

Synthesis of meta-methoxyphenyl substituted tetraazaporphyrin and corrolazine phosphorus(V) complexes

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Synthesis of *meta*-methoxyphenyl substituted tetraazaporphyrin and corrolazine phosphorus(V) complexes

Taniyuki Furuyama^{a,b}, Yusuke Sugiya^b, Takuya Yoshida^b, and Nagao Kobayashi^{*b,c}

^a*Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan*

^b*Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

^c*Faculty of Textile Science and Technology, Shinshu University, Tokida, Ueda, 386-8567, Japan*

Dedicated to Professor Tomás Torres on the occasion of his 65th birthday

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ABSTRACT: Octa-(*meta*-methoxyphenyl) substituted tetraazaporphyrin (TAP, **1**) and corrolazine (Cor, **4**) phosphorus(V) complexes have been synthesized and characterized. **1** has a blue-shifted, small charge transfer (CT) band while *para*-methoxyphenyl substituted PTAP **2** has a red-shifted, intense CT band. The difference could be interpreted as an inductive effect of the *meta*-methoxy groups. The position and intensity of the absorption bands of **1** are well matched to the trend of *para*-substituted PTAPs. The synthesis of PCor from free-base TAP was also investigated. The PCor was not generated directly but from a PTAP intermediate.

KEYWORDS: tetraazaporphyrin, phosphorus, substitution effect, electronic structure, absorption spectra.

*Correspondence to: Nagao Kobayashi, email: nagaok@shinshu-u.ac.jp tel/fax +81-268-21-5499

INTRODUCTION

Azaporphyrinoids, such as tetraazaporphyrins (TAPs), corrolazines (Cors), and phthalocyanines (Pcs) are well-established artificial organic dyes and pigments. Many easily-synthesized azaporphyrinoids have a symmetrical 18π electron aromatic macrocycle and unique optical and electrochemical properties. Since their optical properties in solution often correlate with function for practical applications, tuning the absorption properties is one of the most fascinating research topics in porphyrinoid chemistry.[1] We have recently proposed a novel and simple “ π electron-unmodified” approach by the introduction of the phosphorus(V) ion into the central core of azaporphyrinoid macrocycles.[2] Here, the choice of macrocycles is critical, since the effect of the phosphorus(V) ion depends on the type of macrocycle. In the case of TAPs, an intense charge-transfer (CT) band appeared between the Soret and Q bands in the absorption spectrum of the TAP phosphorus(V) complex (PTAP). The position and intensity of the CT bands could be tuned by peripheral aryl substitution groups,[3] axial ligands of the phosphorus atom[4] and the introduction of heteroatoms.[5] Most previous approach for modulating optical properties have focused on the “two” intense absorption bands (Q and Soret bands),[6] while for PTAPs, “the third” intense absorption band (CT band) can be utilized in the visible region (Fig. 1).

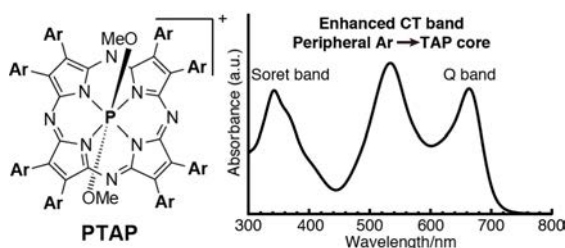


Fig. 1. Representative absorption spectrum of tetraazaporphyrin phosphorus(V) complex (PTAP).

In this article, we have synthesized and characterized octa-(*meta*-methoxyphenyl) substituted PTAPs (Fig. 2). Although the electronegativity of oxygen is larger than that of carbon, a *para*-substituted methoxy group is a well-known electron donating group (EDG). This EDG ability originates from the mesomeric effect (*M* effect) of oxygen lone pairs. However, *meta*-substituted methoxy groups cannot use the *M* effect, so that an inductive effect (*I* effect) dominates the substitution effect. The Hammett equation has been one of the most widely used means for the quantitative analysis of these electronic effects.[7] The Hammett σ values of *para*- and *meta*- substituted methoxy group are -0.27 and 0.12 , respectively, indicating that the role of the methoxy group depends on its position. The Hammett value can be useful for rationalizing the physical properties for new functional molecules.[8] In our previous research, the absorption spectra of octa-(*para*-substituted phenyl) substituted PTAP exhibit a correlation with the Hammett σ_p values value of substituents on the peripheral moieties.[3] Comparisons between *meta*- and *para*-substituted PTAPs with the same functional group can estimate the generality of this trend.

