

Olefin-Mediated Interaction Observed for Nickel Tetraphenylporphyrins with an Acceptor Substituted on the β -Carbon

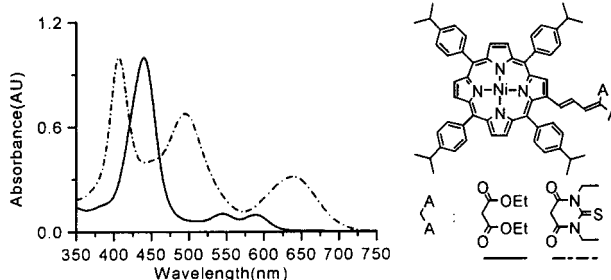
Chin-Ti Chen,^{*,†} Hsiu-Chih Yeh,[†] Xuequn Zhang,[†] and Jenwei Yu^{*,‡}

Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, R.O.C., and
Department of Chemistry, National Kaohsiung Normal University, Kaohsiung,
Taiwan 802, R.O.C.

cchen@chem.sinica.edu.tw

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ABSTRACT



A new series of acceptor-substituted nickel tetraphenylporphyrins were synthesized in order to examine the efficiency of the π -conjugation through the olefinic linkages to the β -carbon of porphyrins. Perturbed absorption spectra were found for the substituted porphyrins and may be attributed to the reduced symmetry of porphyrins, although such a symmetry factor is acceptor strength dependent. A stronger interaction than previously realized for the β -carbon-substituted porphyrins exists between the porphyrin π -system and through an olefin-linked electron acceptor.

Covalently linked porphyrin systems have attracted considerable interest. They have been vigorously pursued as the molecular models for studying electron or energy transfer to mimic analogous processes found in photosynthetic organisms.¹ There is also growing interest in oligo- and polymeric π -conjugated porphyrins as “molecular photonic wires” and nonlinear optical materials.² All these interesting properties hinge more or less on the effective π -overlap between the central porphine unit and the peripheral substituents. The edge-to-edge fused porphyrins or substituents bridged by alkynyl moieties are among the few structures that are amenable toward building an effective π -conjugated con-

nection. It is widely believed that due to the steric crowding unsaturated bridges such as olefinic and aryl moieties would limit the desired π -conjugation on either the β or *meso* carbon of the porphine ring.³ In this Letter we report the first evidence for a remarkable electronic interaction between the

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(3) Recently β -substituted styryl tetraphenylporphyrins have been prepared, and the porphine rings have been observed to be coplanar with the styryl substituent. However, spectroscopic data suggest that side-chain conjugated interaction in β -substituted styryl tetraphenylporphyrins is still limited. (a) Burrell, A. K.; Officer, D. L.; Reid, D. C. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 900. (b) Bonfantini, E. E.; Burrell, A. K.; Officer, D. L.; Reid, D. C. W.; McDonald, M. R.; Cocks P. A.; Gordon, K. C. *Inorg. Chem.* **1997**, *36*, 6270.

[†] Academia Sinica.

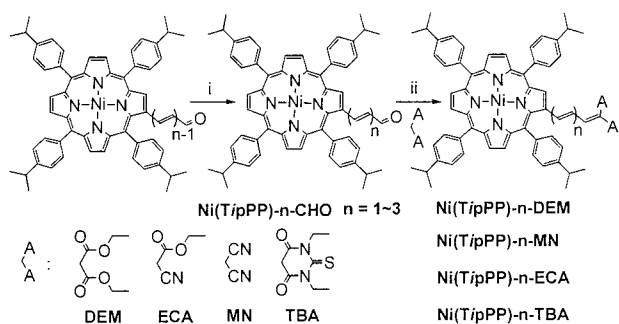
[‡] National Kaohsiung Normal University.

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porphine ring and its electronic acceptor through the olefinic bridge on the β position in a series of acceptor-substituted nickel complexes of 5,10,15,20-tetra(4-isopropylphenyl)-porphyrin Ni(TipPP).

