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Phenanthroline-appended porphyrazines: synthesis and conversion into solitaire Ru(II) complexes

Antonio Garrido Montalban [a], Efstathia G. Sakellariou [a], Eric Riguet [a], Quentin J. McCubbin [a], Anthony G.M. Barrett [a,*1], Brian M. Hoffman [b,*2]

[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW 7 2AY, UK*
[b] *Department of Chemistry, Northwestern University, Evanston, IL 60208, USA*

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Abstract

Unsymmetrical porphyrazines (tetraazaporphyrins) bearing a single bidentate phenanthroline chelating group M[pz(t-butylphenyl)$_6$phen] have been prepared by the base-catalyzed cross condensation of 3,4-bis(4-*tert*-butylphenyl)pyrroline-2,5-diimine (in excess) with 6,7-dicyanodipyridoquinoxaline. Treatment of these centrally metalated (M = Mg, Zn) ligands with various Ru(II) salts has yielded several bimetallic complexes including the first coordinatively linked porphyrazine trimer. The optical properties of these complexes are shown to be a function of the additional ligands surrounding the asymmetric ruthenium center.

Keywords: Porphyrinoid complexes; Phenanthroline complexes; Ruthenium complexes

1. Introduction

Coordination compounds prepared from ligand systems containing photo- and/or redox-active units allow the possibility of long distance delocalization of electron density and metal–metal interactions between multiple metal centers [1]. One strategy for the design of such architectures is based on porphyrinic macrocycles, and, in most of the systems studied so far, the porphyrins are covalently linked to external coordination sites without any extended π conjugation [2]. Our efforts in this area utilize the tetraazaporphyrin (porphyrazine, pz) ligand as a structural motif for the rigid organization of the metal centers, and we have developed a new family of tetraaza macrocycles that have metal-binding sulfur [3], nitrogen [4], or oxygen atoms [5] attached to the pz periphery.

Peripherally functionalized porphyrazines of the form M[pz(A_n:B_{4-n})], in which A and B symbolize functional groups fused directly to the β-positions of the pyrrole rings, can be synthesized with $n = 1$ to 4. Although the peripheral A moieties generally involve heteroatoms (S, N, O) appended to the porphyrazine ring and are designed in order to bind an exocyclic metal ion, the B groups are intended to confer a desired solubility. Unsymmetrical porphyrazines having a single peripheral metal-chelation site form complexes that are designated as *solitaire*-porphyrazines [6]. In such systems the metal in the central macrocyclic cavity and periphery can be chosen independently [7], thus giving rise to physical properties not seen in the pz or metal fragments alone [8]. Another way to assemble multimetallic arrays is to fuse an aromatic ligand onto the porphyrazine fragment. The 1,10-phenanthroline nucleus, a well-known metal-chelating agent, is ideally suited for the incorporation into multichromophore systems [9]. Herein we report the synthesis and optical properties of porphyrazines in which a 1,10-phenanthroline is fused directly onto the β-positions of the macrocycle, thus extending the π conjugation beyond the tetrapyrrolic structure. In addition, we demonstrate that, besides the metal in the central macrocyclic cavity, these novel ligands can coordinate a metal ion at the peripheral phenanthroline unit, including the first te-

[1] *Corresponding author. Tel.: +44-207-594 5766; fax: +44-207-594 5805; e-mail: agmb@ic.ac.uk
[2] *Corresponding author.

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tranuclear metal-linked porphyrazine trimer via mutual chelation of a ruthenium(II) ion.

2. Experimental

2.1. General procedures

All reactions were conducted in oven- or flame-dried glassware. Solvents used for reactions were distilled prior to use: DMF [predried over BaO, distilled from alumina (activity I)]; butanol (from Mg); quinoline (from Zn). 3,4-bis(4-*tert*-Butylphenyl)pyrroline-2,5-diimine (**8**) [10], 1,10-phenanthroline-5,6-dione (**3**) [12] and *cis*-$RuCl_2(bipy^*)_2$ (**13**) [15] were synthesized according to published procedures. All other reagents were used as commercially supplied. TLC was carried out on E. Merck precoated silica gel 60 F_{254} plates, which were visualized using UV radiation (254 nm). Chromatography refers to flash chromatography on E. Merck silica gel 60, 40–60 μm or deactivated neutral aluminum oxide (5% H_2O), ~150 μm (eluants are given in parentheses). Size exclusion chromatography was performed on Bio-Beads SX3 or Sephadex LH20.