Corrolazine (triazacorrole) is an aza-analog of corrole, in which one *meso* nitrogen atom is missing. A facile synthesis of PCors and metal complexes has been reported by Goldberg *et al.*[9] and many applications of Cors proposed to date.[2d,10] A typical synthesis of PCors is the direct ring contraction of free-base TAP by phosphorus(III) reagents. However, we observed in our experiments that the PCor may be generated by a stepwise reaction via a PTAP. The reaction mechanism is also discussed in this article.

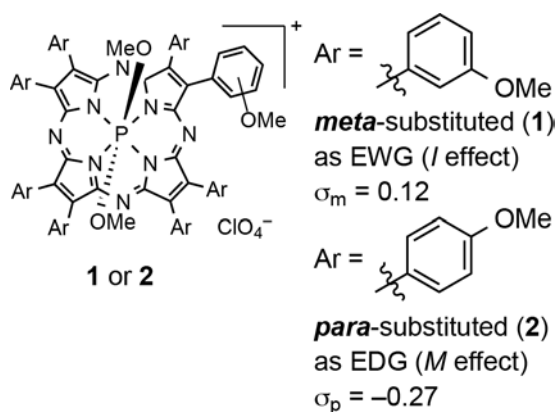


Fig. 2. Structures of PTAPs in this work.

EXPERIMENTAL

Measurements

Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. NMR spectra were obtained on a Bruker AVANCE III 500 spectrometer using CDCl_3 as solvent unless otherwise noted. Chemical shifts and coupling constants are expressed in δ (ppm) values and in hertz (Hz), respectively. ^1H -NMR spectra were referenced to the residual solvent as an internal standard. ^{31}P -NMR spectra were referenced to an external 85% H_3PO_4 solution (0.0 ppm). The following abbreviations are used: s = singlet, d = doublet, and m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics Apex-III spectrometer.

Synthesis

Free-base tetraazaporphyrin **3** and *para*-substituted PTAP **2** were prepared according to the literature.[3]

Preparation of (*m*-MeOPh) $_8$ TAP phosphorus(V) complex (1**).** POBr_3 (150 mg, 0.52 mmol) was added to a solution of **3** (15 mg, 13 μmol) in 1 mL of pyridine and stirred for 1 h at 90°C . After removing the solvent *in vacuo*, the residue was dissolved in a mixed solvent of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1/1 v/v) and stirred for 2 h at room temperature. The organic layer was collected, washed with 2N HCl aq, sat. NaHCO_3 aq and water, and the solvent removed to yield a dark green product. The resulting solid was dissolved in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1/1 v/v), then NaClO_4 added. After stirring the mixture for 3 h at room temperature, the solvent was removed, and the residue recrystallized from $\text{CH}_2\text{Cl}_2/n$ -hexane, to afford the title compound as a green-purple powder (11 mg, 68%). 500 MHz ^1H -NMR (CDCl_3) δ (ppm): 7.81 (br, 8H), 7.78 (s, 8H), 7.55 (br, 8H), 7.25-7.23 (m, 8H), 3.69 (s, 24H), -1.79 (d, 6H, $^3J_{\text{PH}} = 28.3$ Hz). 200 MHz ^{31}P -NMR (CDCl_3) δ (ppm): -179. LR-MALDI Calcd for $\text{C}_{74}\text{H}_{62}\text{N}_8\text{O}_{10}\text{P} [\text{M}-\text{ClO}_4]^+$: 1253.4. Found: 1253.4. UV-vis ($\text{CH}_2\text{Cl}_2/\text{TFA} = 99/1$) λ_{max} : 644, 533, 361 nm.

Preparation of (*m*-MeOPh) $_8$ Corrolazine phosphorus(V) complex (4**).** PBr_3 (0.20 mL, 2.2 mmol) was added to a solution of **3** (100 mg, 86 μmol) in 2 mL of pyridine and stirred for 2 h at rt. Then, 1 mL of MeOH was added, and the mixture stirred for 2 h under reflux. The organic layer was collected, washed with 2N HCl aq, sat. NaHCO_3 aq and water, and the organic layer dried over MgSO_4 , and concentrated *in vacuo*. The product was purified by silica gel column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 95/5$), to give the title compound as a green solid (70 mg, 70%). 500 MHz ^1H -NMR (CDCl_3) δ (ppm): 7.95 (br, 2H), 7.90 (br, 2H), 7.83-7.75 (m, 6H), 7.68 (br, 2H), 7.53-7.48 (m, 6H), 7.41-7.38 (m, 2H), 7.15-7.14 (m, 6H), 7.05 (br, 4H), 6.85-6.84 (m, 2H), 3.75 (br, 6H), 3.71 (br, 6H), 3.67 (br, 6H), 3.63 (br, 6H). 200 MHz