Acceptor-substituted porphyrins Ni(TipPP)-*n*-DEM, Ni(TipPP)-*n*-ECA, Ni(TipPP)-*n*-MN, and Ni(TipPP)-*n*-TBA were synthesized and characterized in this study (Scheme 1). Acceptors diethyl malonate (DEM), ethyl cyanoacetate (ECA)

Scheme 1. Synthesis of Acceptor-Containing β -Substituted Nickel Porphyrins^a



^a(i) (1) 1,3-Dioxan-2-yl methyltributylphosphonium bromide in DMF, sodium ethoxide, ethanol, and toluene; (2) 2% aqueous HCl in THF; (ii) aluminum oxide.

(ECA), malononitrile (MN), and 1,3-diethyl-2-thiobarbituric acid (TBA), in order of increasing electron-withdrawing strength, were attached to the β -carbon of the porphine ring through olefin bridges of varying length ($n = 0, 1, 2,$ and 3). Porphyrins Ni(TipPP) and Ni(TipPP)-*n*-CHO ($n = 0$) were synthesized by standard procedures^{4a,b} and the Vilsmeier formylation method,^{4c} respectively. Porphyrin aldehydes Ni(TipPP)-*n*-CHO were readily synthesized by repeating the Wittig oxypropenylation procedure on the shorter aldehyde homolog.^{4d} The acceptor-attached porphyrins were prepared by reacting Ni(TipPP)-*n*-CHO with the appropriate acceptors using Knoevenagel condensation under modified conditions. In our work, we used aluminum oxide as the base for the acceptor condensation. To drive the reaction toward completion, a range of reaction conditions were adopted depending on the strength of the acceptor. For instance, the condensations were carried out at room temperature for 6 h in chloroform for MN and 48 h at refluxing temperature of chloroform for TBA. For stubborn acceptors, the reaction was heated at $\sim 110^\circ\text{C}$ in toluene for 48 h in the case of ECA, and the porphyrin aldehyde was heated directly with DEM at $\sim 150^\circ\text{C}$ for 16 h in the absence of solvent. The ease and the yield of the acceptor condensation reaction related directly to the acceptor strength. The longer reaction time required for the stronger acceptor TBA relative to MN could be attributed to steric hindrance in the case of TBA. Isolated yields of Ni(TipPP)-1-acceptor ranged from poor

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(<30% for Ni(TipPP)-1-DEM), to moderate (<50% for Ni(TipPP)-1-ECA), to good (80–90% in the cases of Ni(TipPP)-1-MN and Ni(TipPP)-1-TBA) after purification by flash column chromatography. All new porphyrin compounds were fully characterized by elemental analysis, FAB-MS, UV–visible, FTIR, and ¹H NMR spectroscopies.

UV–visible absorption spectra of Ni(TipPP)-1-CHO (as a control), Ni(TipPP)-1-DEM, Ni(TipPP)-1-ECA, Ni(TipPP)-1-MN, and Ni(TipPP)-1-TBA are shown in Figure 1. These

