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Neutral π-radicals of lithium porphyrins: synthesis and characterization

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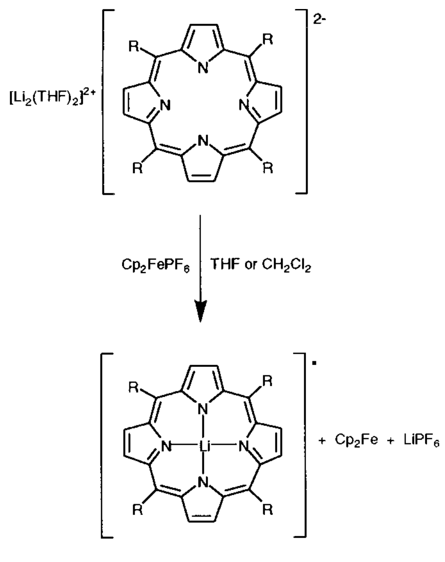
Neutral π-radicals of three lithium porphyrins (tetraphenylporphyrin [Li(TPP)$^{\bullet}$], 1, tetra(pentafluorophenyl)porphyrin [Li(PFP)$^{\bullet}$], 2, and tetra(3,5-bis-*tert*-butylphenyl)porphyrin [Li(TBP)$^{\bullet}$], 3) have been prepared and characterized using UV-vis, EPR, and IR spectroscopy, and, in the case of 1, X-ray crystallography.

Porphyrins are of great importance in biological oxidation and reduction reactions. Their metal complexes participate in the primary photosynthetic process, oxygen transport, electron transport, and the metabolism of drugs and xenobiotics.[1–5] They also form the core of all heme proteins, with cation radicals identified as intermediates in many catalytic cycles.[1] It has further been suggested that future electronic devices used in memory or logic application could rely specifically on tuning the electronic properties of porphyrins and their π cation radicals.[6,7]

Stable π cation radicals of metalloporphyrins have been obtained with the transition metals cobalt,[8] iron,[9–13] copper,[14] zinc,[8,15–17] and the main group metal magnesium.[8,15,18] Additionally, π anion radicals with metals such as zinc and iron have been prepared.[19–21]

In this communication we report the first neutral π-radical prepared from a dilithium porphyrin. This type of complex has precedence only in the chemistry of phthalocyanines, *i.e.*, a neutral lithium phthalocyanine π-radical.[22–26]



1. R = phenyl
2. R = C_6F_5
3. R = (3,5-bis-*tert*-butyl)phenyl

Scheme 1

The dilithium porphyrins, which were prepared using literature procedures,[27–29] were oxidized using one equivalent of ferrocenium hexafluorophosphate in THF or dichloromethane (Scheme 1). The resulting lithium porphyrin radicals were isolated by crystallization.† [Li(TPP)$^{\bullet}$], **1**, is insoluble in acetone and in nonpolar solvents such as hexanes and diethyl ether, is slightly soluble in THF, and is moderately soluble in methylene chloride and chloroform. In contrast, the radicals [Li(PFP)$^{\bullet}$], **2**, and [Li(TBP)$^{\bullet}$], **3**, are soluble in acetone, with radical **3** being slightly soluble even in toluene and benzene.

The UV-vis spectra of the radicals show one weaker absorption band (at 356, 413, and 419 nm for **1**, **2**, and **3**, respectively) followed by one strong Soret-like band (at 418, 430, and 436 nm, for **1**, **2**, and **3**, respectively) in addition to several Q-type absorption bands.† The observation of negligible Λ_M in acetonitrile suggest the compounds exist as tight ion pairs in solution.[30] This result contrasts with that observed for Li_2porphyrin compounds which show Λ_M's consistent with the formation of solvent separated ion pairs.[27–29]

The absence of signals in ^{1}H NMR spectra of the compounds suggested paramagnetism, a notion that was confirmed by EPR measurements.‡ From room temperature to 1.7 K, solid and THF solutes of the three porphyrin radicals show *g*-values of 2.00 consistent with the presence of an organic radical. In the case of **1**, a split into parallel and perpendicular *g*-values of 2.002 and 2.003, respectively, was observed.