^{31}P -NMR (CDCl_3) δ (ppm): -111 . HRMS-MALDI Calcd for $\text{C}_{72}\text{H}_{56}\text{N}_7\text{O}_9\text{P}$ [M-H]: 1193.3872. Found: 1193.3871. UV-vis (CH_2Cl_2) λ_{max} ($10^{-4}\epsilon$): 631 (6.70), 585 (1.55), 440 (11.0) nm.

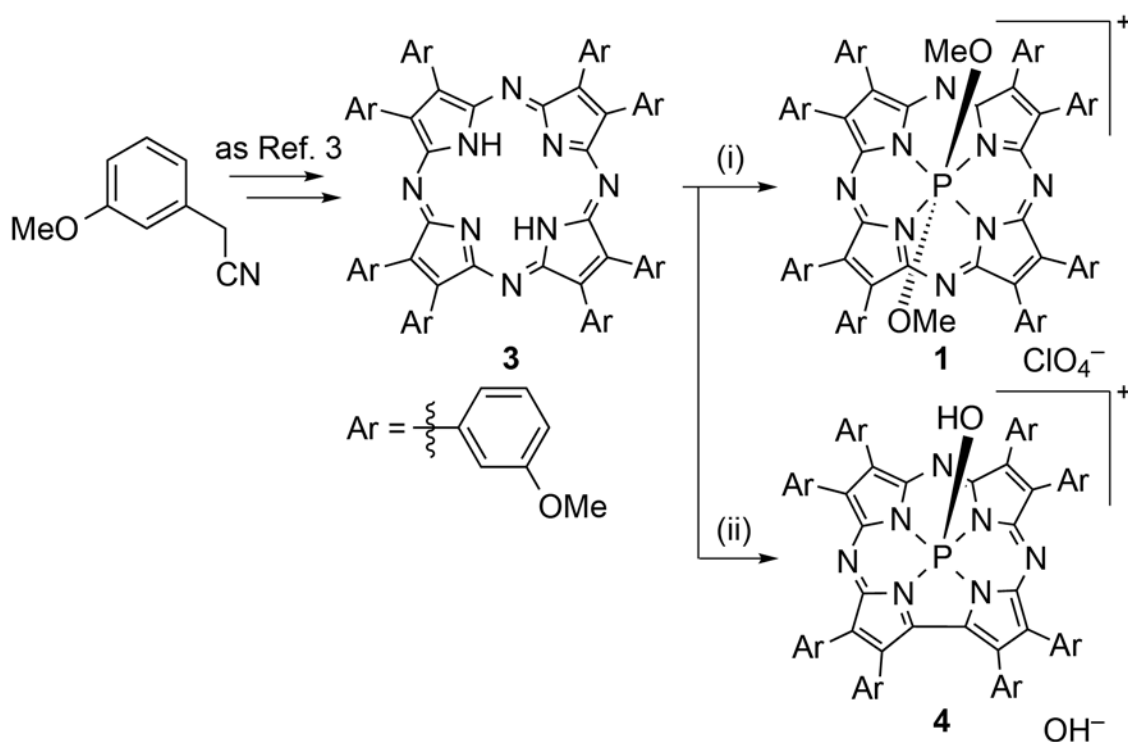
Computational details

Geometry optimization for all molecules was performed at the DFT level, by means of the hybrid Becke3LYP[11] (B3LYP) functional as implemented in Gaussian 2009.[12] The 6-31G* basis set was used for all atoms. After the geometry optimization, time-dependent (TD) DFT calculations[13] were performed to evaluate the stick absorption spectrum, employing BLYP functionals with long-range correction (LC)[14] (LC-BLYP) with the same basis set. All stationary points were optimized without any symmetry assumptions and characterized by normal coordinate analysis at the same level of theory (number of imaginary frequency, Nimag , 0).