2.2. 6,7-Dicyanodipyridoquinoxaline (dicnq) (4)

1,10-Phenanthroline-5,6-dione (**3**) (5.0 g, 23.8 mmol), diaminomaleonitrile (**2**) (2.57 g, 23.8 mmol), acetic acid (five drops) and EtOH (300 ml) were heated to reflux for 2 h. The mixture was allowed to cool and the resultant precipitate filtered and washed with EtOH to give dinitrile **4** (3.07 g, 46%) as orange–brown needles: m.p. 335°C (EtOH); IR (Nujol) 2240, 1584, 1505, 1262, 1222, 1141, 1074 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 8.05 (dd, $J = 4.4$ and 8.2 Hz, 2H), 9.36 (dd, $J = 1.7$ and 4.4 Hz, 2H), 9.42 (dd, $J = 1.7$ and 8.2 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 115.3, 125.2, 125.8, 132.6, 134.3, 141.7, 143.9, 148.7, 154.8; MS (EI) m/z 282 ($M^{+\cdot}$); HRMS (EI) calc. for $C_{16}H_6N_6$: [$M^{+\bullet}$], 282.0654; found: [$M^{+\bullet}$], 282.0634. *Anal.* Found: C, 67.83; H, 2.07; N, 29.58. Calc. for $C_{16}H_6N_6$: C, 68.08; H, 2.14; N, 29.77%.

2.3. Mg[pz(t-butylphenyl)$_6$phen] (5)

A mixture of butanol (30 ml), Mg (0.12 g, 5 mmol) and I_2 (one small crystal) was heated to reflux for 12 h under N_2. The suspension was cooled and dicnq **4** (0.28 g, 1.0 mmol) followed by pyrroline **8** (1.08 g, 3.0 mmol) were added and the mixture further heated at reflux for 48 h. The deep-green suspension was allowed to cool, filtered (Celite) and the solids washed with CH_2Cl_2. Rotary evaporation and chromatography on silica ($CHCl_3$; $CHCl_3$:MeOH 9:1) gave Mg–porphyrazine **5** (0.3 g, 23%) as a dark-green solid: m.p. >350°C; R_f 0.17 ($CHCl_3$:MeOH 9:1); IR (CH_2Cl_2) 1731, 1606, 1488, 1460, 1366, 1266, 984, 778 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 381 (4.45), 487 (3.61), 649 (4.20), 682 (4.15) nm; ^1H NMR (300 MHz, pyridine-d_5) δ 1.50 (s, 36H), 1.55 (s, 18H), 7.81 (d, $J =$ 8.4 Hz, 4H), 7.84 (d, $J = 8.7$ Hz, 4H), 7.98 (d, $J = 8.4$ Hz, 4H), 8.02 (dd, $J = 4.7$ and 7.4 Hz, 2H), 8.75 (d, $J = 8.4$ Hz, 4H), 8.82 (d, $J = 8.4$ Hz, 4H), 8.93 (d, $J = 8.7$ Hz, 4H), 9.50 (m, 2H), 10.36 (d, $J = 7.4$ Hz, 2H); MS (FAB) m/z 1334 [$M^{+\bullet}$]; HRMS (FAB) calc. for $C_{88}H_{86}MgN_{12}$: $[M + 2H]^+$, 1334.6949; found: $[M +$ 2H]$^+$, 1334.7082. *Anal.* Found: C, 76.17; H, 6.42; N, 11.79. Calc. for $C_{88}H_{84}MgN_{12}\cdot 3H_2O$: C, 76.15; H, 6.53; N, 12.11%.