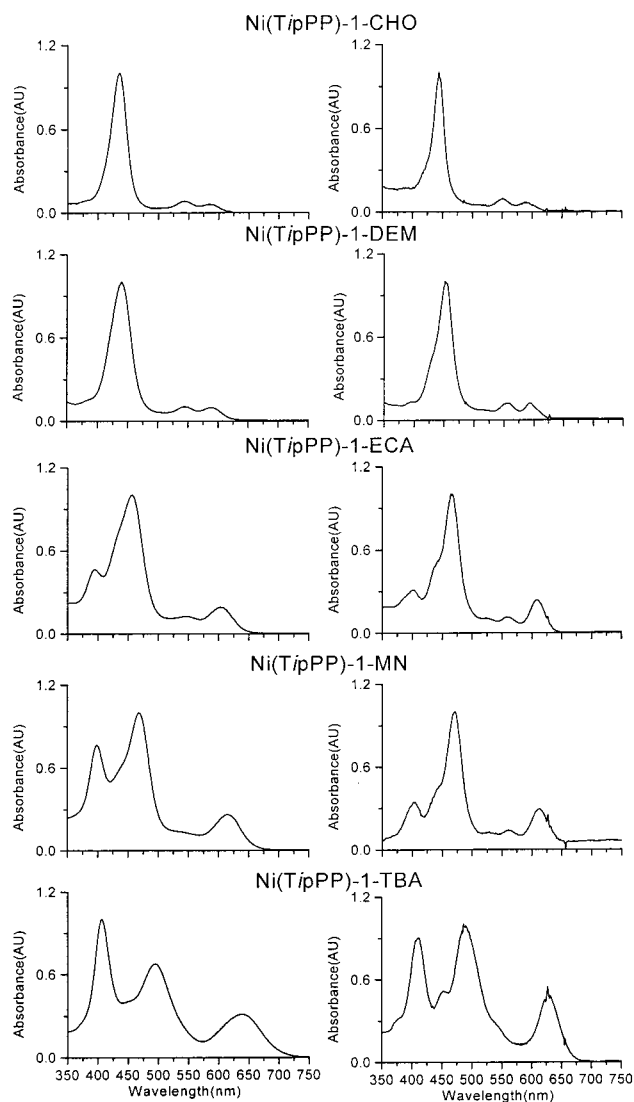


Figure 1. UV–Visible absorption spectra of Ni(TipPP)-1-CHO, Ni(TipPP)-1-DEM, Ni(TipPP)-1-ECA, Ni(TipPP)-1-MN, and Ni(TipPP)-1-TBA (from top to bottom) in dichloromethane at room temperature (left column) and in 2-methyltetrahydrofuran at $\sim 90\text{ K}$ (right column).

data reveal an increasing electronic interaction between the substituent and the porphine ring in these nickel tetraarylporphyrins. To our knowledge, the strikingly perturbed spectra, observed for Ni(TipPP)-1-ECA, Ni(TipPP)-1-MN, and Ni(TipPP)-1-TBA, have not been previously noted for other

known 2-substituted *meso*-5,10,15,20-tetraphenylporphyrin (TPP) metal complexes.⁵ Perturbed absorption spectra due to the excitonic splitting of linear-linked multiple porphyrins have been reported.⁶ A similar theory of excitonic splitting is unlikely valid for the system of single porphyrin units reported here. Therefore, an intriguing question concerning the absorption spectra is whether the reduced symmetry of the porphyrin or the intramolecular charge-transfer absorption causes the perturbed spectra?

From Gouterman's four-orbital model, one would expect that transitions of both Q and B bands of metalloporphyrins with low symmetry would be split into two components, namely, B_x , B_y , Q_x , and Q_y , respectively.⁷ Thus, including vibronic excitations, a total of up to eight transitions, i.e., $Q_x(0,0)$, $Q_x(1,0)$, $Q_y(0,0)$, $Q_y(1,0)$, $B_x(0,0)$, $B_x(1,0)$, $B_y(0,0)$, and $B_y(1,0)$, may appear in the spectra of low-symmetry metalloporphyrins, such as the nickel porphyrins under study here.⁸ As shown in Figure 1, low-temperature absorption spectra (~ 90 K in 2-methyltetrahydrofuran) of all the Ni(TipPP)-1-acceptor complexes, with the exception of Ni(TipPP)-1-TBA, exhibit multiple absorption profiles (three absorption bands) in the Q band region between 500 and 650 nm indicative of split Q bands. However, four split B bands, $B_x(0,0)$, $B_x(1,0)$, $B_y(0,0)$, and $B_y(1,0)$, are clearly discernible for Ni(TipPP)-1-TBA in the low-temperature spectrum. Both split Soret and Q bands have also been observed in the low-temperature absorption spectra of some 10,20-disubstituted push-pull 5,15-diphenylporphyrins, al-