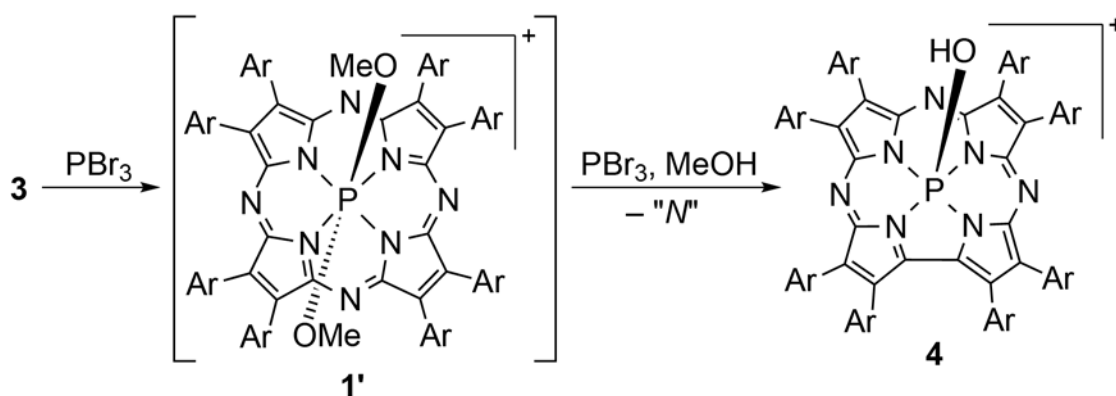
RESULTS AND DISCUSSION

Synthesis

The synthetic procedure for tetraazaporphyrin and corrolazine phosphorus(V) complexes is shown in Scheme 1. The common precursor free-base TAP **3** was first prepared according to literature procedures in moderate yields.[1] For the preparation of PTAP **1**, phosphorus oxybromide (P(V) reagent) was used as previously reported.[2–4] Finally, the desired complex was isolated as the perchlorate salt. For the preparation of PCor **4**, phosphorus tribromide (P(III) reagent) was first used as in Goldberg's procedure.[9b] However, the MS spectrum of the reaction mixture indicated that only PTAP was generated. When heteroatom-substituted PTAPs were synthesized, we also observed the similar phenomenon.[5] Surprisingly, when a mixture of the reaction mixture and methanol was heated, PTAP was converted to the desired PCor. A plausible mechanism is shown in Scheme 2. PTAP appeared to be generated at first (a portion of the phosphorus tribromide may be oxidized by air), and then the good electron acceptor PTAP[2a] was reduced by the remaining phosphorus tribromide, generating PCor. A similar reaction mechanism was reported in the synthesis of a tetrabenzotriazacorrole germanium complex via reduction of a Pc germanium complex.[15]



Scheme 1. Synthesis of tetraazaporphyrin and corrolazine phosphorus(V) complexes. *Reagents and conditions:* (i) POBr₃ (40 eq), pyridine, 90°C, 1 h, then NaClO₄, CH₂Cl₂/MeOH, rt 2 h, 68%; (ii) PBr₃ (25 eq), pyridine, rt, 2 h, then MeOH, reflux, 2 h, 70%.



Scheme 2. Plausible mechanism for the formation of **4**.

Both compounds **1** and **4** could be fully characterized by NMR and MS spectroscopy. The ¹H NMR spectrum of **1** exhibited a characteristic doublet assignable to axial methoxy groups at high field (ca. -1.8 ppm). No signal was observed at this field in the ¹H NMR of **4**, supporting the premise that the axial ligand of **4** is a hydroxyl group. The ³¹P NMR spectra of **1** and **4** exhibit signals at -179 and -111 ppm, respectively. ³¹P NMR spectroscopy is sensitive to the coordination number of the phosphorus center[10e,16] so that the number of axial ligands of **1** and **4** can be determined (2 and 1, respectively). The MS spectra also supported their coordination number. Unfortunately, suitable single crystals for X-ray diffraction analysis could not be obtained.