2.4. Zn[pz(t-butylphenyl)$_6$phen] (6)

A mixture of dicnq **4** (0.14 g, 0.5 mmol), pyrroline **8** (0.54 g, 1.5 mmol), $Zn(OAc)_2$ (0.27 g, 1.5 mmol) and quinoline (5 ml) was heated rapidly to 170°C using a heat gun under N_2. At the appearance of an intense green color (~5 min) the reaction mixture was allowed to cool, diluted with CH_2Cl_2 (10 ml) and washed successively with 1 M HCl (3 × 15 ml), aqueous $NaHCO_3$ (3 × 15 ml) and H_2O (3 × 15 ml). The organic layer was dried ($MgSO_4$), rotary evaporated and the residue chromatographed on silica ($CHCl_3$; $CHCl_3$:MeOH 9:1) to give Zn–porphyrazine **6** (0.13 g, 19%) as a dark-green solid: m.p. >350°C; R_f 0.34 ($CHCl_3$:MeOH 9:1); IR (CH_2Cl_2) 1733, 1657, 1391, 1365, 1266, 1104, 1012, 755 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 379 (4.51), 488 (3.72), 652 (4.23), 665 (4.30) nm; ^1H NMR (270 MHz, pyridine-d_5) δ 1.51 (s, 36H), 1.56 (s, 18H), 7.82 (d, $J = 8.4$ Hz, 4H), 7.84 (d, $J = 8.7$ Hz, 4H), 7.97 (d, $J = 8.4$ Hz, 4H), 8.04 (dd, $J = 4.1$ and 8.2 Hz, 2H), 8.78 (d, $J = 8.4$ Hz, 4H), 8.85 (d, $J = 8.4$ Hz, 4H), 8.97 (d, $J = 8.7$ Hz, 4H), 9.53 (dd, $J = 2.0$ and 4.1 Hz, 2H), 10.36 (dd, $J = 2.0$ and 8.2 Hz, 2H); MS (FAB) m/z 1375 [$M^{+\bullet}$]; HRMS (FAB) calc. for $C_{88}H_{86}N_{12}Zn$: $[M + 2H]^+$, 1374.6390; found: $[M + 2H]^+$, 1374.6316. *Anal.* Found: C, 73.78; H, 5.94; N, 11.15. Calc. for $C_{88}H_{84}N_{12}Zn\cdot 3H_2O$: C, 74.02; H, 6.36; N, 11.78%.

2.5. [(Zn[pz(t-butylphenyl)$_6$phen])Ru(Cp)(PPh$_3$)]Cl (11)

$RuCl(Cp)(PPh_3)_2$ (**9**) (42 mg, 58 mmol) was added to porphyrazine **6** (40 mg, 29 mmol) in DMF (4 ml) and the mixture heated at 80°C for 1 h under N_2. The mixture was allowed to cool and rotary evaporated and the dark-green residue was dissolved in CH_2Cl_2 (20 ml) and filtered. Rotary evaporation and chromatography on alumina ($CHCl_3$:MeOH 9:1) followed by gel filtration (Sephadex, $CHCl_3$) gave complex **11** (29 mg, 55%) as a dark-green solid: m.p. >350°C; R_f 0.15 ($CHCl_3$:MeOH 9:1); IR (CH_2Cl_2) 1606, 1480, 1366, 1266, 1139, 1104, 983, 841 cm^{-1}; UV–Vis (CH_2Cl_2)

λ_{max} (log ε) 399 (4.66), 662 (4.77) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.47 (s, 18H), 1.50 (s, 36H), 5.15 (s, 5H), 7.01–7.19 (m, 15H), 7.78 (d, $J = 8.5$ Hz, 4H), 7.80 (d, $J = 8.3$ Hz, 4H), 7.86 (d, $J = 8.3$ Hz, 4H), 8.00 (m, 2H), 8.72 (d, $J = 8.5$ Hz, 4H), 8.76 (d, $J = 8.3$ Hz, 4H), 8.90 (d, $J = 8.3$ Hz, 4H), 10.00 (m, 2H), 10.10 (m, 2H); MS (FAB) m/z 1804 $[M-Cl]^+$. *Anal.* Found: C, 72.62; H, 5.73; N, 9.50. Calc. for $C_{111}H_{104}ClN_{12}PRuZn$: C, 72.47; H, 5.70; N, 9.14%.

2.6. [(Zn[pz(t-butylphenyl)$_6$phen])Ru(p-cymene)Cl]Cl (12)