(5) A wide range of β -substituted tetraphenylporphyrin metal complexes are known, but they all exhibit absorption spectra with common features: (1) a single intense absorption Soret (or B) band (with $\epsilon = 1-4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) in the range of 415 to 430 nm and (2) a relatively weak absorption (with $\epsilon = 5-20 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) Q-band, $Q(0,0)$, accompanied by its vibronic component $Q(1,0)$ in the range of 530 to 600 nm. The β -substituent of M(TPP) (M = Ni, Cu, Zn) ranges from nonacceptors, such as alkyl and vinyl groups, to weakly withdrawing groups, such as acetylenyl, formyl, *trans*-acrylate ester, and *trans*-acrylamide, to strong acceptors, such as cyano and nitro. (a) Callot, H. J. *Bull. Soc. Chim. Fr.* **1973**, 3413. (b) Callot, H. J. *Bull. Soc. Chim. Fr.* **1974**, 1492. (c) Momenteau, M.; Loock, B.; Bisagni, E.; Rougee, M. *Can. J. Chem.* **1979**, *57*, 1804. (d) Giraudeau, A.; Callot, H. J.; Jordan, J.; Ezhar, I.; Gross, M. *J. Am. Chem. Soc.* **1979**, *101*, 3857. (e) More, K. M.; Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1981**, *20*, 2641. (f) Baldwin, J. E.; Crossley, M. J.; DeBernardis, J. *Tetrahedron* **1982**, *38*, 685. (g) Rish, I. G.; Pshchetskii, V. S.; Askarov, K. A.; Ponomarev, G. V. *Chem. Heterocycl. Compd. Engl. Transl.* **1985**, *21*, 777. (h) Crossley, M. J.; King, L. G. *J. Org. Chem.* **1993**, *58*, 4370. (i) Crossley, M. J.; Harding, M. M.; Tansey, C. W. *J. Org. Chem.* **1994**, *59*, 4433.

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(7) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1-165. The lowest unoccupied molecular orbital (LUMO) is doubly degenerate with e_g symmetry in the case of the unsubstituted symmetrical metalloporphyrin (e.g., Ni(TPP)). The LUMO of a metalloporphyrin will not be degenerate for the low-symmetry (*Ci*) β -substituted Ni(TipPP) examined in this study. Thus, a split Soret is to be expected. Here we qualitatively take the x direction along opposite pyrrole rings with the acceptor substituent and the y axis along a perpendicular direction to the x axis.

(8) In practice, of course, not all of the split absorption bands are observable. In the Soret band region, some absorption bands are only partially resolved due to the narrow energy separation ($1100-1600 \text{ cm}^{-1}$ between vibronic and electronic transitions). In the Q band region, in addition to the small energy separation, the split Q bands might extend into the 500-550 nm region and become obscured by the much stronger Soret bands that also appear here.

though these porphyrins have effective π -conjugation ethynyl linkages on the *meso* carbon.⁹

On the other hand, it is evident that the reduced symmetry of the porphyrin π -system cannot be the only reason for split Soret and Q bands. For instance, 2-triphenylphosphonium-5,10,15,20-tetraporphyrinato zinc(II) perchlorate which contains bulky substituent at the β -carbon exhibits an absorption spectrum with only minor perturbations.^{5,10} Similarly, in this study, the aldehyde-containing Ni(TipPP)-*n*-CHO porphyrins all show common absorption spectra (Figure 2) with little