Electronic absorption spectra and substitution effect of PTAPs

The absorption spectra of PTAPs (**1** and **2**) and PCor **4** in CH₂Cl₂ are shown in Fig. 3. An intense absorption assignable to a CT band from peripheral aryl moieties to the central TAP core appeared in the 500-600 nm region in the absorption spectra of PTAPs.[3] Although aryl moieties are located outside the 18π-conjugation system of the TAP, the substitution groups at the aryl moieties affect the position and intensity of the CT band. In the case of *para*-substituted **2**, the CT and Q bands appear at 572 and 675 nm and the bases of the bands overlap. On the other hand, the absorption spectrum of *meta*-substituted **1** shows blue-shifted CT and Q bands at 533 and 644 nm, respectively. The weak, blue-shifted CT band resembles the absorption spectrum of electron-withdrawing group (F or CF₃) substituted PTAPs. The wavelength or energy difference between the CT bands of **1** and **2** (39 nm, 1280 cm⁻¹) was larger than that of the Q bands (31 nm, 710 cm⁻¹), supporting the premise that the blue-shifted bands of **1** originate from the substitution effect of the *meta*-OMe groups. Finally, the absorption properties of **1** could be interpreted through plots of the position and intensity of the Q and CT bands *versus* the Hammett σ_p and σ_m constant of the substituents (Fig. 4). The parameters of *meta*-substituted **1** constitute a modified straight line for a series of *para*-substituted PTAPs. Hence, the *meta*-OMe groups behave as electron-withdrawing groups.

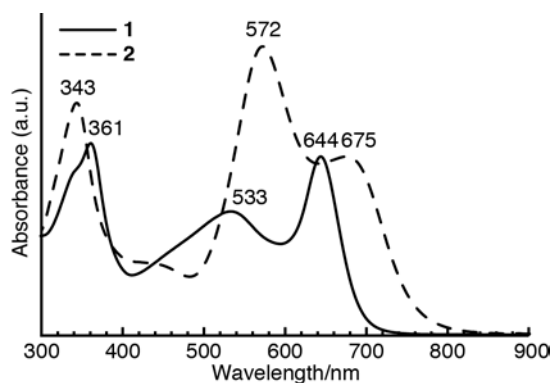


Fig. 3. UV-vis-NIR absorption spectra of **1** (solid line) and **2** (dashed line) in CH_2Cl_2 .

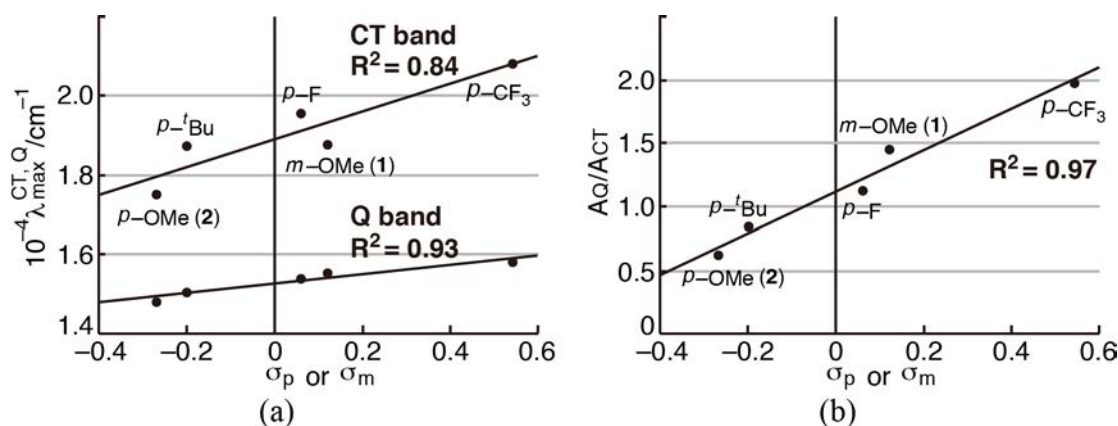


Fig. 4. Plots of (a) position of the CT and Q bands, and (b) ratio of A_Q to A_{CT} versus Hammett σ -values derived from the PTAPs. The data of p - t Bu, p -F, and p - CF_3 were taken from Ref. [3].

The absorption spectrum of **4** shows two intense absorption bands (Fig. 5). Two bands could be assigned to the Soret (440 nm) and Q (631 nm) bands, while no intense CT band was observed. Cor is a trivalent ligand, so that the MO levels of the macrocycle are different from those of TAPs. Thus, the interaction between peripheral moieties and the PCor core is less than that between peripheral moieties and the PTAP core. The intense, red-shifted Soret band is a characteristic of Cors.[1,9] The Soret band of **4** is broader than that of tetrabenzotriazacorrole phosphorus(V) complexes.[2d,17] This broad Soret band might be correlated with the peripheral groups, and further synthetic and theoretical approaches are currently underway.