It has been well established that the electron removed from metalloporphyrins during oxidation can be removed from either of the highest occupied orbitals, a_{1u} and a_{2u}, which are almost degenerate in the unoxidized species.[6] Therefore a neutral π-radical produced by electron abstraction from one or the other of these orbitals would lead to either a $^2A_{1u}$ or $^2A_{2u}$ ground state. These two states, in turn, differ significantly in their EPR spectroscopic behavior. In the $^2A_{2u}$ ground state, spin electron density is localized on the *meso*-carbons and the nitrogen atoms, while the $^2A_{1u}$ state has low spin density on these atoms. In the latter state the spin density is primarily confined to α-pyrrolic carbon atoms. The absence of hyperfine splitting for radicals **1** and **2** at room temperature in solution and the solid state suggests that these radicals exist in the $^2A_{1u}$ ground state. This would stand in contrast to what is observed for most *meso*-substituted cationic π-radical porphyrins such as [Fe(TPP)Cl], which are generally found to exist in the $^2A_{2u}$ ground state.[6,8] The $^2A_{1u}$ ground state is usually found for β-substituted species such as cationic π-radicals of metallo-octaethylporphyrins.

The small energy gap between these orbitals implies that peripheral substituents on the porphyrin ring or the metal might influence which ground state is lowest in energy. To investigate the effect of substituents further, attempts were made to prepare the analogous neutral lithium octaethylporphyrin π-radical ([Li(OEP)$^{\bullet}$]). However the [Li(OEP)$^{\bullet}$] derivative appears to be much less stable in the presence of traces of O_2 and/or water, and all attempts to prepare this radical were unsuccessful. Thus, it remains to be determined if this different behavior of the neutral π-radical described here is due to the difference in charge, in substitution, or to the bound lithium ion.

Crystallization of [Li(TPP)$^{\bullet}$] **1** from dichloromethane and diethyl ether afforded bright purple block-like crystals.§ The solid state structure shows that the remaining lithium atom is bound in the plane of the porphyrin (Fig. 1). The porphyrin macrocycle is slightly ruffled, with opposite pyrrolic carbons up

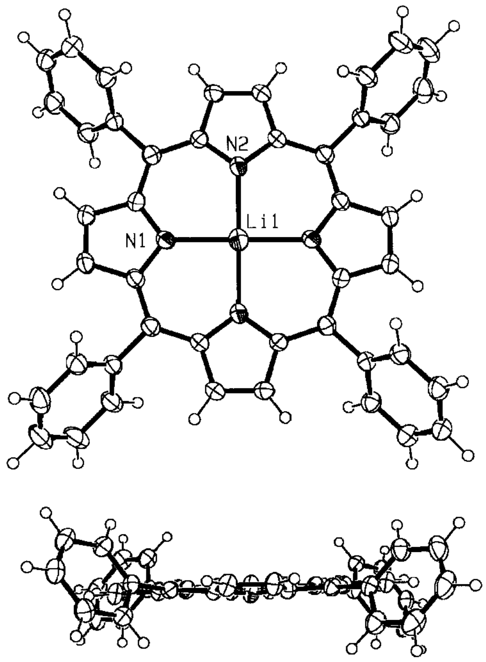


Fig. 1 Top and side views of the solid state structure of **1**. Selected bond distances (Å): N(1)–Li 2.039(2), N(2)–Li 2.069(2), N(1)–Cα(2) 1.371(3), N(1)–Cα(5) 1.366(3), N(2)–Cα(7) 1.371(3), N(2)–Cα(10) 1.373(3), Cm(1)–Cα(2) 1.408(4), Cm(1)–Cα(10*) 1.417(4), Cm(6)–Cα(5) 1.413(4), Cm(6)–C(7) 1.414(3), Cα(2)–Cβ(3) 1.452(4), Cα(5)–Cβ(4) 1.447(4), Cα(7)–Cβ(8) 1.443(4), Cα(10)–Cβ(9) 1.445(4), Cβ(3)–Cβ(4) 1.345(4), Cβ(8)–Cβ(9) 1.351(4). Selected bond angles (degrees): N(1)–Li–N(2) 90.33(8), N(1)–Li–N(2)* 89.67(8), Cα(2)–Cm(1)–Cα(10) 125.8(2), Cα(5)–Cm(6)–Cα(7) 125.8(2), Cα(2)–N(1)–Cα(5) 106.0(2), Cα(7)–N(2)–Cα(10) 105.8(2).