[RuCl(μ_2-Cl)(*p*-cymene)]$_2$ (**10**) (22 mg, 36.3 mmol) was added to porphyrazine **6** (25 mg, 18.1 mmol) in DMF (4 ml), the mixture heated at 80°C for 5 h under N_2, cooled, rotary evaporated and the dark-green residue taken up in CH_2Cl_2 (20 ml) and filtered. Rotary evaporation and chromatography on alumina ($CHCl_3$:MeOH 9:1) followed by gel filtration (Sephadex, $CHCl_3$) gave complex **12** (3.4 mg, 11%) as a dark-green solid: m.p. >350°C; R_f 0.20 ($CHCl_3$:MeOH 9:1); IR (CH_2Cl_2) 1731, 1606, 1489, 1366, 1264, 987, 779 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 390 (4.97), 668 (4.95) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.06 (d, $J = 6.8$ Hz, 6H), 1.45 (s, 18H), 1.50 (s, 36H), 2.36 (s, 3H), 2.85 (h, $J = 6.8$ Hz, 1H), 6.32 (d, $J = 6.2$ Hz, 2H), 6.54 (d, $J = 6.2$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 4H), 7.80 (d, $J = 8.4$ Hz, 4H), 7.85 (d, $J = 8.4$ Hz, 4H), 8.38 (dd, $J = 4.9$ and 8.4 Hz, 2H), 8.72 (d, $J = 8.4$ Hz, 4H), 8.76 (d, $J = 8.4$ Hz, 4H), 8.87 (d, $J = 8.4$ Hz, 4H), 10.30 (d, $J = 8.4$ Hz, 2H), 10.35 (d, $J = 4.9$ Hz, 2H); MS (FAB) m/z 1646 $[M-Cl]^+$. *Anal.* Found: C, 67.95; H, 6.12. Calc. for $C_{98}H_{98}Cl_2N_{12}RuZn\cdot 3H_2O$: C, 67.82; H, 6.12%.

2.7. [(Mg[pz(t-butylphenyl)$_6$phen])Ru(bpy*)$_2$]Cl$_2$ (14)

cis-RuCl$_2$(bpy*)$_2$ (**13**) (41.0 mg, 58.0 mmol) (bipy* = 4,4′-di-*tert*-butyl-2,2′-bipyridine) was added to porphyrazine **5** (40.0 mg, 29.9 mmol) in DMF (4 ml), and the mixture heated at reflux for 4 h under N_2. The mixture was allowed to cool, rotary evaporated and the dark-green residue was dissolved in CH_2Cl_2 (20 ml) and filtered. Rotary evaporation and chromatography on alumina (CH_2Cl_2; $CHCl_3$:MeOH 9:1) followed by gel filtration (Sephadex, $CHCl_3$) gave complex **14** (19.2 mg, 31%) as a dark-green solid: m.p. >350°C; R_f 0.23 ($CHCl_3$:MeOH 5.7:1); IR (CH_2Cl_2) 1726, 1612, 1480, 1368, 1264, 1245, 1137, 1105, 983, 842 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 390 (4.88), 460sh, 672 (4.89) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.31 (s, 18H), 1.37 (s, 18H), 1.43 (s, 18H), 1.50 (s, 18H), 1.51 (s, 18H), 7.38 (dd, $J = 1.5$ and 6.2 Hz, 2H), 7.46 (dd, $J = 1.5$ and 5.9 Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 4H), 7.79 (d, $J = 8.2$ Hz, 4H), 7.82 (d, $J = 8.2$ Hz, 4H), 8.03 (dd, $J = 5.7$ and 8.2 Hz, 2H), 8.18 (d, $J = 5.9$ Hz, 2H), 8.28 (d, $J = 6.2$ Hz, 2H), 8.72 (d, $J = 8.2$ Hz, 4H), 8.77 (d, $J = 8.2$ Hz, 4H), 8.84 (d, $J = 8.4$ Hz, 4H), 9.73 (d, $J = 5.7$ Hz, 4H), 10.24 (d, $J = 8.2$ Hz, 2H); MS (FAB) m/z 1972 $[M-2Cl]^+$. HRMS (FT-ICR) calc. for $C_{124}H_{132}MgN_{16}Ru$: $[M-2Cl]^{2+}$, 985.4858; found: $[M-2Cl]^{2+}$, 985.4807.

2.8. [(Zn[pz(t-butylphenyl)$_6$phen])Ru(bpy*)$_2$]Cl$_2$ (15)

Treatment of porphyrazine **6** (40.0 mg, 29.0 mmol) under the same reaction conditions as above gave complex **15** (6.7 mg, 11%) as a dark-green solid: m.p. >350°C; R_f 0.06 ($CHCl_3$:MeOH 9:1); IR (CH_2Cl_2) 1739, 1612, 1481, 1368, 1264, 1245, 1138, 1105, 982, 842 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 399 (4.77), 460sh, 673 (4.88) nm; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.31 (s, 18H), 1.37 (s, 18H), 1.42 (s, 18H), 1.50 (s, 36H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.45 (d, $J = 6.9$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 4H), 7.79 (d, $J = 8.2$ Hz, 4H), 7.81 (d, $J = 8.2$ Hz, 4H), 8.03 (dd, $J = 5.4$ and 8.1 Hz, 2H), 8.16 (d, $J = 5.4$ Hz, 2H), 8.26 (d, $J = 5.7$ Hz, 2H), 8.71 (d, $J = 8.2$ Hz, 4H), 8.75 (d, $J = 8.2$ Hz, 4H), 8.84 (d, $J = 8.2$ Hz, 4H), 9.76 (br s, 4H), 10.25 (d, $J = 8.1$ Hz, 2H); MS (FAB) m/z 2013 $[M-2Cl]^+$. HRMS (FT-ICR) calc. for $C_{124}H_{132}N_{16}RuZn$: $[M-2Cl]^{2+}$, 1005.4578; found: $[M-2Cl]^{2+}$, 1005.4533.