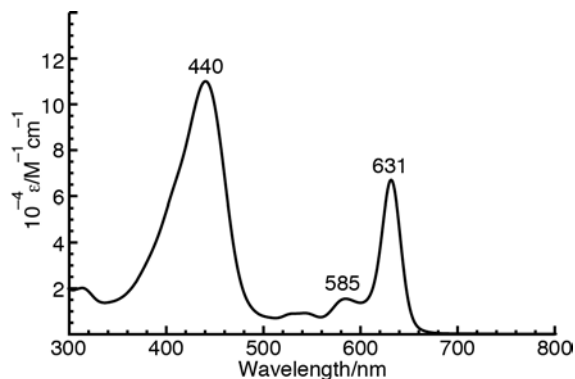


Fig. 5. UV-vis-NIR absorption spectrum of **4** in CH_2Cl_2 .

Molecular orbital calculations

In order to enhance the interpretation of the electronic structures of PTAPs, MO calculations of the cationic segments of PTAPs **1** and **2** (1^+ and 2^+) were performed. The molecular geometries were first optimized at the DFT level using B3LYP/6-31G(d). The LC-BLYP[14]/6-31G(d) level was used as in our previous paper[2a,3,4] to calculate the molecular orbitals and excited states. Partial MO energy diagrams with the calculated absorption spectra are shown in Fig. 6, with the calculated transition energies, oscillator strengths (f), and configurations summarized in Table 1. For both compounds, the HOMO, LUMO, and LUMO+1 are dominated by the TAP orbitals, which correspond to the a_{1u} -, e_{gy} - and e_{gx} -like orbitals in Gouterman's model.[18] The calculated HOMO-LUMO energy gap of 1^+ is slightly larger than that of 2^+ so that the position of the Q band of **1** shifts slightly to shorter wavelength. The bands calculated at around 400 nm (for 1^+) or 440 nm (for 2^+) are composed of transitions from orbitals under the HOMO-1 to the LUMO and LUMO+1 (almost degenerate). The occupied orbitals are delocalized over the entire complex, implying that the CT transitions from the aryl moieties to the TAP core can occur easily. The CT bands of 1^+ were estimated to be weaker than those of 2^+ in the shorter wavelength region. These results nicely reproduce the experimental absorption spectra of **1** and **2**, supporting the conclusion that the methoxy group position can affect the entire absorption spectrum of PTAPs.

