

Structural changes in non-planar octaaryl substituted phthalocyanine phosphorus complexes

Taniyuki Furuyama⁰, Ryosuke Harako and Nagao Kobayashi*⁰

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

Dedicated to Professor Shunichi Fukuzumi on the occasion of his retirement

Received 28 October 2014 Accepted 7 January 2015

ABSTRACT: Phosphorus complexes of non-planar α -octaaryl phthalocyanine derivatives ((α -Ar)₈Pc), **3a** and **3b** have been synthesized by introduction of phosphorus(V) ions into free-base Pcs **2a** and **2b**. **3a** and **3b** were characterized by MS, ¹H and ³¹P NMR spectra. The solid state structure of **3a** indicated a ruffled Pc structure due to the small atomic radius of phosphorus, although the corresponding free-base Pc **2a** has a saddled Pc structure. The phosphorus complexes showed intense absorption bands (Q-bands) in the near-IR region, while the introduction of electron-donating groups at the peripheral phenyl groups was efficient for additional red-shifting of the Q-band. Electrochemical data revealed that the red-shift of the Q-band is attributable to a decrease in the HOMO–LUMO gap due to significant and moderate stabilization of the LUMO and HOMO, respectively. MO calculations suggested that the phosphorus(V) ion intensified the electronic interaction between the peripheral aryl moieties and the Pc macrocyclic core.

KEYWORDS: phosphorus phthalocyanine, ruffled structure, electronic structure, near-infrared absorption.

INTRODUCTION

Phthalocyanines (Pcs) are some of the most wellknown and successful artificial dyes and pigments in modern materials chemistry. Pcs have a symmetrical 18π electron aromatic macrocycle, and an intense absorption band (the so-called Q-band) appears in the visible (650–700 nm) region. The optical properties of Pcs often correlate with their function in practical applications, so that changing the absorption properties of Pcs is one of the most attractive research topics in their chemistry [1]. Recently, we reported that the introduction of phosphorus(V) ions into appropriate Pcs can shift their Q-band beyond 1000 nm [2]. Interestingly, the effect of the phosphorus atom is completely different between Pcs and tetraazaporphyrins (TAPs) [3], the congeners of Pc. Hence, the combination of a central phosphorus ion, peripheral substituents, and the macrocyclic core appears critical, in order to obtain novel absorption properties.

A rigid planar structure for the macrocycle is also a feature of Pcs. However, we [4], Cook [5], and McKeown [6] reported "non-planar Pcs" with bulky peripheral substituents at the so-called α positions of Pcs. X-ray crystallography revealed that this type of derivative has a highly-saddled conformation due to the steric hindrance of the peripheral substituents. These Pcs also retain 18π aromaticity, namely curved π -conjugation [7], and an intense Q absorption band still appears. In the case of octraaryl-substituted non-planar Pcs, these show a significantly red-shifted Q-band (at around 800 nm) [4a], while the Q-bands of octaalkyl-substituted non-planar Pcs appear at a similar wavelength to typical Pcs (at around 700 nm) [5]. On the other hand, Kojima and Fukuzumi demonstrated that the saddled structure of Pcs could assemble with protonated porphyrins, and that the resulting complex undergoes photoinduced intrasupramolecular electron transfer [8]. Moreover, unique effects dependent on phenyl substitution [9] and the central element [10]

[◊]SPP full member in good standing

^{*}Correspondence to: Nagao Kobayashi, email: nagaok@m. tohoku.ac.jp, tel/fax +81 22-795-7719

of octaphenyl-substituted non-planar Pcs have also been reported by our group. Although the effect of aryl groups is still not completely clear, the modified octaarylsubstituted non-planar Pcs may be attractive targets in materials chemistry. In this paper, we report the synthesis and properties of phosphorus(V) complexes of nonplanar α -octaaryl phthalocyanine derivatives (α -Ar)_sPc). The crystallographic structures of Pc [2] and TAP [3a] phosphorus complexes show ruffled configurations due to the small atomic radius of the phosphorus. Peripheral substitution effects in the phosphorus complexes are also significant, where the absorption envelope of phosphorus TAP was proven to be changed markedly by changing the peripheral moieties, since the aryl substituents are directly linked to the TAP core. Hence, phosphorus(V) complexes of any arylated non-planer Pc ($(\alpha$ -Ar)₈PcP(V)) appear to be attractive subjects for examining their structural and spectroscopic properties.

