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Rationally Designed Phthalocyanines Having Their Main Absorption Band beyond 1000 nm

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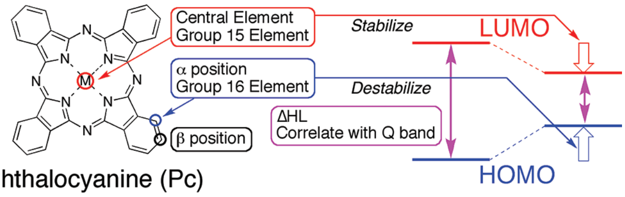
Supporting Information

ABSTRACT: Highly air-stable phthalocyanines (Pcs) having their main absorption band beyond 1000 nm have been synthesized using main-group elements as peripheral and central (core) substituents. The resultant $[(PhS)_8PcP(OMe)_2][PF_6]$ and $[(PhSe)_8PcP(OMe)_2][PF_6]$ show a single Q-band peak at 1018 and 1033 nm, respectively, which was achieved by carefully taking into account the spectroscopic properties of Pcs and the characteristics of the frontier orbitals. The large red shift can be considered to originate from synergistic effects involving both the group-15 and -16 elements.

Considerable effort has been made to develop various types of near-IR organic compounds because of their potential applications in various fields, such as organic solar cells, photodynamic therapy for cancer, heat absorbers, and near-IR imaging.[1] With respect to their practical implementation, the compounds must be easy to produce in a small number of steps and are required to have high stability. Phthalocyanines (Pcs) are good candidates in this regard, since they have been mass-produced (annually more than 5000 tons) in relatively high yields for many years and are known to be one of the most robust organic compounds. However, most Pcs have their main absorption band (called the Q band) at 650−700 nm, and it is unusual to find Pcs having this band beyond 800 nm.[2,3] Although the Q-band position can be shifted to the near-IR by benzoannulation to form naphthalocyanine (Nc) and further anthracocyanine (Ac), this has the disadvantage that the HOMO level destabilizes, making the resulting Ncs and Acs prone to oxidation and hence sensitive to air. Considering also that the reaction sequences leading to Ncs and Acs are longer and their yields lower than those of Pcs,[4] it is of considerable interest to design new Pcs having main bands in the deep near-IR region, particularly when we consider practical applications in high-tech fields.

To achieve our goal in developing these new types of Pc, we have to take into account several factors that influence the position of absorption band of Pcs. (1) Since the Q band is assigned to a transition between the HOMO and the LUMO or LUMO+1,[4,5] the HOMO−LUMO band gap must be smaller than that of normal Pcs. (2) Electron-donating substituent groups at the so-called α-positions generally shift the Q band to longer wavelengths, but simultaneously they undesirably destabilize the HOMO level.[5] (3) Deformation of the Pc plane shifts the Q band to longer wavelengths, but again this is due to the undesired destabilization of the HOMO level.[6] (4) Central elements also affect the position of the Q band.[2] Careful inspection of the molecular orbitals (MOs) of Pcs[4] reveals that (2) results from the fact that the MO coefficient of the α-carbon of the HOMO is large, causing the introduction of electron-donating groups at this position to destabilize the HOMO energy, thereby shifting the Q band to longer wavelengths.[5] Furthermore, the MO coefficient of the pyrrole nitrogens of the LUMO is quite large, from which it is easily inferred that the introduction of electron-withdrawing groups at the pyrrole nitrogen would dramatically stabilize the LUMO orbitals, thereby making it possible to shift the Q band to longer wavelengths. If high-valency elements with a small ionic radius (i.e., strongly electron-deficient groups) are used, the (LU)MOs of Pcs should be strongly stabilized. On the basis of this rational concept, we chose main-group elements as substituents because of their notable features such as effective orbital interactions and diversity of coordination. In this communication, we report the design of phosphorus(V) Pcs containing electron-donating group-16 elements (S and Se), with which we have succeeded in shifting the Q band beyond 1000 nm through synergistic effects (Scheme 1).

Scheme 1. Molecular Design of NIR Phthalocyanines



We chose phosphorus(V) instead of transition metals for the following reasons: (i) P has a large electronegativity (ca. 2.3) and in particular can have a +5 oxidation state that can withdraw electrons strongly, thus satisfying the requirements of this study. (ii) The interaction between P and the Pc ligand is anticipated to be larger than those between transition metals and the Pc ligand because C and N, the elements that constitute the Pc ligand, are closer to P than to transition metals in the periodic table. Hence, the electron-withdrawing effect of P should be stronger than that of a transition metal in the same oxidation state.

