Near-IR absorption of porphyrin methylcarbocations

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Abstract—Syntheses of stabilized *meso*-and β-carbocations of nickel(II) porphyrins are reported and compared. A novel dimeric porphyrin cation absorbing at 1030 nm is also described.
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The stability of carbocations depends upon the entire molecular framework, with substituents playing a crucial part.[1] Long-lived carbocations, such as arylcarbocations,[2] which are stable enough to have their electronic, vibrational, and NMR spectra recorded, have been described. A common feature of aryl and alkenyl cations and also those with cyclic π-systems is the shift to long wavelength of their electronic absorption spectra. For example, diphenylmethyl carbocation has a λ_{max} at 422 nm, significantly red-shifted relative to diphenylcarbinol (312 nm).[3]

Because of their highly conjugated aromatic systems, porphyrinoids are capable of efficiently stabilizing a positive charge. While metalloporphyrin π-dications are highly reactive,[4] metalloporphyrin π-cation radicals, prepared by one-electron oxidation of the corresponding porphyrins, are moderately stable and useful synthetic intermediates.[5]

Porphyrin π-cation radicals typically display an intense absorption band above 700 nm, while the Soret band is broadened, blue-shifted and lower in intensity compared with that of the parent porphyrin.[6] The λ_{max} of cationic zinc(II) isoporphyrins, such as those prepared by the reaction of dibenzoyl peroxide with ZnTPP[7] or by total synthesis,[8] appear around 800–900 nm, presumably as a consequence of the π-delocalization of the positive charge over the isoporphyrin moiety. Cu(II) porphyrin-stabilized *meso*-methylcarbocations obtained by acid addition to *meso*-hydroxymethyl-, *meso*-

methoxymethyl- and *meso*-dimethylaminomethyl–Cu(II)–etioporphyrin I, have been shown to display a broad Soret band at ∼450 nm and an intense absorption band around 1015 nm.[9] Herein we report the synthesis of stabilized both *meso*- and β-methylcarbocations of Ni(II)–porphyrins, as well as a novel route to porphyrin dimeric cationic species displaying remarkably intense near-IR absorptions.
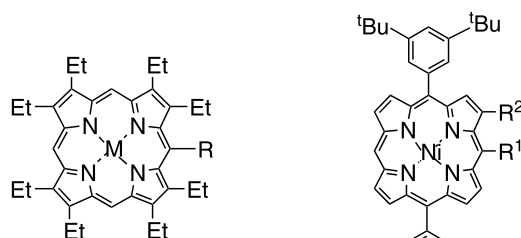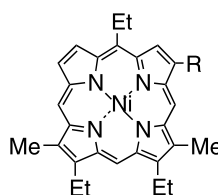

1: R = CH₂OH; M=Ni
2: R = CHO; M=Ni
15: R = CHO; M=Cu

3: R¹=CH(OH)Ph; R²=H
4: R¹=CHO; R²=H
5: R¹=R²=H
6: R¹=H; R²= C(O)Ph

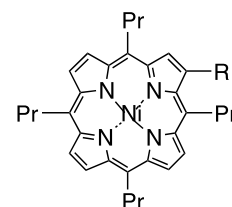7: R=H
8: R=CHO
11: R=CH(OMe)₂

12: R=H
13: R=CHO
14: R =CH₂OH

Upon addition of a few drops of trifluoroacetic acid (TFA) to a solution of nickel(II) 5-hydroxymethyl-octaethylporphyrin **1** in CH_2Cl_2, prepared by reduction of aldehyde **2** with sodium borohydride,[10] we observed an intense absorption band around 1100 nm (Table 1), attributed to the *meso*-methylcarbocation as previously reported.[9] This absorption spectrum reverted to that of a typical nickel(II) porphyrin upon neutralization with triethylamine. Similar results were observed with 5-hydroxymethylphenylporphyrin **3**, prepared in 70% yield by Vilsmeier formylation of nickel(II) porphyrin **5**[11] followed by treatment of **4** with phenyl magnesium bromide. Our first approach to **3** involved Friedel–Crafts acylation of **5** in CH_2Cl_2 using benzoylchloride and 2 equiv. of $AlCl_3$; whereas porphyrin electrophilic substitutions take place preferentially at the less hindered more reactive *meso*-positions,[12] the major Friedel–Crafts product isolated was β-acylporphyrin **6**. A radical mechanism stemming from the oxidation of the porphyrin macrocycle by the acyl carbocation, followed by radical recombination, could explain this unexpected regioselectivity.