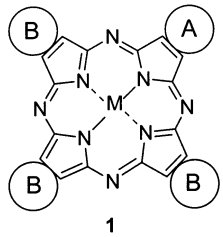
2.9. (Mg[pz(t-butylphenyl)$_6$phen])$_3$RuCl$_2$ (16)

$RuCl_3\cdot H_2O$ (4.0 mg, 19.2 mmol), LiCl (2.5 mg, 57.6 mmol) and EtOH (five drops) were added to a solution of porphyrazine **5** (90.0 mg, 67.4 mmol) in DMF (5 ml), and the mixture heated at reflux for 10 h under N_2. The solution was allowed to cool and the dark-green precipitate that formed upon the addition of H_2O (13 ml) filtered and washed with H_2O. Chromatography of the crude residue on alumina (CH_2Cl_2; $CHCl_3$:MeOH 9:1) followed by gel filtration (Bio-Beads, CH_2Cl_2 then Sephadex, $CHCl_3$) gave compound **16** (80.0 mg, 56%) as a dark-green solid: m.p. >350°C; R_f 0.40 ($CHCl_3$:MeOH 5.7:1); IR (CH_2Cl_2) 1605, 1478, 1366, 1245, 1138, 1104, 986, 841 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 385 (5.32), 459 (4.75), 673 (5.33) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.49 (s, 54H), 1.50 (s, 108H), 7.74–7.90 (m, 36H), 8.28 (m, 6H), 8.75 (t, $J = 7.9$ Hz, 24H), 8.85 (d, $J = 7.7$ Hz, 12H), 9.14 (d, $J = 4.0$ Hz, 6H), 10.42 (d, $J = 8.2$ Hz, 6H); HRMS (FT-ICR) calc. for $C_{264}H_{253}Mg_3N_{36}Ru$: $[M+H-2Cl]^{3+}$, 1366.9833; found: $[M+H-2Cl]^{3+}$, 1367.0006. *Anal.* Found: C, 76.06; H, 6.24; N, 11.99. Calc. for $C_{264}H_{252}Cl_2Mg_3N_{36}Ru$: C, 75.97; H, 6.08; N, 12.08%.

3. Results and discussion

3.1. Synthesis of phenanthroline-appended porphyrazines

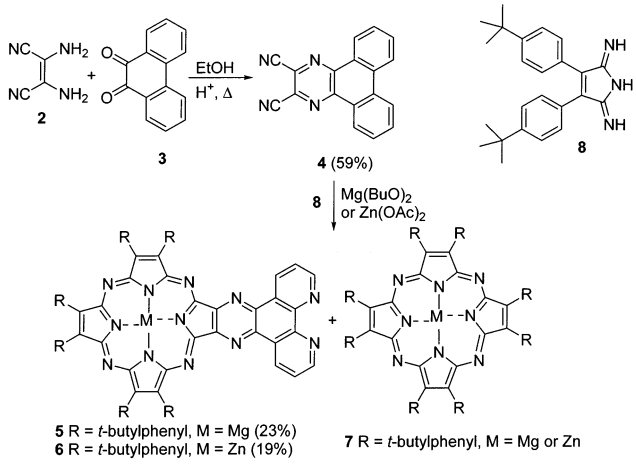
As we have already shown, unsymmetrical porphyrazines of the form M[pz(A:B_3)] **1** (Chart 1) are best obtained by using one of the two maleonitrile derivatives in excess (B) [6].



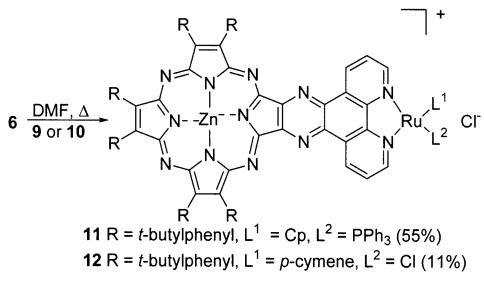
1

Chart 1.