EXPERIMENTAL

Measurements

Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic circular dichroism (MCD) spectra were obtained on a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet capable of producing magnetic fields of up to 1.03 T (1 T = 1 tesla) with both parallel and antiparallel fields. The magnitudes were expressed in terms of molar ellipticity per tesla ($[\theta]_{M}$, deg.M⁻¹.cm⁻¹.T¹). NMR spectra were obtained on a Bruker AVANCE III 500 spectrometer using CDCl₃ as solvent unless otherwise noted. Chemical shifts and coupling constants are expressed in $\delta(ppm)$ values and in hertz (Hz), respectively. ¹H NMR spectra were referenced to the residual solvent as an internal standard. ³¹P NMR spectra were referenced to external 85% H₃PO₄ solution (0.0 ppm). The following abbreviations are used: s = singlet, d = doublet, and m = multiplet. High-resolutionmass spectra (HRMS) were recorded on a Bruker Daltonics Apex-III spectrometer. CV measurements were recorded with a Hokuto Denko HZ5000 potentiostat under a nitrogen atmosphere in o-dichlorobenzene (o-DCB) with 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Measurements were made with a glassy carbon electrode (area = 0.07 cm^2), an Ag/ AgCl reference electrode, and a Pt wire counter electrode. The concentration of the solution was fixed at 1.0 mM and the sweep rates were set to 100 mV/s. The ferrocenium/ ferrocene (Fc⁺/Fc) couple was used as an internal standard

Crystallographic data collection

A red, plate shaped single crystal of $3a 0.20 \times 0.10 \times 0.05$ mm, was selected for measurement. The diffraction data were collected using a Bruker APEXII CCD

diffractometer with Bruker Helios multilayered confocal mirror monochromatized MoK α radiation (λ =0.71073 Å) at -173 °C. The structures were solved by a direct method (SIR2004) [11] and refined using a full-matrix least squares technique (SHELXL-97) [12]. Yadokari-XG 2009 software was used as a GUI for SHELXL-97 [13]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated geometrically, and refined by applying riding models. Some large electron peaks due to solvent molecule(s) were found in the unit cell. As we failed to model these properly, the rest of the molecules were refined without the effect of the solvent molecules by the Platon squeeze technique [14].

Synthesis

Free-base phthalocyanines **2a** [4] and **2b** [9] were prepared according to the literature.

Preparation of $(\alpha$ -Ph)₈Pc phosphorus(V) complex (3a). POBr₃ (150 mg, excess) was added to a solution of 2a (30 mg, 26.7 µmol) in 2 mL of pyridine and stirred for 1 h at room temperature. After removing the solvent in vacuo, the residue was dissolved in a solution of CH₂Cl₂/ MeOH (2/1 v/v) and stirred for 1 h at room temperature. The organic layer was collected, washed with water, and the solvent removed, to yield a dark red product (phosphorus(V) Pc). The resulting solid was dissolved in CH_3CN/CH_2Cl_2 (1/1 v/v), then KPF₆ (25 mg, 140 μ mol) added. After stirring the mixture for 3 h at room temperature, the solvent was removed, and the residue recrystallized from CH₂Cl₂/n-hexane. The title compound was obtained (20 mg, 55%) as a red powder. ¹H NMR (500 MHz, CDCl₃): δ, ppm 7.89 (s, 8H), 7.37–7.33 (m, 24H), 7.28–7.26 (m, 16H), 0.01 (d, 6H, ${}^{3}J_{PH} = 28.5$ Hz). ³¹P NMR (200 MHz, CDCl₃): δ , ppm -144 (septet, PF₆, J = 700 Hz), -173 (s, P(OMe)₂). HRMS-MALDI: m/zcalcd. for $C_{82}H_{54}N_8O_2P$ [M - PF₆]⁺ 1213.4102. Found 1213.4101. Anal. calcd. for C₈₂H₅₄F₆N₈O₂P₂: C, 72.46; H, 4.00; N, 8.24. Found C, 72.40; H, 4.37; N, 7.98. UV-vis $(CH_2Cl_2): \lambda_{max}, nm (10^{-5} \varepsilon) 852 (1.10).$