Table 1. Absorption spectra data for porphyrin methyl-carbocations (**A**) and their precursors (**B**)

Cmpd	(**B**) λ^a nm (ε^a)	(**A**) λ^b nm (ε^b)
1	404 (149,500);	386 (55,000);
	569 (13,500)	880 (1,500);
		>1100 (>2,500)
3	408 (191,500);	473 (57,500);
	523 (14,000)	621 (12,500);
		963 (8,000)
9	398 (117,500);	361 (34,500);
	517 (11,500);	397 (44,500);
	553 (14,500)	421 (25,500);
		494 (18,500);
		925 (24,000);
		1030 (41,500)
14	418 (159,500);	406 (78,000);
	539 (10,500)	602 (6,000);
		686 (6,000)

[a] In dichloromethane.
[b] In dichloromethane with trifluoroacetic acid [0.2% (v/v)].

Upon addition of 2–3 drops of TFA to a solution of **3** in CH_2Cl_2, the longest wavelength of absorption red-shifted to 963 nm, and demonstrated reversibility when the solution was neutralized with triethylamine.

The ^{1}H NMR spectrum of **1** in CD_2Cl_2 containing some deuterated TFA displayed a broad peak at −40 ppm, presumably resulting from a change in the oxidation state from nickel(II) to nickel(III) and concomitant delocalization of the positive charge over the entire porphyrin ring (Scheme 1).

In contrast to the methylcarbocation prepared from **1**, the diamagnetic ^{1}H NMR spectrum of **3** in the presence of d-TFA suggested no such participation of the nickel ion in the stabilization of the carbocation. However, the π-delocalization of the positive charge over the porphyrin macrocycle yielded eight non-equivalent and upfield shifted β-proton signals, indicative of an asymmetric structure.

Formylation of **7**[13] in TFA with trimethyl orthoformate took place under strong steric control[14] and the brown-colored β-formylporphyrin **8** was obtained as the main product, along with an unexpected red porphyrin dimer **9**, in about 20% yield. The formation of **9** was strongly dependent upon the amount and rate of trimethyl orthoformate addition and appeared only after some β-formylporphyrin was formed, as monitored by TLC. The most striking feature of this dimeric species resulted from addition of a drop of TFA to a solution of **9** in CH_2Cl_2, which generated a very intense and broad absorption band at 1030 nm (Fig. 1), typical of a porphyrin methylcarbocation. Furthermore, while the LDI-ToF analysis of porphyrin **9** displayed peaks at 969.8 and 999.8 Da, a single peak at 969.8 Da (M+−OMe) was observed after TFA treatment. ^{1}H, gCOSY, gHSQC and NOE NMR experiments confirmed the β,β-dimeric porphyrin structure. The stabilized cationic form **10** (Scheme 2) displays a near-infrared absorption band strikingly similar to that observed for the methylcarbocation obtained from **1**.
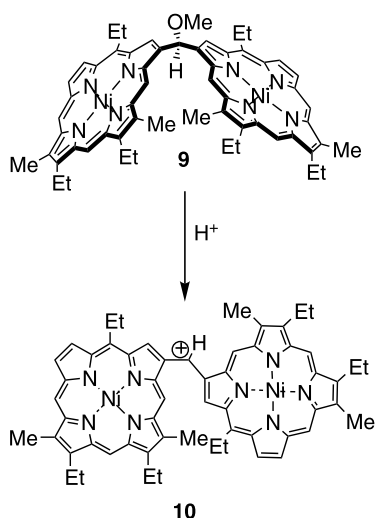
The dimeric species **9** is presumably formed via an intermolecular Friedel–Crafts alkylation using the intermediate porphyrin ketal **11** as alkylating agent.[15]
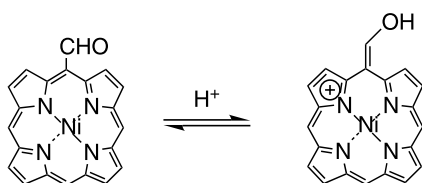
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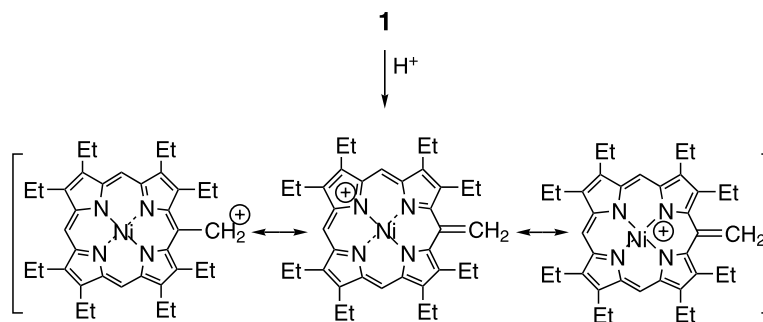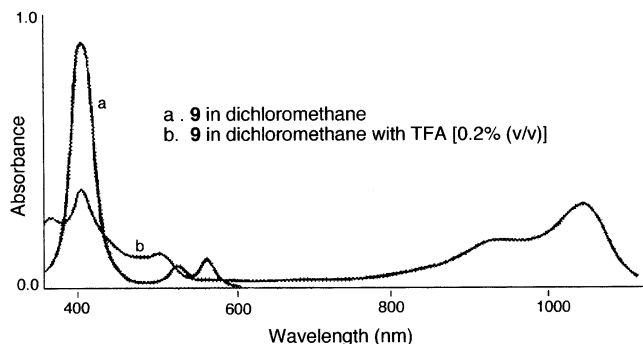
Scheme 1.

