10,15,20-Tetraphenylporphinato)chloroiridium(III) **2**. UV-VIS [$CHCl_3$, λ_{max}/nm (log ε)]: 395 (sh., 3.91), 418 (5.78), 476 (sh., 3.60), 508 (sh., 3.73), 549 (4.42), 588 (3.81), 640 (3.63). IR (chaotic layer, ν/cm^{-1}): 465 and 526 ($\nu_{as\,Ir-N}$, skeletal vibrations of the macrocycle and $\nu_{s\,Ir-N}$, skeletal vibrations of the macrocycle), 573 and 662 ($\nu_{as\,Ir-O}$ and $\nu_{s\,Ir-O}$), 702 and 754 (m and s, γ_{C-H} of the benzene ring), 802 (s, γ_{C-H} of the pyrrole ring, N–H), 1012 (s, δ_{C-H} of the pyrrole ring), 1045, 1072 and 1207 (m and s, δ_{C-H} of the benzene ring), 1277 (ν_{C-N}), 1320 ($\nu_{C=N}$), 1351 (δ_{O-H}), 1441 (m, skeletal vibrations of the pyrrole ring), 1488, 1597 and 1622 ($\nu_{C=C}$ of the benzene ring), 2853 and 2924 (m and s, ν_{C-H} of the pyrrole ring), 3026, 3054 (ν_{C-H} of the benzene ring).

[¶] *(5,10,15,20-Tetraphenyl-21*H*,23*H*-porphinato)(phenoxo)rhenium(III)* **3**. EAS [$CHCl_3$, λ_{max}/nm (log ε)]: 660 (sh.), 551 (2.3), 436 (sh.), 425 (4.3). IR (chaotic layer, ν/cm^{-1}): phenyl – 702, 758 (γ_{C-H}), 1068, 1178 (δ_{C-H}), 1487, 1578, 1600 ($\nu_{C=C}$), 2956, 3060 (ν_{C-H}); pyrrole ring – 806 (γ_{C-H}), 997 (C^3–C^4, ν_{C-N}, δ_{C-H}), 1340 (ν_{C-N}), 1377 ($\nu_{C=N}$); coordination centre – 418 (Re–N), 663 (Re–O), axial ligand – 1265, 1462, 1542 (–OPh). ^{1}H NMR ($CDCl_3$) δ: 8.95 (d, 8β-H), 8.25, 8.15 (d, m, 8*o*-H), 7.80 (m, 8*m*-H), 7.55 (m, 4*p*-H), 3.63 (s, 2*o*-H_{OPh}), 4.71 (s, 2*m*-H_{OPh}), 5.37 (s, *p*-H_{OPh}).

*(5,10,15,20-Tetraphenyl-21*H*,23*H*-porphinato)chlororhenium(III)* **4**. EAS ($CHCl_3$, λ_{max}/nm): 555 (sh.), 525, 495 (sh.), 416. EAS (AcOH, λ_{max}/nm): 540 (sh.), 520, 480, 437 (sh.), 417. IR (KBr, ν/cm^{-1}): phenyl – 705, 759 (γ_{C-H}), 1075, 1172 (δ_{C-H}), 1466, 1595, 1614 ($\nu_{C=C}$); pyrrole ring – 799 (γ_{C-H}), 1029 (C^3–C^4, ν_{C-N}, δ_{C-H}), 1350 (ν_{C-N}), 1377 ($\nu_{C=N}$); coordination centre – 408 (Re–N), 374, 392 (Re–Cl).