Preparation of (α-4-OMe-Ph)₈Pc phosphorus(V) complex (3b). The procedure described for 3a was used with 2b, to give the title compound as a gray powder (72%). ¹H NMR (500 MHz, CDCl₃): δ, ppm 7.87 (s, 8H), 7.41 (d, 16H, J = 8.5 Hz), 6.79 (d, 16H, J = 8.5 Hz), 3.97 (s, 24H), 0.16 (d, 6H, ${}^{3}J_{PH} = 28.5$ Hz). ³¹P NMR (200 MHz, CDCl₃): δ, ppm -144 (septet, PF₆, J = 700 Hz), -172 (s, P(OMe)₂). HRMS-MALDI: m/z calcd. for C₉₀H₇₀N₈O₁₀P [M – PF₆]⁺ 1453.4947. Found 1453.4948. UV-vis (CH₂Cl₂): λ_{max} , nm (10⁻⁵ ε) 916 (1.01).

Computational details

Geometry optimization for all molecules was performed at the DFT level, by means of the hybrid Becke3LYP[15] (B3LYP) functional, as implemented in Gaussian 2009 [16]. The 6-31G* basis set was used for all atoms. After the geometry optimization, timedependent (TD) DFT calculations [17] were performed to evaluate the stick absorption spectrum employing BLYP functionals with long-range correction (LC) [18] (LC-BLYP) using the same basis set. All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the same level of the theory (number of imaginary frequency, Nimag, 0).

RESULTS AND DISCUSSION

Synthesis

The synthetic procedures for the phosphorus(V) complexes are shown in Scheme 1. Free-base Pcs 2a and 2b were first prepared according to the literature procedures in moderate yields. For the introduction of a phosphorus ion into the macrocyclic core, phosphorus oxybromide was used, as previously reported. Finally, the desired complexes **3a** (α -octa(phenyl)) and **3b** $(\alpha - octa(p - methoxyphenyl))$ were isolated as the hexafluorophosphate salts. The color of **3a** and **3b** is red and gray, respectively, rather than the typical blue-green color of Pc. 3a and 3b showed excellent solubility in general organic solvents, and could be fully characterized by NMR and HR-MALDI-FT-ICR mass spectroscopy. The observed MS spectrum of 3a and calculated isotropic distributions are shown in Fig. 1. The strongest peak was found at m/z = 1213.4101, and the isotropic distribution patterns provided a reasonable match with experiment for the compound whose molecular formula is C₈₂H₅₄N₈O₂P as a cationic part of **3a** ($[M - PF_6]^+$). The ¹H NMR spectra show only one kind of peripheral aryl group, at the β -position of the Pc macrocycle, and a doublet assignable to axial methoxy groups at high field (ca. 0 ppm); hence the conformation of the phosphorus(V) complexes appears to retain a highly symmetrical, unaggregated

structure in solution. The ³¹P NMR spectra exhibit only one peak at -173 ppm for **3a** and -172 ppm for **3b**, supporting hexa-coordinated phosphorus representations [19] lying within the central cavity of the Pc macrocycle.

Solid-state structure

The structure of 3a was unambiguously elucidated by X-ray diffraction analysis of crystals obtained from the diffusion of *n*-pentane into a CH_2Cl_2 solution of **3a**. The X-ray crystallographic structure of **3a** is shown in Fig. 2. Figure 3 shows the displacement of the 24 core atoms from the 4N mean plane of 2a (crystallographic data was taken from Ref. 4b) and 3b. The degree of distortion of the core (Δr) , which was calculated as the square root of the sum of square of the deviation of each atom from the mean plane, rationalizes the nonplanarity of the Pcs. Although the Δr value of **3a** (0.57) is close to that of **2a** (0.58), the type of distortion is different. **3a** has a ruffled structure rather than the typical saddled structure reported for non-planar Pcs. The distances between the two pyrrolenitrogen atoms at opposite sides in the core (3.675(4) and 3.685(4) Å) for **3a** are shorter than those of **2a** (3.804(5)) and 3.983(4) Å) and reported metallo and free-base Pcs (3.8–4.0 Å) [2a]. The small macrocyclic Pc core of **3a** originates from the small atomic radius (106 pm) of the phosphorus(V) atom, resulting in a bond length of 1.84 Å between phosphorus and nitrogen in the core of 3a, which is reasonable for a single bond of hexacoordinated phosphorus(V)-nitrogen [20]. Therefore, the structural influence of only one phosphorus(V) atom is stronger than the bulky phenyl substituents at the peripheral position.