The synthetic procedures for the Pcs are shown in Scheme 2. Free-base Pcs were prepared in moderate yield by the so-called lithium method[7] at 120 °C. Phosphorus oxybromide was used for the introduction of a phosphorus atom into the center of the Pc ring. After the reaction was completed, the mixture was quenched

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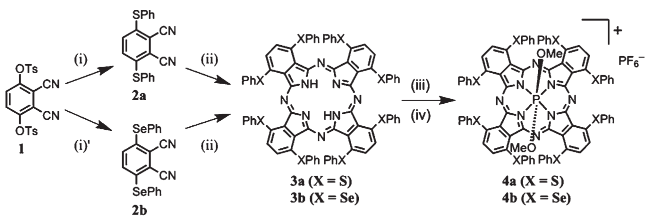
Scheme 2. Synthesis of Substituted Phthalocyanines[a]



[a] Reagents and conditions: (i) PhSH (8 equiv), K_2CO_3 (4 equiv), DMSO, rt, 14 h, 66%; (i)′ PhSeSePh (1.4 equiv), $NaBH_4$ (3.2 equiv), DMSO, rt, 3 h, 37%; (ii) Li (excess), 1-butanol, 120 °C, 2 h, 56−74%; (iii) $POBr_3$ (excess), pyridine, reflux, 1.5 h (X = S), rt, 30 min (X = Se); (iv) CH_2Cl_2/MeOH, rt, 30 min, then KPF_6 (4 equiv), CH_2Cl_2, rt, 12 h, 16−40%.

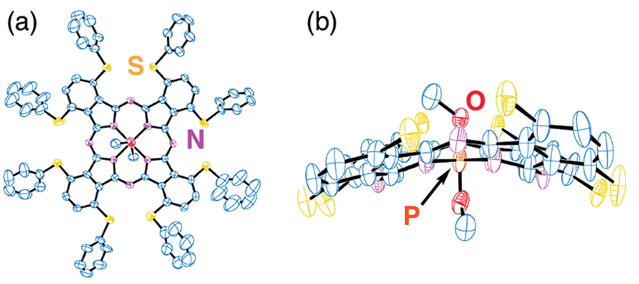


Figure 1. Thermal ellipsoid (50%) diagrams of the molecular structure of **4a**: (a) top view; (b) side view (peripheral substitutents omitted). H atoms, the counteranion of **4a**, and the solvent molecule have been omitted for clarity.

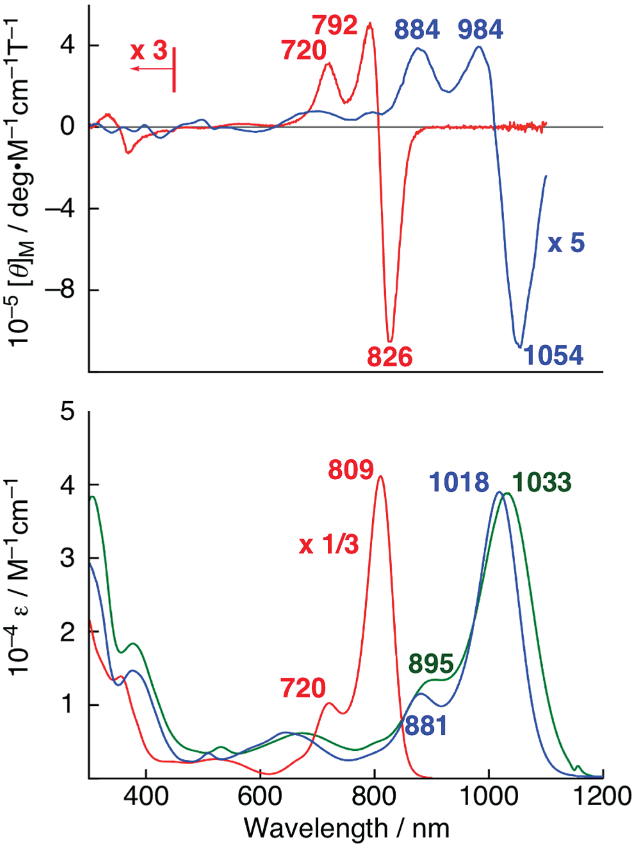


Figure 2. (bottom) UV−vis−NIR and (top) MCD spectra of **3a** (red), **4a** (blue), and **4b** (green) in $CHCl_3$.