*μ-Oxo-bis[(oxo)(5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato)]rhenium(V)* **5**. EAS [$CHCl_3$, λ_{max}/nm (log ε)]: 620 (sh.), 582 (4.51), 461 (5.34), 333 (4.88). IR (chaotic layer, ν/cm^{-1}): phenyl – 702, 754 (γ_{C-H}), 1072, 1179 (δ_{C-H}), 1485, 1575, 1597 ($\nu_{C=C}$), 2954, 3056 (ν_{C-H}); pyrrole ring – 801 (γ_{C-H}), 1018 (C^3–C^4, ν_{C-N}, δ_{C-H}), 1341 (ν_{C-N}), 1440 ($\nu_{C=N}$); coordination centre – 418 (Re–N), 568, 630, 854 (Re–O–Re), 961, 946 (Re=O). ^{1}H NMR ($CDCl_3$) δ: 9.07 (d, 8*o*-H, J_{HH} 7.6 Hz), 8.79 (s, 16β-H), 8.01 (t, 8*m*-H, J_{HH} 7.6 Hz), 7.60 (t, 8*p*-H, J_{HH} 7.6 Hz), 7.47 (d, 8*o*′-H, J_{HH} 7.6 Hz), 7.04, 6.87 (2t, 8*m*-H, J_{HH} 7.6 Hz). ^{1}H NMR (D_2SO_4) δ: 9.13 (m, 8β-H), 8.52, 8.23 (2t, 8*o*-H), 8.06 (t, 8*m*-H, 4*p*-H). Found (%): C, 63.15; H, 3.5; N, 5.6. Calc. for $C_{88}H_{56}N_8O_3Re_2$ (%): C, 64.2; H, 3.4; N, 6.8.

TPP^{2-} (complexes **3** and **4**) and the complex of rhenium(V) with the dianion TPP^{2-} in the μ-oxo-bridge form, $[O{=}ReTPP]_2O$.

In order to confirm a coordination sphere composition for complexes **1**–**5**, the IR and NMR signals of potential ligands were explored.[§] Thus, the pophyrin ligand in a molecular form was found for **1** due to –2.13 ppm (s, 2H, NH) absorption in NMR spectra. In addition, there are the IR signals at 615 ($\nu_{s\,Ir-O}$), 1378 cm^{-1}(δ_{O-H}) and the hydride ligand signal at 968 cm^{-1} (γ_{N-H}, bending Ir–H) and high-field NMR signal –50.82 ppm (m, 2H, Ir–H)[§] in corresponding spectra of **1** after treatment with benzene–1 M AcOH (or C_6D_6–CF_3COOH). The hydride and AcO^- ligands appear in a coordination sphere due to the oxidizing bonding reaction and the $Ir^I \rightarrow Ir^{III}$ transition. Signal at 968 cm^{-1} (γ_{N-H}, bending Ir–H) demonstrates the isotopic shift in the IR spectrum in C_6D_6. The absorption of Ir–D is observed at 1612 cm^{-1} (ν), N–D at 720 (γ), 812 (δ), 3230 (ν) and 1159 cm^{-1}. At last a non-traditional structure of compound **1** is clearly manifested in the splitting of signals of the *ortho* and *meta* protons of the benzene rings[§] due to the pair wise deviation of pyrrole rings to opposite sides relative to the N_4 plane away from two Ir atoms. The individuality and the chemical purity of chelate salt **2** was examined by luminescence spectroscopy.[††] The one exponential law of decay of a molecular fluorescence in the areas of 580–700 nm, which is characterized by two maxima at 600 and 656 nm (λ_{exc} = 415 nm), shows that other forms of a complex or porphyrin are absent. Analogously, –OPh and Cl^- were established in the sphere of **3** and **4**, –O– and O^{2-} in those of **5** as well as TPP^{2-} anion in all three complexes.[¶] In addition, the composition of μ-oxo bridged complex **5** was determined by elemental analysis.[¶]