Electronic absorption and MCD spectroscopy

The absorption and MCD spectra of the Pcs in CH_2Cl_2 are shown in Fig. 4. The absorption spectra of all compounds show intense Q-bands in the near-IR



Scheme 1. Synthesis of octaaryl substituted phthalocyanine phosphorus(V) complexes. *Reagents and conditions*: (i) "BuOLi (4 eq), "BuOH, reflux, 1 h; (ii) POBr₃ (20 eq), pyridine, rt, 1 h, then MeOH, rt, 1 h; (iii) KPF₆, CH₃CN/CH₂Cl₂, rt, 3 h



Fig. 1. Observed high-resolution mass spectrum (a) of 3a and the theoretical distribution pattern for $C_{82}H_{54}N_8O_2P$ ([M – PF₆]⁺) (b)



Fig. 2. X-ray crystal structure of **3a**. The thermal ellipsoids were scaled to the 50% probability level. (a) top view; (b) side view. H atoms, and solvent molecules have been omitted for clarity

region. The Q-bands of free-base Pc **2a** and **2b** might be split theoretically into four peaks, but they show only two peaks or shoulders (Q_{00} and Q_{01} bands). In the MCD spectra of **2a** and **2b**, dispersion-type signals were observed corresponding to their Q_{00} bands. It is considered that the splitting of the Q-band is so small that the superimposition of two oppositely signed Faraday *B* terms give seemingly *A* term-like MCD signals, the



Fig. 3. Views of the skeletal deviation of the atoms from the 4N mean plane for (a) 2a (crystallographic data was taken from Ref. 4b) and (b) 3a. The black circles indicate carbon atoms. The black squares and gray triangles indicate nitrogen atoms at the *meso*-position and coordinating nitrogen atoms, respectively

so-called pseudo Faraday A term. As we previously reported [4, 9], the introduction of eight aryl groups at the α positions can shift the Q-band to the near-IR region; in particular, 2b has a sharp Q-band in the region beyond 800 nm. The insertion of a phosphorus(V) ion into 2a produces a red-shift of ca. 70 nm (ca. 990 cm⁻¹), while the difference between the free-base α -(ArS)₈Pc and its phosphorus(V) complex is *ca*. 210 nm (*ca*. 2500 cm⁻¹) [2]. The extent of the red-shift upon phosphorus insertion into the core of the Pc was different from substituent to substituent, so that octaaryl substitution at the α position is not efficient for further red-shifting beyond 1000 nm by the phosphorus(V) ion, which is different from the case of α -octathioaryl group substituted Pc [2]. In contrast, the substitution effect at the aryl group is enhanced by phosphorus insertion. The difference in Q-band position between methoxy substituted 3a and **3b** (64 nm, *ca.* 820 cm⁻¹) is significantly larger than that between unsubstituted **2a** and **2b** (25 nm, *ca*. 390 cm⁻¹). The Q-band of **3b** appears at 916 nm, which is sufficiently long enough for application in the near-IR photodynamic therapy of cancer [21]. Since Pcs having a O-band at around 900 nm are still rare, the combination of a central phosphorus atom and appropriate aryl groups at the α position appears to be an efficient method for accessing near-IR light at around 900 nm. The Faraday A MCD term

of **3a** and **3b** in the Q-band region further indicates that the practical chromophore symmetry of these complexes is close to D_{4h} , similarly to typical metallo Pcs. A broad, weak absorption band appeared between the Soret and Q-bands (at around 500 nm) for the phosphorus complexes. The MCD spectra corresponding to these absorptions cannot be interpreted simply, since their complex character suggests an overlap of several transitions. Although the detailed assignment will be discussed later, these bands could be assigned to a charge-transfer (CT) band from peripheral aryl groups to the macrocyclic Pc core. Emission of phosphorus(V) complexes are very weak ($\Phi_{\rm F} < 0.01$), so that the fluorescence spectra of both **3a** and **3b** could not be obtained.