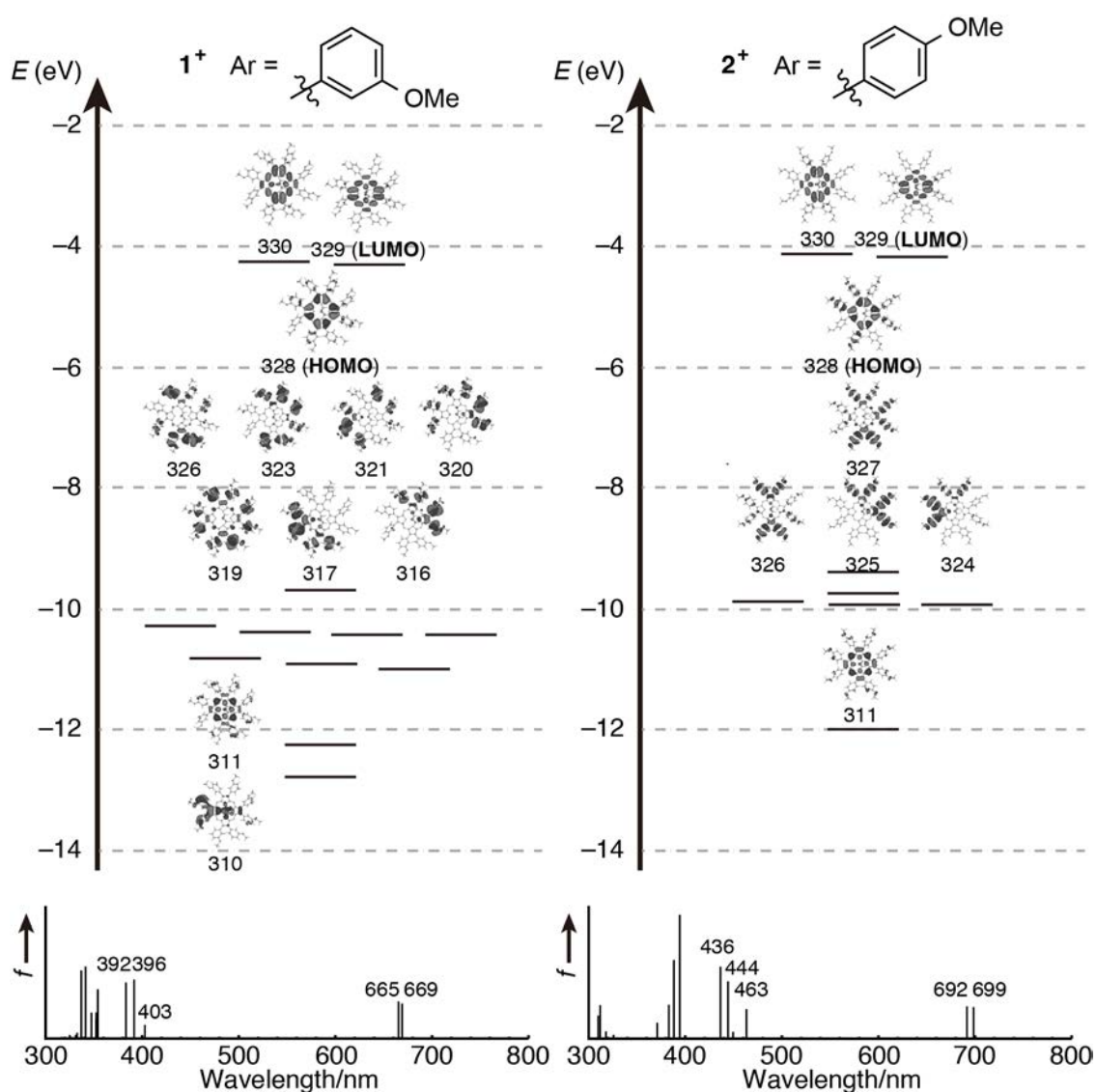


Fig. 6. Partial molecular energy diagram and orbitals of cationic part of **1** and **2** (top) and their calculation absorption spectra (bottom). Calculations were performed at the LC-BLYP/6-31G*//B3LYP/6-31G* level.

Table 1. Calculated excited wavelength (λ) and oscillator strengths (f) for components of selected transition energies.

Compound	λ (nm)	f	Composition (%)
1 ⁺	669.1	0.22	311→329 (6%), 328→329 (16%), 328→330 (68%)
	665.3	0.22	311→330 (5%), 328→329 (69%) 328→330 (15%)
	402.8	0.08	310→329 (8%), 317→329 (18%), 320→329 (13%), 321→329 (15%)
	391.6	0.36	316→330 (5%), 317→330 (6%), 319→330 (11%), 321→330 (9%), 326→330 (39%)
	383.2	0.34	316→329 (16%), 320→329 (24%), 321→329 (6%), 323→329 (14%), 326→329 (6%)
2 ⁺	698.5	0.19	311→330 (6%), 327→330 (5%), 328→329 (59%) 328→330 (20%)
	691.6	0.19	311→329 (6%), 328→329 (20%), 328→330 (59%)
	463.2	0.19	324→329 (7%), 326→330 (38%), 327→330 (29%)
	444.2	0.34	324→330 (7%), 325→329 (23%), 325→330 (15%) 326→330 (8%), 327→329 (5%), 327→330 (19%)
	436.4	0.43	324→330 (7%), 325→329 (19%), 326→329 (11%) 326→330 (9%), 327→329 (21%)

CONCLUSIONS

Octa-(*meta*-methoxyphenyl) substituted tetraazaporphyrin and corrolazine phosphorus(V) complexes have been synthesized and characterized. The PTAP and PCor could be synthesized from the common free-base TAP with different phosphorus reagents. PTAP appears to be an intermediate in generating PCor, so that a stepwise synthesis improves the yield of PCor. The absorption spectrum of PTAP **1** was rationalized by the Hammett equations and theoretical calculations. The absorption envelope of **1** was quite different from its *para*-substituted regioisomer **2**. The trends of absorption parameters correlate well with the Hammett σ_m or σ_p constants corresponding to the substituents. The results of theoretical calculations support the premise that the electronic structure of **1** is similar to that of **2**. Hence, the *meta*-substituted methoxy groups of **1** behaved as electron-withdrawing groups. No clear, intense CT band was observed in the absorption spectrum of PCor **4**, although the broad Soret band suggested some interaction with the peripheral aryl groups. The optical properties of **1**, thus, expanded the generality of the trends of the absorption spectra of PTAPs. Moreover, the spectral changes between **1** and **2** demonstrated that the absorption spectrum can be manipulated without changing the molecular formula, by just altering the substituent position on the peripheral aryl groups. This methodology provides another tool for manipulating the optical properties of PTAPs.