Figure 1. Optical spectra of porphyrin **9** in CH_2Cl_2 with and without TFA.

Scheme 2.

Scheme 3.

Formylation of nickel(II) *meso*-tetrapropylporphyrin **12**[16] with TFA/HC(OMe)$_3$ gave β-formylporphyrin **13** in low yield; no dimeric species were isolated suggesting that the Friedel–Crafts reaction is highly sensitive to the steric environment. Reduction of **13** with sodium borohydride in THF gave carbinol **14** quantitatively, which upon acid treatment generated a stabilized β-methylcarbocation. This species displayed a broad absorption band at 686 nm, significantly less red-shifted than dimeric **10** and than the *meso*-methylcarbocation obtained from **1**.

Similar spectral changes were observed upon treatment of *meso*- and β-formylporphyrins in CH_2Cl_2 with a large amount of acid (see below), presumably as a

Table 2. Absorption spectral data for formylporphyrins

Cmpd	λ^a nm (ε^a)	λ^b nm (ε^b)
2	399 (78,500); 421 (70,000); 525 (4,500); 559 (8,000); 643 (7,000)	426 (4,500); 563 (3,000); 687 (3,000); 951 (6,000)
13	433 (118,500); 554 (8,500); 600 (7,500)	411 (51,500); 621 (4,500); 747 (4,000); 861 (4,000)
15	397 (200,500); 528 (10,000); 565 (15,000)	385 (68,000); 880 (2,500)

[a] In dichloromethane.
[b] In dichloromethane with trifluoroacetic acid [50% (v/v)].

consequence of the formation of cationic enol-type structures (Scheme 3).

The acid driven mesomerism of three nickel(II) formylporphyrins in TFA/CH_2Cl_2 is summarized in Table 2. For example, addition of an equal volume of acid to a solution of **2** in CH_2Cl_2 yielded a broad absorption around 951 nm.[17] A similar band is observed at 880 nm for copper(II) *meso*-formyloctaethylporphyrin **15**. A related process, involving reversible conversion of a porphyrin Schiff base into a phlorinoid compound by protonation, has been previously described;[18] in this case, the λ_{max} shifted to 720 nm. β-Formylporphyrin **13** gave a less red-shifted absorption band (600 nm) relative to that of *meso*-formylporphyrins in the presence of acid, as was also observed for porphyrin β-relative to *meso*-methylcarbocations. However, the β-cationic dimer **10** has a visible spectrum very similar to that of the *meso*-methylcarbocations obtained from **1**.