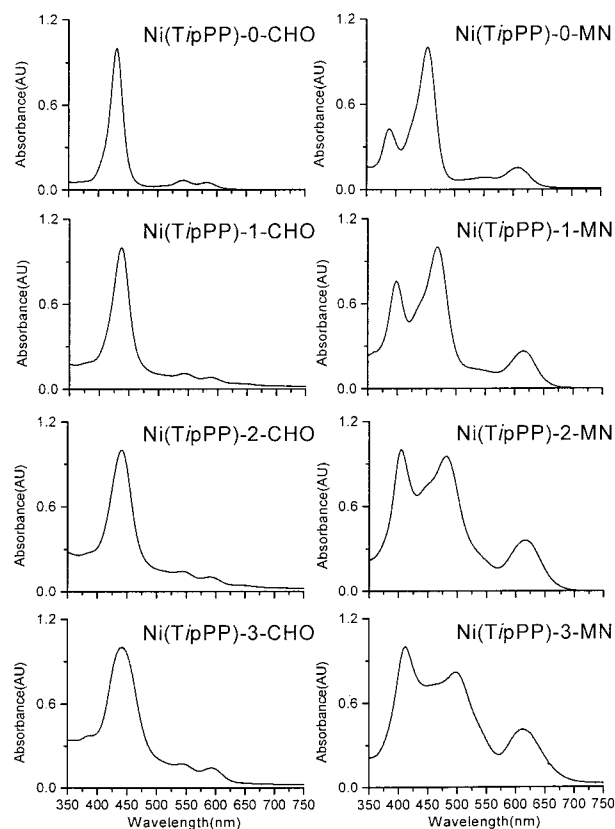


Figure 2. UV-Visible absorption spectra of Ni(TipPP)-*n*-CHO and Ni(TipPP)-*n*-MN in dichloromethane at room temperature.

perturbation, irrespective of the size of conjugation ($n = 0, 1, 2$, or 3), although with increasing conjugation length the absorption bands become progressively red-shifted and broadened, a signature of weak interaction.

We therefore conclude that the splitting of Soret and Q bands of β -substituted metalloporphyrins depends on acceptor strength in addition to a symmetry factor. A weak electron accepting power,⁵ an obstacle on the conjugation pathway (aromatic phenyl ring),³ or steric hindrance as in metallo-

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2-nitro-5,10,15,20-tetraphenylporphyrin could be the reason for the essentially unperturbed absorption spectra observed for many of the 2-substituted tetraphenylporphyrins examined to date.^{3,5,9}

Among Ni(TipPP)-1-acceptor porphyrins, Ni(TipPP)-1-TBA has the strongest acceptor and the largest solvatochromic shift, although none of the absorption bands shifts more than ~10 nm from toluene to dimethyl sulfoxide. Usually, the solvatochromism associates with intramolecular charge-transfer (ICT) absorption bands, which, in the present case, could be a manifestation of donor–acceptor interactions through π -conjugation. Such an ICT contribution to the overall electronic structure has been strongly suggested by our preliminary semiempirical CI calculations using the ZINDO/S parameter set.¹¹ The electron density of HOMO in Ni(TipPP)-2-TBA is concentrated on the porphine ring, whereas the electron density of LUMO and other energetically nearby orbitals is spread out as far as to the sulfur atom of the acceptor. A detailed account of the ICT of these acceptor-substituted porphyrins will be given in the future.

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In summary, we have demonstrated in this study evidence for the π -conjugation in β -substituted olefinic-bridged porphyrins that could lead to substantial interaction between the porphyrin π -system and an electronic acceptor, provided that acceptor strength is sufficiently strong. These findings point to an alternate approach toward rational designing and construction of π -conjugated porphyrin systems for novel optical materials.

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Supporting Information Available: Spectroscopic (UV–visible, FTIR, FAB-MS, ¹H NMR) and elemental analysis data for Ni(TipPP)-*n*-CHO (*n* = 0, 1–3), Ni(TipPP)-*n*-MN (*n* = 0, 1–3), and Ni(TipPP)-1-acceptor (acceptor = DEM, ECA, TBA). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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