with methanol, which provided axial methoxide ligands for the central phosphorus atom. The resulting phosphorus(V) Pcs were cationic salts containing a mixture of several counteranions (mainly $[OH]^-$). With the aim of isolating a discrete counteranion for further characterization, counteranion exchange with potassium hexafluorophosphate was carried out, producing the desired stable Pcs as the hexafluorophosphate salts **4a** (for S) and **4b** (for Se) in yields of 40 and 16%, respectively. The ^{1}H NMR spectrum of **4a** in CD_2Cl_2 shows only one kind of peripheral phenylthio group (7.76 and 7.53 ppm), one signal for the Pc β-hydrogens (7.29 ppm), and a doublet assignable to axial methoxy groups at high field (0.6 ppm). The ^{31}P NMR spectrum exhibits only one peak at −179 ppm and follows the same trends of [(porphyrin)P(V)(L)$_2$].[8] Hence, the conformation of **4a** appears to retain a highly symmetrical structure in solution, with the phosphorus atom lying in the center of the macrocycle and methoxy groups bound to the phosphorus (J_{P-H} = 24 Hz). The methoxy groups are affected by the strong shielding effect of the diatropic ring current resulting from the macrocycle.

To our knowledge, no X-ray crystallographic structure of a phosphorus(V) Pc has been previously reported. To determine the detailed structure of the P(V) Pcs (Figure 1), single crystals of **4a** suitable for X-ray crystallography were grown by slow diffusion of *n*-hexane into a chloroform solution of **4a**.[9] The ionic radius of P(V) (0.38−0.52 Å, six-coordinate octahedral)[10] is small enough to allow the P(V) ion to sit in the center of the Pc 4N mean plane (Δ4N < 0.005 Å). On the other hand, **4a** is not planar but rather is severely ruffled (Δr = 0.472 Å),[11] as reported for P(V) porphyrins,[8] which helps to shift the Q band to longer wavelengths relative the free base **3a**, based on the above characteristic (3). The peripheral phenyl rings are oriented essentially perpendicular to the 4N mean plane, suggesting only a weak electronic interaction between the substituent phenyl groups and the Pc core. Since **4a** has two axial ligands and sterically hindered substituents, no Pc−Pc packing interaction was observed [Figure S1 in the Supporting Information (SI)].

Figure 2 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **3a** and **4a** and the absorption spectrum of **4b**. Free base **3a** shows a single Q-band peak at 809 nm. The position of the Q band is similar to that of $H_2(BuS)_8Pc$ (805 nm in THF),[5] so we can conclude that the phenyl rings of **3a** only marginally affect the electronic nature of the Pc. In contrast, the Q band of P(V)-inserted **4a** is at 1018 nm, confirming a large red shift upon insertion of the P(V) ion due to an effective orbital interaction typical of main-group elements. The absorption spectrum in chloroform is typical of nonaggregated Pcs, which strictly follow the Beer−Lambert law (Figure S2).[12] In a similar manner, free base **3b** and P(V)-inserted **4b** show Q bands at 812 and 1033 nm, respectively. Since the Q band of substituent-free H_2Pc is at ca. 678 nm (=center of the Q_{x00} and Q_{y00} bands) in the same solvent,[2] the above data indicate that eight chalcogen atoms such as S and Se at the so-called α-positions can shift the Q band to the red by ca. 130 nm (2420 cm^{-1}), while the central P(V) ion can provide an additional red shift of 210−220 nm (2570−2630 cm^{-1}). The absorption coefficients of **4a** (and **4b**) are smaller than those of the corresponding metal-free species **3a**, but the reason for this is not yet known (several metallo-Pcs having Q bands at longer wavelength are also known to have weaker Q bands).[3d] The Faraday *A*-term MCD spectra

