

Crystal Structures and Electronic Properties of Saddle-Distorted and Protonated Phthalocyanines**

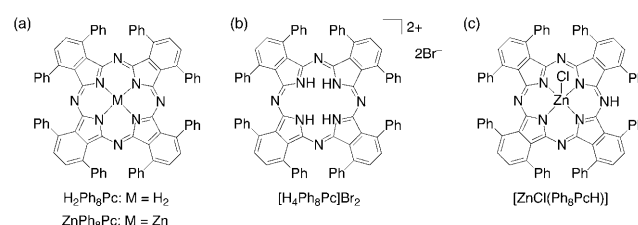
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Phthalocyanines (Pcs) are one of the most developed heteromacrocycles, together with porphyrins, in particular as dyes and pigments. Recently, they have been utilized in a variety of applications such as photosensitizers, photovoltaic materials, and so on.^[1,2] However, the properties of protonated species resulting from the acid–base reaction have been little known because of their low basicity arising from the rigid structure of the phthalocyanine ring as compared with the porphyrin ring.^[3,4] In sharp contrast to the protonation of the porphyrin ring, which always occurs at pyrrole nitrogen atoms,^[5,6] phthalocyanines may undergo protonation at two different sites: the isoindole nitrogen atom and the *meso*-nitrogen atom. To date, the protonation of phthalocyanines has been limited to overly acidic conditions such as in concentrated sulfuric acid and in trifluoroacetic acid (TFA) because of the small formation constants of protonated species.^[3] Moreover, there have been no reports on either the detection of inner protonation at the isoindole nitrogen atom or of the crystal structure determination of protonated phthalocyanines.

We previously investigated the formation of supramolecular assemblies based on the protonation of saddle-distorted dodecaphenylporphyrin (H₂DPP), which has high basicity derived from the lone pairs of pyrrole nitrogen atoms.^[6] We have also reported on the free base and the metal complex of

saddle-distorted 1,4,8,11,15,18,22,25-octaphenylphthalocyanine (Ph₈Pc),^[7] whose structural features are expected to enhance the proton-accepting ability of the phthalocyanine ring as well as H₂DPP.

We report herein for the first time the formation and the crystal structure determination of *meso*- and isoindole-protonated phthalocyanines by using saddle-distorted Ph₈Pcs (Scheme 1). We also report the spectroscopic and electrochemical properties of these protonated phthalocyanines, which provide novel features such as near-IR absorption and highly positively shifted redox potentials as compared with unprotonated phthalocyanines.



Scheme 1. Chemical structures of a) Ph₈Pcs, b) [H₄Ph₈Pc]Br₂, and c) [ZnCl(Ph₈PcH)].

We examined the reaction of Ph₈Pcs with a variety of acids, and we used excess amounts of hydrobromic acid (HBr) and hydrochloric acid (HCl) for H₂Ph₈Pc and [ZnPh₈Pc], respectively. We succeeded in obtaining single crystals of the respective protonated species suitable for X-ray crystallography (see the Experimental Section). As shown in Figure 1, the crystal structure of inner-protonated H₂Ph₈Pc, [H₄Ph₈Pc]Br₂, shows a significant increase in the out-of-plane distortion of the Pc ring owing to the steric hindrance among protons in the central cavity compared with its free-base form, while structural deformations are almost the same in outer-protonated [ZnPh₈Pc], [ZnCl(Ph₈PcH)].^[8] In the crystal structure, [H₄Ph₈Pc]Br₂ forms hydrogen bonds between two N–H protons of isoindole and a bromide ion both above and below the phthalocyanine mean plane with interatomic distances of 3.26–3.32 Å (Figure S1 in the Supporting Information). To verify the extent of deformation of the Pc ring, the displacement of each atom from the least-square mean plane of 24 atoms of the phthalocyanine core (Δ RMS) in H₂Ph₈Pc^[9] and [H₄Ph₈Pc]Br₂ was calculated to be 0.57 and 0.81 Å, respectively. This result clearly indicates that the inner protonation at the isoindole nitrogen atom induces severe saddle deformation because of the repulsion of inner protons in a manner similar to diprotonated porphyrins.^[5,6] In the crystal structure of [ZnCl(Ph₈PcH)], the chloride ion is found to coordinate to the central zinc ion at a distance of

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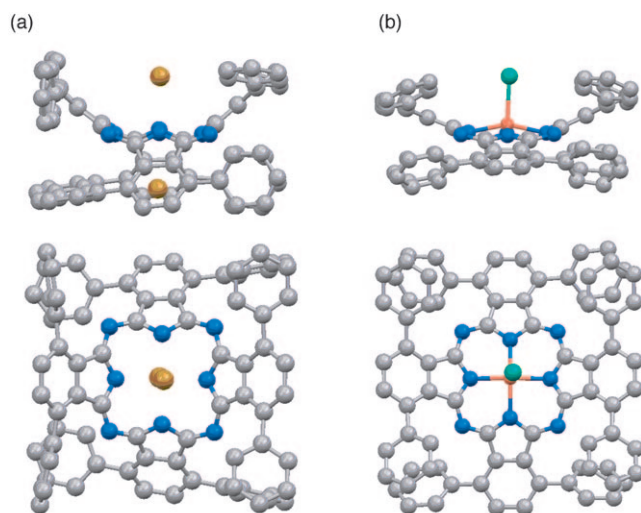
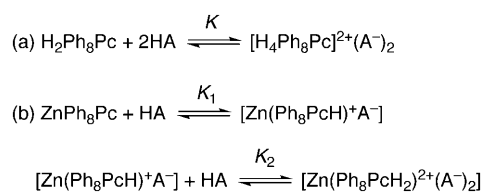