In conclusion, porphyrin methylcarbocations are stable enough to have their electronic spectra and, in some instances, NMR spectra recorded. Metalloporphyrins, with their large aromatic system, are very capable stabilizing substituents for the methylcarbocations and could be incorporated into molecular probes with regard to the intense near infrared absorption of their methylcarbocations.

References

1. Olah, G. A.; Schleyer, von R. P. *Carbonium Ions*, Volume 1: General Aspects and Methods of Investigation; Interscience: New York, 1968.
2. Bethell, D.; Gold, V. *Carbonium Ions*: *An Introduction*; Academic Press: New York, 1967.

3. Olah, G. A.; Pittman, C. U., Jr.; Waack, R.; Doran, M. *J. Am. Chem. Soc.* **1966**, *88*, 1488.

4. Dolphin, D.; Felton, R. H.; Borg, D. C.; Fajer, J. *J. Am. Chem. Soc.* **1970**, *92*, 743.

5. (a) Shine, H. J.; Padilla, A. G.; Wu, S.-M. *J. Org. Chem.* **1979**, *44*, 4069; (b) Smith, K. M.; Barnett, G. H.; Evans, B.; Martynenko, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5953; (c) El Kahef, L.; Gross, M.; Giraudeau, A. *J. Chem. Soc., Chem. Commun.* **1989**, 963; (d) El Kahef, L.; Giraudeau, A. *Can. J. Chem.* **1991**, *69*, 1161; (e) Giraudeau, A.; Ruhlmann, L.; El Kahef, L.; Gross, M. *J. Am. Chem. Soc.* **1996**, *118*, 2969; (f) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Chem. Commun.* **1998**, 337.

6. (a) Kadish, K. M.; Rhodes, R. K. *Inorg. Chem.* **1981**, *20*, 2961; (b) Gans, P.; Buisson, G.; Duee, E.; Marchon, J.-C.; Erler, B. S.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1223.

7. Takeda, Y.; Takahaara, S.; Kobayashi, Y.; Misawa, J.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1990**, 2103.

8. (a) Xie, H.; Smith, K. M. *Tetrahedron Lett.* **1992**, *33*, 1197; (b) Xie, H.; Leung, S. H.; Smith, K. M. *J. Porphyrins Phthalocyanines* **2002**, *6*, 607.

9. Ponomarev, G. V. *Khim. Geterotsikl. Soedin.* **1977**, 90.

10. Arnold, D.; Johnson, A. W.; Winter, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1643.

11. Yeung, M.; Ng, A. C. H.; Drew, M. G. B.; Vorpagel, E. M.; McMahon, R. J.; Ng, D. K. P. *J. Org. Chem.* **1998**, *63*, 7143.

12. (a) Nudy, L. R.; Schieber, C.; Longo, F. R. *Heterocycles* **1987**, *26*, 1797; (b) Callot, H. J.; Schaeffer, E. *J. Chem. Res. (M)* **1978**, 690; (c) Longo, F. R.; Drach, J. E. *J. Org. Chem.* **1974**, *39*, 3282; (d) Schlozer, R.; Fuhrhop, J.-F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 363. 5,15; (e) Arnold, D. P.; Bott, R. C.; Eldridge, H.; Elms, F. M.; Smith, G.; Zojari, M. *Aust. J. Chem.* **1997**, *50*, 495; (f) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135.

13. Wickramasinghe, A.; Jaquinod, L.; Nurco, D.; Smith, K. M. *Tetrahedron* **2001**, *57*, 4261.

14. Montforts, F.-P.; Scheurich, G.; Meier, A.; Haake, G.; Hoper, F. *Tetrahedron Lett.* **1991**, *32*, 3477.

15. For an example of intramolecular alkylation with ketals as alkylating agents: Fan, J.-F.; Wu, Y.-L. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1189.

16. Senge, M. O.; Bischoff, I.; Nelson, N. Y.; Smith, K. M. *J. Porphyrins Phthalocyanines* **1999**, *3*, 99.

17. Upon bubbling hydrogen chloride into a solution of **2** in CD_2Cl_2, a clean and rapid deformylation could be monitored by ^1H NMR and UV–vis spectra. Deformylation in TFA was slow (taking several hours). A base-catalyzed deformylation has been reported: Callot, H. J. *Bull. Soc. Chim. Fr.* **1973**, *12*, 3413.

18. Witte, L.; Fuhrhop, J.-H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 361.