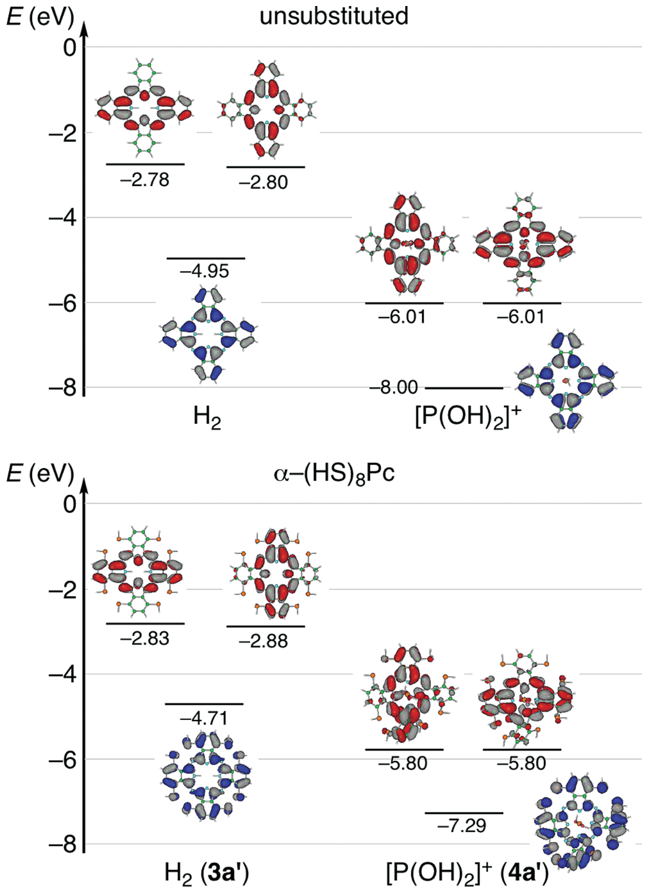


Figure 3. Energy levels of frontier MOs and their contour plots obtained from calculations. Blue and red plots indicate occupied and unoccupied MOs, respectively. Calculations were performed at the B3LYP/6-31G* level (for details, see the SI).

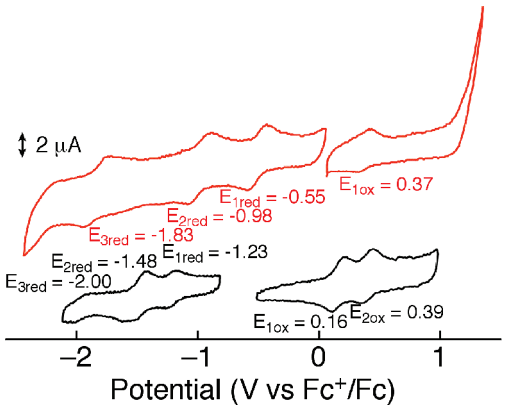


Figure 4. Cyclic voltammetry data for **3a** (bottom, black lines) and **4a** (top, red lines). Cyclic voltammograms were acquired from 1.0 mM solutions of analyte in 0.1 M $^{n}Bu_4NClO_4$/*o*-DCB. Ferrocene was used as an internal standard and set to 0 V.

in the Q_{00} band region further indicate that the practical chromophore symmetry of **4a** is close to D_{4h}, similarly to regular metallo-Pcs.

Our Pcs are remarkably air- and photostable. For example, the UV−vis−NIR spectrum of **4a** remained unchanged when **4a** was stored as a solid in air under ambient light for over 6 months. In air-saturated $CHCl_3$ under ambient light, the decrease in intensity of the Q band of **4a** was less than that of *tert*-butylated CuPc, which is considered to be one of the most stable metallo-Pcs (Figure S4).

To enhance the interpretation of the electronic structure of **4a** and **4b**, MO calculations were performed for unsubstituted H_2Pc and its $[P(OH)_2]^+$ derivative and for α-$(HS)_8H_2Pc$ **3a′** and its $[P(OH)_2]^+$ derivative **4a′** (Figure 3). The optimized structure of **4a′** is also ruffled ($\Delta r = 0.477$ Å), in good agreement with the crystal structure of **4a**. As has already been reported,[5] the HOMO−LUMO energy gap (ΔHL) becomes smaller on going from unsubstituted H_2Pc (ca. 2.2 eV) to α-$(HS)_8H_2Pc$ **3a′** (ca. 1.8 eV). The introduction of strongly electron-withdrawing $[P(OH)_2]^+$ into the Pc center stabilizes both the HOMO and LUMO significantly, reducing ΔHL to ca. 2.0 and 1.5 eV, respectively, for the unsubstituted and α-$(HS)_8$-substituted species, making them robust against oxidation and shifting the Q band to even longer wavelengths. An important implication of these calculations is that the extent of the red shift upon element insertion is different from ligand to ligand. Thus, in the above case, the shift is larger for the α-$(HS)_8$-substituted species. The frontier orbitals of α-$(HSe)_8H_2Pc$ **3b′** and its $[P(OH)_2]^+$ derivative **4b′** can also be explained in a manner similar to that for **3a′** and **4a′** (Figure S7).