3,4-bis(4-*tert*-Butylphenyl)pyrroline-2,5-diimine (**8**), used previously as the B component and found to enhance the solubility of the resulting porphyrazines and complexes thereof [10], proved suitable for this study (vide infra). The required 1,10-phenanthroline-appended dinitrile **4** (dicnq = dicyanodipyridoquinoxaline) [11], was obtained via condensation of 1,10-phenanthroline-5,6-dione (**3**) [12] with commercially available diaminomaleonitrile **2** (Scheme 1). Although dicnq **4** failed (decomposition under the reaction conditions) to undergo macrocyclization on its own (presumably due to steric reasons), co-cyclization with an excess of diimine **8**, using magnesium butoxide in refluxing butanol or zinc acetate in quinoline, gave the unsymmetrical porphyrazines **5** and **6** respectively, along with the octa(*tert*-butylphenyl) porphyrazine **7** (Scheme 1). Owing to the different polarities of porphyrazines **5** (23%) and **6** (19%) when compared with byproduct **7**, separation was easily achieved via chromatography. However, their proton NMR spectra in $CDCl_3$ displayed very broad signals. This broadening could be overcome by recording the NMR spectra in pyridine-d_5. Both, **5** and **6**, show six well-resolved doublets in the aromatic region (attributable to the three different t-butylphenyl groups) and three resonances associated with the phenanthroline part of the porphyrazines. In addition, ligands **5** and **6** seem to retain residual water (despite heating under vacuum), as indicated from their elemental analyses and proton NMR spectra, very likely directly coordinated to the central metals and phenanthroline part of the macrocycles via hydrogen bonding [13]. All other spectroscopic data were fully consistent with the proposed structures.



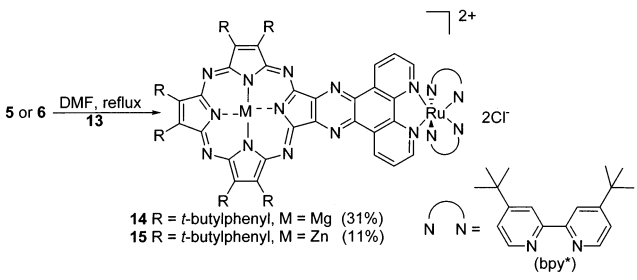
Scheme 1.



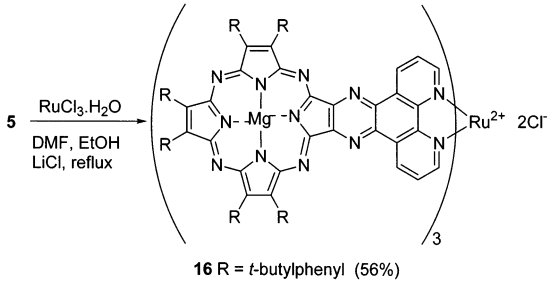
Scheme 2.

3.2. Peripheral metalation

In order to probe the coordination properties of our two novel ligands **5** and **6**, we decided to synthesize diamagnetic low spin [$(t_{2g})^6$] Ru(II) complexes. Oligonuclear Ru(II) complexes of polypyridyl ligands are currently subject to much investigation because of their rich electro- and photo-chemical properties, known to play a crucial role in numerous biological processes such as photosynthetic mimetics and DNA oxidative cleavage [14]. Thus, a number of experiments showed that peripheral metalation was best achieved with DMF as the solvent. Treatment of porphyrazine **6**, for example, with commercially available $RuCl(Cp)(PPh_3)_2$ (**9**) or $[RuCl(\mu_2\text{-}Cl)(p\text{-cymene})]_2$ (**10**) in hot DMF gave the stable 18-electron tetracoordinated d^6 complexes **11** and **12** in 55% and 11% yields respectively (Scheme 2). Both complexes **11** and **12** were freely soluble in chlorinated solvents and easily separated from the reaction mixture by chromatography on alumina and subsequent gel filtration. Proton NMR spectra of solitaire porphyrazines **11** and **12** in pyridine-d_5 clearly showed, in addition to the characteristic signature of the macrocycles (vide supra), the distinctive singlet (5.15) of the η^5-cyclopentadienyl (η^5-Cp) and doublets (6.32 and 6.54) of the η^6-coordinated *p*-cymene respectively. Unfortunately, all attempts to grow crystals suitable for an X-ray crystallographic study were unsuccessful. However, elemental analysis and mass ion measurement of complexes **11** and **12** are fully consistent with their identity.