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REFERENCES

1. *Handbook of Porphyrin Science*; Kadish KM, Smith KM and Guillard R. (Eds.) World Scientific: 2010.
2. a) Yoshida T, Zhou W, Furuyama T, Leznoff DB and Kobayashi N. *J. Am. Chem. Soc.* 2015; **137**: 9258-9261. b) Furuyama T, Harako R and Kobayashi N. *J. Porphyrins Phthalocyanines* 2015; **19**: 500-509. c) Furuyama T, Satoh K, Kushiya T and Kobayashi N. *J. Am. Chem. Soc.* 2014; **136**: 765-776. d) Furuyama T, Sugiya Y and Kobayashi N. *Chem. Commun.* 2014; **50**: 4312-4314.
3. Furuyama T, Yoshida T, Hashizume D and Kobayashi N. *Chem. Sci.* 2014; **5**: 2466-2474.
4. Furuyama T, Asai M and Kobayashi N. *Chem. Commun.* 2014; **50**: 15101-15104.
5. Yoshida T, Furuyama T and Kobayashi N. *Tetrahedron Lett.* 2015; **56**: 1671-1674.
6. Rio Y, Rodríguez-Morgade MS and Torres T. *Org. Biomol. Chem.* 2008; **6**: 1877-1894.
7. Hansch C, Leo O and Taft RW. *Chem. Rev.* 1991; **91**: 165-195.
8. a) Higashino T, Rodríguez-Morgade MS, Osuka A and Torres T. *Chem. Eur. J.* 2013; **19**: 10353-10359. b) Berg S, Thomas KE, Beavers CM and Ghosh A. *Inorg. Chem.* 2012; **51**: 9911-9916. c) Namba K, Osawa A, Ishizaka S, Kitamura N and Tanino K. *J. Am. Chem. Soc.* 2011; **133**: 11466-11469.
9. a) Goldberg DP. *Acc. Chem. Res.* 2007; **40**: 626-634. b) Ramdhanie B, Stern CL and Goldberg DP. *J. Am. Chem. Soc.* 2001; **123**: 9447-9448.
10. a) Zhang X-F. *Coord. Chem. Rev.* 2015; **285**: 52-64. b) Zaragoza JPT, Siegler MA, Goldberg DP. *Chem. Commun.* 2016; **52**: 167-170. c) Neu HM, Jung J, Baglia RA, Siegler MA, Ohkubo K, Fukuzumi S, Goldberg DP. *J. Am. Chem. Soc.* 2015; **137**: 4614-4617. d) Cho K, Leeladee P, McGown AJ, DeBeer S, Goldberg DP. *J. Am. Chem. Soc.* 2012; **134**: 7392-7399. e) Fox DP, Goldberg DP. *Inorg. Chem.* 2003; **42**: 8181-8191.
11. a) Becke AD. *Phys. Rev.* 1988; **A38**: 3098-3100. b) Becke AD. *J. Chem. Phys.* 1993; **98**: 1372-1377. c) Becke AD. *J. Chem. Phys.* 1993; **98**: 5648-5652. d) Lee C, Yang W and Parr RG. *Phys. Rev.* 1988; **B37**: 785-788.
12. Gaussian 09, Revision D.01, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery, Jr. JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J and Fox DJ. Gaussian, Inc., Wallingford CT, 2013.
13. a) Bauernschmitt Rd and Ahlrichs R. *Chem. Phys. Lett.* 1996; **256**: 454-464. b) Dreuw A and Head-Gordon M. *Chem. Rev.* 2005; **105**: 4009-4037.
14. Iikura H, Tsuneda T, Yanai T and Hirao K. *J. Chem. Phys.* 2001; **115**: 3540-3544.
15. Fujiki M, Tabei H and Isa K. *J. Am. Chem. Soc.* 1986; **108**: 1532-1536.

16. Akiba K-y, Nadano R, Satoh W, Yamamoto Y, Nagase S, Ou Z, Tan X, Kadish KM. *Inorg. Chem.* 2001; **40**: 5553-5567.
17. a) Mkhize C, Britton J, Mack J and Nyokong T. *J. Porphyrins Phthalocyanines* 2015; **19**: 192-204. b) Shi M, Tian J, Mkhize C, Kubheka G, Zhou J, Mack J, Nyokong T and Shen Z. *J. Porphyrins Phthalocyanines* 2014; **18**: 698-707.
18. Gouterman M. in *The Porphyrins* Dolphin D. (Ed) Academic Press, New york: 1978, vol. 3, Part A, p. 1.