to 0.3 Å above or below the mean porphyrin plane. The porphyrin plane is distorted from planarity to a much greater degree than is found for $[Li(C_6H_{12}O_{12})_2]^+[Li(TMPP)]^-$, which is virtually planar, or $Li_2(TPP)(Et_2O)_2$.[27–29] S_4 distortions, but not S_2, have been observed in other tetraphenylporphyrin radical complexes.[12,14–16]

The bond lengths of the porphyrin macrocycle are very similar to those of tetraphenylporphyrin dianions and cation radicals.[12,14,16,17,21] In contrast to octaethylporphyrin radicals, an alternating shortening and lengthening of the bond lengths of the tetraphenylporphyrin macrocycle is not observed upon oxidation. This is probably due to the fact that the HOMO from which an electron was removed is of a different symmetry type (see above).

Preliminary reactivity studies suggest that **1** reacts with phenyl iodinium chloride to afford *meso*-phenyl substitution of the TPP skeleton, resulting in an isoporphyrin-like macrocycle[31–33] with a centrally bound lithium ion (as determined by ^7Li and ^1H NMR spectroscopy). Full details will be presented later.

In summary, we have presented the synthesis and characterization of three neutral *meso*-substituted porphyrin π-radicals. These compounds were found to show different EPR behavior than that observed for π-cation radicals of *meso*-substituted porphyrins. Reasons for this difference are currently under investigation.

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Notes and references

† General synthesis of lithium porphyrin radicals: THF was added *via* cannula to a mixture of Cp_2FePF_6 (217 mg, 0.65 mmol) and the respective dilithium porphyrin (0.65 mmol) and the mixture was stirred for 3 h at room temperature. The precipitate formed after cooling overnight to −40 °C was collected by filtration. [Li(TPP)] **1**: bright purple solid, 55%. Mp >350 °C. UV/vis: 356, 418, 508, 546, 644, 696 nm. IR: ν 1329, 1258, 1213, 1197, 1174, 1069, 1033, 973, 922, 829, 793, 758, 718, 701, 656, 590 cm^{-1}. EPR: $g_{\parallel} = 2.002$; $g_{\perp} = 2.003$. [Li(PFP)] **2**: bright red solid, 60%. Mp >350 °C. UV/vis: 413, 430, 504, 550, and 584 nm. IR: ν 2955, 2923, 2854, 1518, 1487, 1463, 1378, 1329, 1261, 1067, 1048, 1019, 987, 931, 799, 760 cm^{-1}. EPR: $g = 2.002$. [Li(TBP)] **3**: bright purple solid, 58%. Mp >350 °C. UV/vis: 419, 436, 513, 550, 580, and 647 nm. IR: ν 2955, 2923, 2854, 1591, 1462, 1378, 1261, 1093, 1018, 921, 799, 714 cm^{-1}. EPR: $g = 2.003$.

‡ EPR spectra were measured as solids, solutions, or frozen glasses using a Varian E-12 spectrometer. The microwave frequency was measured using an EIP-548 microwave frequency counter, and the magnetic field was measured using a Varian E-500 NMR Gaussmeter.

§ *Crystal data* for $C_{44}H_{28}N_4Li$ **1**: $M = 619.67$, triclinic, $a = 6.4302(1)$ Å $b = 10.3539(4)$ Å, $c = 12.3020(4)$ Å, $\alpha = 95.305(2)°$, $\beta = 99.351(2)°$, $\gamma = 101.149(2)°$, $U = 786.38(4)$ Å^3, space group $P\bar{1}$, $Z = 1$, μ(Mo-Kα) = 0.77 cm^{-1}, 3152 reflections measured, 2197 unique ($R_{int} = 0.049$). The final R_w was 0.053, with a GOF of 2.24. CCDC reference no. 186/1743. See http://www.rsc.org/suppdata/dt/a9/a908956j/ for crystallographic files in .cif format.