Scheme 3.



Scheme 4.

Similarly, treatment of porphyrazines **5** and **6** with *cis*-$RuCl_2(bipy^*)_2$ (**13**) [15] (bipy* = 4,4′-di-*tert*-butyl-2,2′-bipyridine) in refluxing DMF gave, after purification, the soluble (chlorinated solvents) octahedral complexes **14** and **15** in 31% and 11% yields respectively (Scheme 3). The proton NMR spectra (pyridine-d_5) of solitaire porphyrazines **14** and **15** were qualitatively the same, displaying, in addition to the characteristic porphyrazine signature (vide supra), up to five distinct singlets for the t-butyl groups and two sets of two well-resolved doublets associated with the bipyridyl moieties in which the adjacent rings are non-equivalent. In addition, high-resolution mass ion measurements using Fourier transform ion-cyclotron resonance techniques (FT-ICR) were again in full agreement with the proposed structures. Both complexes **14** and **15** displayed doubly charge molecular fragments as the most intense peaks corresponding to $[M-2Cl]^{2+}$.

Finally, treatment of porphyrazine **5** with $RuCl_3 \cdot H_2O$ and ethanol as the reductant in DMF at reflux gave, after repeated chromatography and gel filtration, the microanalytically pure trimer **16** in 56% yield (Scheme 4). The proton NMR spectra (pyridine-d_5) of the soluble (e.g. $CHCl_3$, CH_2Cl_2) homoleptic octahedral complex **16** and the parent porphyrazine **5** are qualitatively the same. However, all resonances are shifted and comparable to the chemical shifts reported for the protons in phenanthroline and those of the analogous D_3 symmetric Ru(II) complex ($[Ru(phen)_3]Cl_2$) [16]. Again, high-resolution mass ion measurements (FT-ICR) were fully consistent with the identity of the tetranuclear complex **16** ($[M+H-2Cl]^{3+}$).

3.3. Optical properties

In accordance with other porphyrazinic macrocycles, the UV–Vis spectra of both **5** and **6** are dominated by intense absorptions in the Soret region at 381 and 379 nm respectively and split Q-bands having Q_x and Q_y absorbances at 649 and 682 nm and 652 and 665 nm respectively. The splitting reflects the C_{2v} symmetry and can be rationalized by Gouterman's four orbital model [17]. In addition, less intense peaks appear at 487 nm and 488 nm respectively. We tentatively assigned these absorptions as the $\pi-\pi^*$ transitions (K-band) of the dipyridoquinoxaline moieties. In comparison with other systems containing the dipyridoquinoxaline group [18] the transitions are red-shifted, thus indicating a lowering in energy of the LUMO due to increased conjugation. Although the B-bands do not change shape significantly upon peripheral metalation, a narrowing (no splitting) of the Q-band is observed. More diagnostic changes occur in the K region and can be interpreted in terms of competitive symmetry (Laporte) allowed ($t_{2g} \rightarrow \pi^*$) metal-to-ligand charge transfer (MLCT) processes. Studies on bipyridine and phenanthroline complexes have demonstrated that increasing the backbonding ability of the ligands results in a shift of the MLCT transition to higher energy [19]. Thus, it is likely that in compounds **11** and **12**, containing the π-complexing ligands Cp and *p*-cymene respectively, the MLCT transition is shifted to higher energy and masked by the broad B-band. In contrast, complexes **14** and **15** with bipyridyls (poorer π acceptor ligands) display a shoulder at 460 nm that we tentatively assigned as the MLCT transition. A similar electronic transition at 459 nm is observed for trimer **16**. Representative UV–Vis spectra are shown in Fig. 1.

4. Conclusions

We have synthesized novel π-extended porphyrazines substituted at their periphery with a single bidentate phenanthroline chelating group and demonstrated that these new ligands will coordinate Ru(II). In continuation of our efforts toward the assembly of multiporphyrazine arrays, we have linked three macrocycles by the mutual chelation of a ruthenium ion, thus forming the first tetranuclear homoleptic porphyrazine trimer. In addition, the optical properties of these complexes can be adjusted through the right choice of ligands. In analogy with their polypyridyl counterparts, it is expected that these materials should have very rich and diverse but more adjustable physicochemical properties. Such work will be reported in due course.