Natural bond orbital (NBO) analysis was carried out to evaluate further the marked effect of phosphorus insertion.[13] Interactions between the lone pairs of the group-16 elements and the π^* orbital of the Pc core were revealed (Table S1 in the SI). While the values of the NBO donor−acceptor interaction energies for free-base Pcs were relatively small and close in value, those of the phosphorus Pcs were much larger than the free-base values and depended significantly on the substituent elements at the Pc periphery. The energies of the S- and Se-substituted phosphorus Pcs were, for example, ca. 2.5 times larger than that of an O-substituted phosphorus Pc. This effective orbital interaction affects the stabilization of the LUMOs. Thus, S (or Se) and P cooperate in narrowing the ΔHL.

Cyclic voltammograms of **3a** and **4a** were measured in *o*-dichlorobenzene (*o*-DCB) for comparison with the above calculations (Figure 4). *tert*-Butylated H_2Pc shows redox couples at 0.94, 0.62, −0.82, and −1.19 V in CH_2Cl_2 ($E_{1ox} - E_{1red} = 1.44$ V).[14] Compound **3a** showed couples at 0.39, 0.16, −1.23, −1.48, and −2.00 V ($E_{1ox} - E_{1red} = 1.39$ V), while **4a** exhibited these at 0.37, −0.55, −0.98, and −1.83 V ($E_{1ox} - E_{1red} = 0.92$ V). Thus, in agreement with the above calculations, the value of $E_{1ox} - E_{1red}$ decreases in going from normal H_2Pc to α-octaphenylthio-substituted **3a** and further to $[P(OMe)_2]^+$-inserted **4a**. In particular, the introduction of the central $[P(OMe)_2]^+$ greatly stabilizes the LUMO level (cf. the change of the first reduction potential from −1.23 to −0.55 V), as anticipated in the introductory section from the large MO coefficient of the pyrrole nitrogen in the LUMO.

In conclusion, we have succeeded in producing highly stable Pcs having Q bands beyond 1000 nm as single chromophores by considering several effects synergistically. The structure and electronic properties of the target phosphorus(V) Pcs were investigated by single-crystal X-ray diffraction (solid phase), NMR spectroscopy (solution phase), and DFT calculations (gas phase). In **4a** and **4b**, destabilization of the HOMO by the introduction of electron-donating elements at the α-positions, deformation of the planarity of the Pc plane, and stabilization of both the HOMO and LUMOs by a strongly electron-withdrawing, high-valency central element function synergistically. The Pc compounds reported here can be synthesized in only a few steps from commercially available compounds in moderate yields, while this magnitude of red-shifted wavelength could not be achieved even for anthracocyanines.[2] This is important, since stable Pcs such as those in this study can be used in society for various purposes. Furthermore, the concept of taking the size of the MO coefficient into account as described here is simple and should be applicable to other organic dyes in adjusting the absorption wavelengths. Further work is currently underway to expand this concept and synthesize other NIR dyes.

ASSOCIATED CONTENT

Supporting Information. Additional spectroscopic data, full details of experimental and calculation procedures, and X-ray crystallographic data of **4a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystallographic data for **4a**: $C_{83}H_{55}Cl_3F_3N_8O_2P_{1.50}S_8$, MW = 1662.63; monoclinic, space group $C2/c$ (No. 15); $a = 17.407(4)$ Å, $b = 37.264(8)$ Å, $c = 29.795(6)$ Å, $\beta = 101.927(3)°$; $V = 18909(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.168$ g cm^{-3}; $T = 100$ K; $R_1 = 0.0879$ [$I > 2\sigma(I)$], $R_w = 0.2526$ (all data), GOF = 0.845; CCDC-843317.

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(11) Δr was calculated as the square root of the average of the squares of the deviations of the atoms from the mean plane. The values of Δr for ruffled phosphorous porphyrins are 0.38−0.54 Å. See ref 8.

(12) The position of the Q band did not depend on the counteranion, so we can conclude that the counteranion does not affect the electronic structure of phosphorous(V) Pc (see Figure S3).

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