Electrochemistry

It is well-established that the HOMO and LUMO energies of Pc derivatives correlate well with their first oxidation and reduction potentials [22]. Estimating the values of the redox potentials is also important in order to determine the origins of the effect of phosphorus insertion. Fig 5 displays cyclic voltammograms of the Pcs in *o*-dichlorobenzene (DCB) with 0.1 M $^{n}Bu_{4}NCIO_{4}$ as the supporting electrolyte. The gap between the first redox potentials ($E_{1ox} - E_{1red}$) correlate well with the



Fig. 4. UV-vis-NIR absorption (bottom) and MCD (top) spectra of Pcs in CH₂Cl₂. (a): **2a** (gray dashed line) and **3a** (black solid line). (b): **2b** (gray dashed line) and **3b** (black solid line)



Fig. 5. Cyclic voltammetry data for (a) **2a** and **3a**, and (b) **2b** and **3b**. Cyclic voltammograms were acquired from 1.0 mM solutions of analyte in 0.1 M ⁿBu₄NClO₄/*o*-DCB. Ferrocene was used as an internal standard and set to 0 V



Fig. 6. Partial molecular energy diagram and orbitals of 2a and cationic part of 3a (top) and their calculated absorption spectra (bottom). Calculations were performed at the LC-BLYP/6-31G*//B3LYP/6-31G* level

positions of the Q-bands. Both of the redox potentials of **2b** are shifted cathodically from those of **2a**, so that it is concluded that the electron donating group (OMe) on the exterior of the π -conjugated system of the Pc ligand can affect the electronic structure of α -octaarylated Pc. After the introduction of a phosphorus(V) ion into the Pc, both the redox potentials are shifted anodically. For

2a and **3a**, the first reduction potential, which is related to the LUMO level, shifted from -1.35 V to -0.59 V, while the first oxidation potential, which is related to the HOMO level, shifted from -0.02 to 0.66 V. These potentials indicate that the stabilization of the LUMO is larger than that of the HOMO after the phosphorus introduction. Similar changes in redox potentials were

7

Compound	λ, nm	f	Composition, % ^a
2a	838.0	0.43	288->294 (7%), 293->295 (92%)
	798.4	0.49	288→295 (4%), 293→294 (94%)
	343.8	0.20	290→295 (11%), 292→294 (11%), 293→297 (66%)
	332.3	0.46	284→294 (12%), 288→294 (58%), 293→295 (6%)
	312.4	0.18	284→295 (3%), 288→295 (31%), 291→294 (31%)
			292→297 (3%), 293→298 (10%)
3a+	917.8	0.42	299–318 (3%), 316–317 (91%), 316–318 (4%)
	904.0	0.41	299→317 (3%), 316→317 (4%), 316→318 (91%)
	370.0	0.19	313→318 (29%), 314→317 (33%), 316→320 (21%)
	349.2	0.07	313→317 (10%), 313→318 (22%), 313→320 (2%)
			314-317 (13%), 314-318 (4%), 315-317 (26%)
	346.8	0.07	313→317 (6%), 313→318 (18%), 314→317 (17%)
			314→320 (2%), 315→317 (26%), 315→318 (6%)
	345.8	0.06	313-317 (4%), 314-317 (8%), 315-317 (9%)
			315→318 (51%), 315→320 (3%), 316→319 (4%)

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

observed on going from **2b** to **3b**. In particular, the cathodic shift (0.22 V) of the first oxidation potential on going from phosphorus-containing **3a** (0.66 V) to **3b** (0.44 V) is larger than that observed (0.08 V) on going from free-base **2a** (-0.02 V) to **2b** (-0.10 V), supporting the conclusion that the substitution effect is enhanced by the phosphorus introduction.