The coordination type and formal charge of a central metal atom were determined by EAS (Figures 1 and 2) and NMR spectra and in view of the found sort of ligands. The NMR spectrum for each complex shows that the complex is diamagnetic. The major absorption in the spectrum of μ-dimers[21,22] as well as the complex **1** in the visible region is the band at 516–518 nm and the absorbance at 544 nm that varies over a broad range depending on a structure of a coordination sphere. A characteristic feature of the UV-VIS spectrum of the mixed Ir^{III} complex with chloride ion and TPP^{2-} porphyrin dianion (complex **2**) is the absorption band in the visible region at 544–549 nm[§] that determines the EAS as a normal type spectrum.[27] The EAS of the complexes (Cl)ReTPP, (PhO)ReTPP and $[O{=}ReTPP]_2O$[¶] (Figure 2) are different. There is an absorption band at 350 nm in the spectrum of the μ-oxo bridged Re^V complex. That is absent in the Re^{III} complex spectrum. Similar bands in the UV region[26] are observed for porphyrin complexes with W^V and Mo^V. So the hyper type spectra of **3** and **4** as well as the normal type spectrum of **2** specify that we deal with the complexes of Re^{III} (**3**, **4**) and Ir^{III} (**2**). It is important that a significant shift of absorption bands in the visible region originates from the OPh → Cl substitution.[¶,26]

Since the 5,10,15,20-tetraphenyl-21*H*,23*H*-pophyrin complexing with Ir or Re occurs at a high temperature, the kinetics and mechanism of the reaction cannot be studied. However, the structure of products allows us to explain the transformation. In view of Scheme 1, both the reaction with H_2IrCl_6 and the coordination with Re proceed with a phenol participation. However, PhOH is oxidized in the first reaction and is bonded as the PhO^- ligand with the Re^{III} cation in the second reaction. Being in equilibrium with HCl small quantity the complex **3** passes in the Cl^- analogue partially. Hence only Re^{IV} cation passing in Re^{III} and Re^V takes part in a redox process. Scheme 1 clarifies a low yield of complex **4**, as well as the experimental fact that relative yields of **3**, **4** and **5** do not depend on a $H_2TPP:H_2ReCl_6$ molar ratio.

We are grateful to the Department of Chemistry of Lanthanides, A. V. Bogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine, for studying the luminescence of (Cl)IrTPP.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.06.008.

References

1 N. Raoul, E. Gallo and E. Rose, *J. Porphyrins Phthalocyanines*, 2011, **15**, 602.

2 C. S. Eberle, A. S. Viana, F.-P. Montforts and L. M. Abrantes, *J. Porphyrins Phthalocyanines*, 2010, **14**, 101.

3 T. N. Lomova, M. E. Klyueva, M. V. Klyuev and O. V. Kosareva, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 719 (*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 748).

4 C. Cretini and P. Tagliatesta, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 2003, vol. 11, p. 161.

5 C.-C. Guo, X.-Q. Liu, Q. Liu, Y. Liu, M.-F. Chu and W.-Y. Lin, *J. Porphyrins Phthalocyanines*, 2009, **13**, 1250.

6 J. P. Collman and K. Kim, *J. Am. Chem. Soc.*, 1986, **108**, 7847.

7 R. Guilard, A. Tabard, E. V. Caemelbecke and K. M. Kadish, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, Boston, 2000, vol. 3, p. 295.

8 H. Kropf and D. J. Will, *Z. Phys. Chem. (N. F.)*, 1971, **60**, 331.

9 I. P. Beletskaya, V. S. Tyurin, A. Yu. Tsivadze, R. Guilard and C. Stern, *Chem. Rev.*, 2009, **109**, 1659.

10 W. Zhang, Y. Chang, F. Wu, J. Mack, N. Kobayashi and Z. Shen, *J. Porphyrins Phthalocyanines*, 2011, **15**, 622.

11 M. Toganoh, S. Ikeda and H. Furuta, *Inorg. Chem.*, 2007, **46**, 10003.

12 L. Cuesta, V. M. Lynch and J. L. Sessler, *J. Porphyrins Phthalocyanines*, 2010, **14**, 41.

13 H. Ogoshi, J.-I. Setsune and Z.-I. Yoshida, *J. Organomet. Chem.*, 1978, **159**, 317.

14 C. P. Hrung, M. Tsutsui, D. L. Cullen, E. F. Meyer, Jr. and C. N. Morimoto, *J. Am. Chem. Soc.*, 1978, **100**, 6068.

15 M. Tsutsui, C. P. Hrung, D. Ostfeld, T. S. Srivastava, D. L. Cullen and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, 1975, **97**, 3952.