1 D. Dolphin and R. H. Felton, *Acc. Chem. Res.*, 1972, **7**, 26.
2 T. L. Poulos and B. C. Finzel, *Pept. Protein Rev.*, 1984, **4**, 155.
3 D. Dolphin, Z. Muljiani, K. Rousseau, D. C. Borg, J. Fajer and R. H. Felton, *Ann. N. Y. Acad. Sci.*, 1973, **206**, 177.
4 D. Dolphin and R. H. Felton, *Acc. Chem. Res.*, 1974, **7**, 26.
5 J. H. Dawson, *Science*, 1988, **240**, 433.
6 R. A. Binstead, M. J. Crossley and N. S. Hush, *Inorg. Chem.*, 1991, **30**, 1259.
7 A. G. Skillman, J. R. Collins and G. H. Loew, *J. Am. Chem. Soc.*, 1992, **114**, 9538.
8 J. Fajer, D. C. Borg, A. Forman, D. Dolphin and R. H. Felton, *J. Am. Chem. Soc.*, 1970, **92**, 3451.
9 J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo and B. J. Evans, *J. Am. Chem. Soc.*, 1981, **103**, 2884.
10 J. T. Groves and Y. Watanabe, *J. Am. Chem. Soc.*, 1986, **108**, 507.
11 K. Rachlewicz and L. Latos-Grazynski, *Inorg. Chem.*, 1995, **34**, 718.
12 P. Gans, G. Buisson, E. Duee, J.-c. Marchon, B. S. Erler, W. F. Scholz and C. A. Reed, *J. Am. Chem. Soc.*, 1986, **108**, 1223.
13 S. Nakashima, H. Ohya-Nishiguchi, N. Hirota, H. Fujii and I. Morishima, *Inorg. Chem.*, 1990, **29**, 5207.
14 H. Song, C. A. Reed and W. R. Scheidt, *J. Am. Chem. Soc.*, 1989, **111**, 6865.
15 Z. Gross and C. Barzilay, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1615.
16 L. D. Spaulding, P. G. Eller, J. A. Bertrand and R. H. Felton, *J. Am. Chem. Soc.*, 1974, **96**, 982.
17 H. Song, C. A. Reed and W. R. Scheidt, *J. Am. Chem. Soc.*, 1989, **111**, 6867.
18 K. M. Barkigia, L. D. Spaulding and J. Fajer, *Inorg. Chem.*, 1983, **22**, 349.
19 J. Teraoka, S. Hashimotot, H. Sugimoto, M. Mori and T. Kitagawa, *J. Am. Chem. Soc.*, 1987, **109**, 180.
20 N. S. Hush and J. R. Rowlands, *J. Am. Chem. Soc.*, 1967, **89**, 2976.
21 R. Cosmo, C. Kautz, K. Merrholz, J. Heinze and K. Muellen, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 604.
22 F. Beensbaa and J.-J. Andre, *J. Phys. Chem.*, 1992, **96**, 5739.
23 M. Brinkmann, P. Turek and J.-J. Andre, *J. Mater. Chem.*, 1998, **8**, 675.
24 P. Turek, J.-J. Andre, A. Giraudeau and J. Simon, *Chem. Phys. Lett.*, 1987, **134**, 471.
25 P. Turek, P. Petit, J.-J. Andre, J. Simon, R. Even, B. Boudjema, G. Guillaud and M. Maitrot, *J. Am. Chem. Soc.*, 1987, **109**, 5119.
26 K. Yakushi, T. Ida, A. Ugawa, H. Yamakado, H. Ishii and H. Kuroda, *J. Phys. Chem.*, 1991, **95**, 7636.
27 D. Y. Dawson and J. Arnold, *J. Porphyrins Phthalocyanines*, 1997, **1**, 121.
28 J. Arnold, D. Y. Dawson and C. G. Hoffman, *J. Am. Chem. Soc.*, 1993, **115**, 2707.
29 H. Brand, J. A. Capriotti and J. Arnold, *Inorg. Chem.*, 1994, **33**, 4334.
30 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
31 D. Dolphin, R. H. Felton, D. C. Borg and J. Fajer, *J. Am. Chem. Soc.*, 1970, **92**, 119.
32 H. Xie and K. M. Smith, *Tetrahedron Lett.*, 1992, **33**, 1197.
33 K. M. Barkigia, M. W. Renner, H. Xie, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1993, **115**, 7894.

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