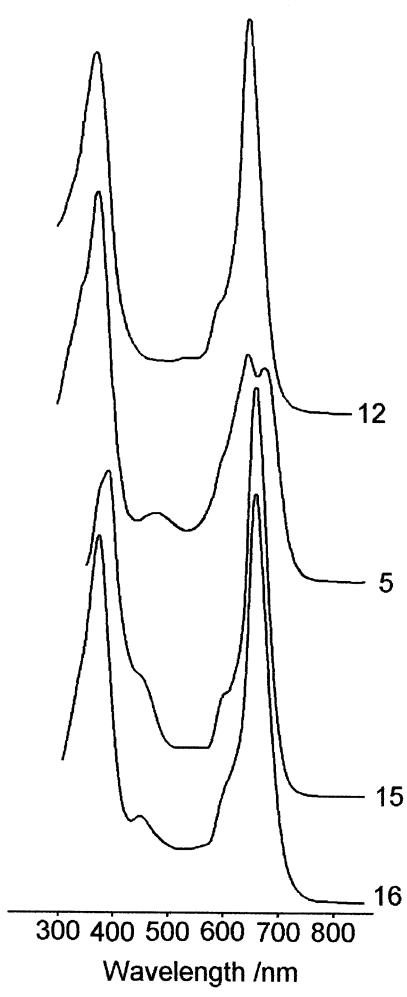


Fig. 1. UV–Vis spectra of porphyrazines **5**, **12**, **15** and **16** in CH_2Cl_2.

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References

[1] (a) J.M. Tour, Chem. Rev. 96 (1996) 537. (b) M.D. Ward, Chem. Soc. Rev. (1995) 121.
[2] T.A. Vannelli, T.B. Karpishin, Inorg. Chem. 38 (1999) 2246 and references cited therein.
[3] C.S. Velazquez, T.F. Baumann, M.M. Olmstead, H. Hope, A.G.M. Barrett, B.M. Hoffman, J. Am. Chem. Soc. 115 (1993) 9997.
[4] N.S. Mani, L.S. Beall, T. Miller, O.P. Anderson, H. Hope, S.R. Parkin, D.J. Williams, A.G.M. Barrett, B.M. Hoffman, J. Chem. Soc., Chem. Commun. (1994) 2095.
[5] A.S. Cook, D.B.G. Williams, A.J.P. White, D.J. Williams, S.J. Lange, A.G.M. Barrett, B.M. Hoffman, Angew. Chem. Int. Ed. Engl. 36 (1997) 760.
[6] T.F. Baumann, M.S. Nasir, J.W. Sibert, A.J.P. White, M.M. Olmstead, D.J. Williams, A.G.M. Barrett, B.M. Hoffman, J. Am. Chem. Soc. 118 (1996) 10479.
[7] S.J. Lange, H. Nie, C.L. Stern, A.G.M. Barrett, B.M. Hoffman, Inorg. Chem. 37 (1998) 6435.
[8] D.P. Goldberg, S.L.J. Michel, A.J.P. White, D.J. Williams, A.G.M. Barrett, B.M. Hoffman, Inorg. Chem. 37 (1998) 2100.
[9] P.G. Sammes, G. Yahioglu, Chem. Soc. Rev. (1994) 327.
[10] T.F. Baumann, A.G.M. Barrett, B.M. Hoffman, Inorg. Chem. 36 (1997) 5661.
[11] While this work was in progress, the synthesis of dicnq was reported: S. Arounaguiri, B.G. Maiya, Inorg. Chem. 38 (1999) 842.
[12] M. Yamada, Y. Tanaka, Y. Yoshimoto, S. Kuroda, I. Shimao, Bull. Chem. Soc. Jpn. 65 (1992) 1006.
[13] L.A. Summers, Adv. Heterocycl. Chem. 22 (1978) 1.
[14] See for example E. Ishow, A. Gourdon, J.-P. Launay, C. Chiorboli, F. Scandola, Inorg. Chem. 38 (1999) 1504.
[15] T.B. Hadda, H. Le Bozec, Polyhedron 7 (1988) 575.
[16] J.E. Baggott, G.K. Gregory, M.J. Pilling, S. Anderson, K.R. Seddon, J.E. Turp, J. Chem. Soc., Faraday Trans. 2 79 (1983) 195.
[17] M. Gouterman, in: D. Dolphin (Ed.), The Porphyrins, vol. 3, Academic Press, New York, 1978.
[18] J. Fees, W. Kaim, M. Moscherosch, W. Matheis, J. Klima, M. Krejcik, S. Zalis, Inorg. Chem. 32 (1993) 166.
[19] W.R. McWhinnie, J.D. Miller, Adv. Inorg. Chem. Radiochem. 12 (1969) 135.