16 R. Guilard and K. M. Kadish, *Chem. Rev.*, 1988, **88**, 1121.

17 T. N. Lomova and B. D. Berezin, *Koord. Khim.*, 1993, **19**, 171 (in Russian).

18 E. W. Buchler, G. Eikelman, L. Puppe, K. Rohbock, H. H. Schneehage and D. Wech, *Liebigs Ann. Chem.*, 1971, **745**, 135.

19 E. W. Buchler, L. Puppe, K. Rohbock and H. H. Schneehage, *Chem. Ber.*, 1973, **106**, 2710.

20 (*a*) E. V. Motorina and T. N. Lomova, *Zh. Neorg. Khim.*, 2010, **55**, 781 (*Russ. J. Inorg. Chem.*, 2010, **55**, 727); (*b*) T. N. Lomova, M. E. Malov, M. V. Klyuev and P. A. Troshin, *Macroheterocycles*, 2009, **2**, 164; (*c*) E. V. Motorina and T. N. Lomova, *Zh. Obshch. Khim.*, 2010, **80**, 681 (*Russ. J. Gen. Chem.*, 2010, **80**, 842); (*d*) E. Yu. Tyulyaeva and T. N. Lomova, *Zh. Fiz. Khim.*, 2010, **84**, 847 (*Russ. J. Phys. Chem. A*, 2010, **84**, 749); (*e*) T. N. Lomova and E. V. Motorina, *J. Porphyrins Phthalocyanines*, 2008, **12**, 617; (*f*) E. V. Motorina and T. N. Lomova, *Zh. Fiz. Khim.*, 2008, **82**, 674 (*Russ. J. Phys. Chem. A*, 2008, **82**, 576); (*g*) T. N. Lomova, E. Yu.Tyulyaeva and E. G. Mozhzhukhina, *J. Porphyrins Phthalocyanines*, 2006, **10**, 751; (*h*) O. V. Molodkina, T. N. Lomova and E. G. Mozhzhukhina, *Izv. Akad. Nauk., Ser. Khim.*, 1998, 2052 (*Russ. Chem. Bull., Int. Ed.*, 1998, **47**, 1996); (*i*) T. N. Lomova, E. Yu. Tulaeva, E. G. Mozhzhukhina and M. E. Klyueva, *Mendeleev Commun.*, 1997, 225; (*j*) T. N. Lomova and L. G. Andrianova, *Mendeleev Commun.*, 2003, 213.

21 A. Antipes and M. Gouterman, *J. Am. Chem. Soc.*, 1983, **105**, 4896.

22 H. Ogoshi, J. Setsune, T. Omura and Z. Yoshida, *J. Am. Chem. Soc.*, 1975, **97**, 6461.

23 S. K. Ghosh, R. Datra and S. P. Rath, *Inorg Chem.*, 2010, **49**, 3449.

24 H. J. Ledon, M. C. Bonnet, Y. Brigandat and F. Varescon, *Inorg. Chem.*, 1980, **19**, 3488.

25 K. J. C. Van Bommel, W. Verbom, P. Hulst, H. Kooijman, A. L. Spek and D. N. Reinhoudt, *Inorg. Chem.*, 2000, **39**, 4099.

26 J. W. Buchler, W. Kokish and P. D. Smith, *Struct. Bond.*, 1978, **34**, 79.

27 T. N. Lomova and B. D. Berezin, *Koord. Khim.*, 2001, **27**, 96 (*Russ. J. Coord. Chem.*, 2001, **27**, 85).

Received: 19th January 2012; Com. 12/3862

[††] For kinetics of molecular fluorescence decay (Figure 1S) of complex **2**, see Online Supplementary Materials.