Molecular orbital calculations

In order to enhance the interpretation of the electronic structures of $(\alpha$ -Ar)₈PcP(V), MO calculations of freebase Pc 2a and the cationic part of the phosphorus complex 3a ($3a^+$) have been performed. The molecular geometries were first optimized at the DFT level using B3LYP/6-31G(d). Since a CT interaction between peripheral aryl groups and the Pc macrocyclic core can be expected from the observed absorption spectrum of 3a, we applied the LC-BLYP [3, 18]/6-31G(d) level to the calculations for the molecular orbitals and excited states of 2a and $3a^+$. Partial MO energy diagrams showing the calculated absorption spectra are shown in Fig. 6, with the calculated transition energies, oscillator strengths (f), and configurations summarized in Table 1. The lowestenergy bands (the Q-bands) of 2a are calculated to lie at 838 and 798 nm, while those of $3a^+$ are calculated to lie at 918 and 904 nm, supporting the experimental absorption spectra. These bands are composed mainly of HOMO \rightarrow LUMO or HOMO \rightarrow LUMO+1 transitions (ca. 90%), and the HOMO, LUMO, and LUMO+1 orbitals included in the transitions correspond to the a_{1u} -, e_{gy} -, and e_{gx} -like

orbitals in Gouterman's model [23], respectively. The central phosphorus(V) ion significantly stabilizes both the HOMO and LUMO, with a higher extent for the LUMO, as expected from the CVs of 2a and 3a (Fig. 5). The calculated bands (370, 349, 347 and 346 nm) of 3a⁺ are composed of transitions from the HOMO-1, HOMO-2 and HOMO-3 to the nearly-degenerate LUMOs. The HOMO-1 to HOMO-3 transitions are localized on the peripheral phenyl rings, so that these bands can be assigned to CT transitions. The complicated transitions in the calculated spectrum indicate quite complicated MCD signals of 3a at around 500 nm. We also calculated the absorption spectrum and molecular orbitals of $[\beta-Ph_8PcP(OMe)_2]^+$ [3a], which is a positional isomer of $[\alpha-Ph_8PcP(OMe)_2]^+$ having phenyl groups at eight β -positions, however, the positions of these transitions were estimated to lie in a shorter wavelength region (356–336 nm) than those of $3a^+$, supporting the conclusion that the substitution effect of α -arylated Pc (3a vs. 3b) is larger than β -arylated Pc.

CONCLUSION

Non-planar α -octaaryl phthalocyanine phosphorus(V) complexes have been prepared in order to estimate the effect of peripheral substituents and a central phosphorus(V) ion. The non-planar structure of α -octaaryl free-base Pcs does not prevent the introduction of the phosphorus ion into the core of the Pc. The synthesized phosphorus(V) Pcs can be fully characterized by MS and NMR spectra; moreover, the X-ray crystallographic

structure of 3a could be obtained. The crystal of 3a has a distorted, ruffled structure, while that of non-metalated 2a adopts a saddled structure, supporting the premise that the small atomic radius of the phosphorus ion can switch the structure of the macrocyclic core, even in Pcs with bulky substituents. The Q-bands of the phosphorus(V) complexes show a significant red shift from those of free-base Pcs. The introduction of an electron-donating methoxy group into the peripheral aryl groups at eight α -positions is quite efficient for shifting the Q-band, so that the O-band of **3b** appeared beyond 900 nm. Cyclic voltammograms of the Pcs also support the red-shifted Q-bands and the substitution effect of phosphorus(V) Pcs, while MO calculations can explain the experimental results. Thus, the combination of α -octaaryl Pcs and a central phosphorus ion can manipulate both the near-IR absorption properties and the solid-state structures, indicating that this strategy can be applied for developing novel near-IR absorbing functional dyes and pigments.

Acknowledgements

This work was partly supported by Grant-in-Aids for Scientific Research on Innovative Areas (25109502, "Stimuli-responsive Chemical Species"), Scientific Research (B) (No. 23350095), Challenging Exploratory Research (No. 25620019) and Young Scientist (B) (No. 24750031) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT). The authors thank Prof. Takeaki Iwamoto and Dr. Shintaro Ishida (Tohoku University) for X-ray measurements. Some of the calculations were performed using supercomputing resources at the Cyberscience Center of Tohoku University.

Supporting information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-1030507. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: data_request@ccdc.cam. ac.uk).

REFERENCES

- 1. *Handbook of Porphyrin Science*, Kadish KM, Smith KM and Guilard R. (Eds.) World Scientific: 2010.
- (a) Furuyama T, Satoh K, Kushiya T and Kobayashi N. J. Am. Chem. Soc. 2014; **136**: 765–776. (b) Kobayashi N, Furuyama T and Satoh K. J. Am. Chem. Soc. 2011; **133**: 19642–19645.
- 3. (a) Furuyama T, Yoshida T, Hashizume D and Kobayashi N. *Chem. Sci.* 2014; 5: 2466–2474.
 (b) Furuyama T, Asai M and Kobayashi N. *Chem. Commun.* 2014; 50: 15101–15104.

 (a) Fukuda T, Homma S and Kobayashi N. *Chem. Eur. J.* 2005; **11**: 5205–5216. (b) Kobayashi N, Fukuda T, Ueno K and Ogino H. *J. Am. Chem. Soc.* 2001; **123**: 10740–10741. 9

- Chambrier I, Cook MJ and Wood PT. Chem. Commun. 2000; 2133–2134.
- McKeown NB, Li H and Helliwell M. J. Porphyrin Phthalocyanines 2005; 9: 841–845.
- Luo J, Xu X, Mao R and Miao Q. J. Am. Chem. Soc. 2012; 134: 13796–13803.
- 8. Kojima T, Honda T, Ohkubo K, Shiro M, Kusukawa T, Fukuda T, Kobayashi N and Fukuzumi S. *Angew. Chem. Int. Ed.* 2008; **47**: 6712–6716.
- Fukuda T, Ishiguro T and Kobayashi N. *Tetrahe*dron Lett. 2005; 46: 2907–2909.
- (a) Fukuda T, Yamamoto K and Kobayashi N. J. Porphyrin Phthalocyanines 2013; 17: 756–762.
 (b) Fukuda T, Homma S and Kobayashi N. Chem. Commun. 2003; 1574–1575. (c) Fukuda T, Ono K, Homma S and Kobayashi N. Chem. Lett. 2003; 32: 736–737.
- Burla MC, Caliandro R, Camalli M, Carrozzini B, Cascarano GL, De Caro L, Giacovazzo C, Polidori G and Spagna R. J. Appl. Cryst. 2005; 38: 381–388.
- Sheldrick GM. SHELXL-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
- (a) Wakita K. Yadokari-XG, Software for Crystal Structure Analyses, 2001. (b) Kabuto C, Akine S, Nemoto T and Kwon E. J. Cryst. Soc. Jpn. 2009; 51: 218.
- (a) Spek AL. J. Appl. Cryst. 2003; 36: 7–13. (b) van der Sluis P and Spek AL. Acta Crystallogr. Sect. A 1990; 46: 194–201.
- (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.
- 16. 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.

- (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.
- 18. Iikura H, Tsuneda T, Yanai T and Hirao K. J. Chem. *Phys.* 2001; **115**: 3540–3544.
- 19. Holmes RR. Chem. Rev. 1996; 96: 927-950.
- 20. Wong CY, Kennepohl DK and Cavell RG. *Chem. Rev.* 1996; **96**: 1917–1952.
- (a) Schmitt J, Heitz V, Sour A, Bolze F, Ftouni H, Nicoud J-F, Flamigni L and Ventura B. *Angew. Chem. Int. Ed.* 2015; 54: 169–173. (b) Tian J,

Ding L, Xu H-J, Shen Z, Ju H, Jia L, Bao L and Yu J-S. *J. Am. Chem. Soc.* 2013; **135**: 18850–18858.

- 22. Kobayashi N, Miwa H and Nemykin VN. J. Am. Chem. Soc. 2002; **124**: 8007–8020.
- 23. Gouterman M. In *The Porphyrins*, Vol. 3, Part A, Dolphin D. (Ed.) Academic Press: USA, 1978; pp 1.