Figure 1. Molecular structures of protonated phthalocyanine a) $[H_4Ph_8Pc]Br_2$ and b) $[ZnCl(Ph_8PcH)]$. C gray, N blue, O red, Br brown, Zn pink, Cl green. Hydrogen atoms and solvent molecules are omitted for clarity.

2.453(2) Å. Furthermore, hydrogen bonds were formed among the coordinating chloride anions and two methanol molecules of crystallization (Figure S2 in the Supporting Information).^[10] The ΔRMS values are almost the same in $[ZnPh_8Pc]$ and $[ZnCl(Ph_8PcH)]$ (0.59 and 0.53 Å, respectively),^[9] which indicates that protonation at the *meso*-nitrogen atom does not affect the phthalocyanine ring conformation.

To elucidate the protonation reaction of Ph_8Pcs in solution, we measured absorption spectral changes upon addition of TFA to the solution of Ph_8Pcs in dichloromethane (CH_2Cl_2) and benzonitrile ($PhCN$). The titration of H_2Ph_8Pc by TFA in CH_2Cl_2 allowed us to observe the one-step spectral change, with isosbestic points as shown in Figure 2a. The Job continuous variation method^[11] clearly indicates that this spectral change has 1:2 stoichiometry (Figures S3 and S4 in the Supporting Information). From the one-step 1:2 stoichiometry equilibrium,^[6b] we determined the equilibrium constant of diprotonation of the phthalocyanine ring K to be $1.2 \times 10^8 M^{-2}$ and $4.8 \times 10^5 M^{-2}$ in CH_2Cl_2 and $PhCN$, respectively (Scheme 2). This apparent one-step diprotonation is ascribed to the high basicity of the inner-monoprotonated phthalocyanine, which is due to the more deformed structure, akin to the monoprotinated porphyrin.^[6b]

In sharp contrast to H_2Ph_8Pc , a two-step spectral change was observed in the course of the titration of $[ZnPh_8Pc]$ with TFA in CH_2Cl_2 , with two isosbestic points (Figure 2b). These spectral changes were assigned to monoprotection and



Scheme 2. The protonation equilibria of a) H_2Ph_8Pc and b) $[ZnPh_8Pc]$ by acid (HA).

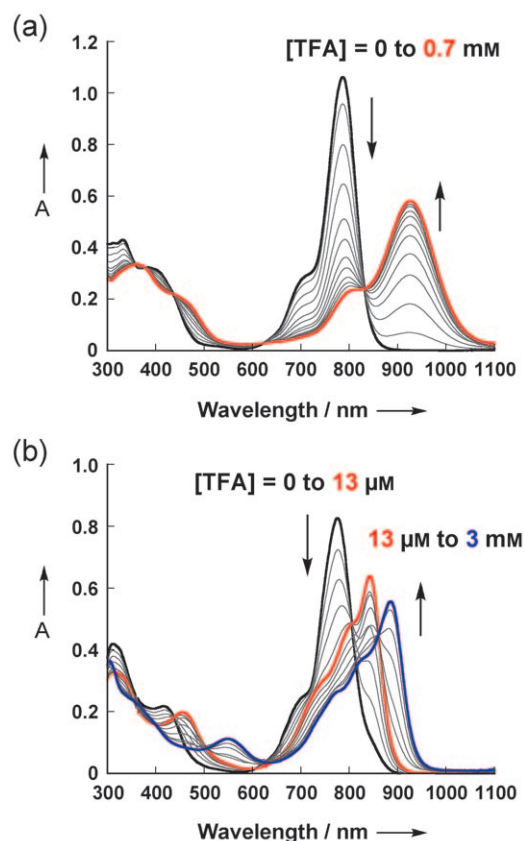


Figure 2. Absorption spectral changes upon addition of TFA to the solution of a) H_2Ph_8Pc ($1.2 \times 10^{-5} M$) and b) $[ZnPh_8Pc]$ ($1.0 \times 10^{-5} M$) in CH_2Cl_2 .

diprotonation of the phthalocyanine ring in light of previous work.^[3] The first spectral change was induced by adding one equivalent of TFA, clearly showing that monoprotection occurred. The equilibrium constants of mono- and diprotonation (K_1 and K_2 , Scheme 2b) were determined to be 1.4×10^5 and $27 M^{-1}$ in $PhCN$, respectively (Figures S5 and S6 in the Supporting Information).^[12] The absorption spectra of the single crystals of $[H_4Ph_8Pc]Br_2$ and $[ZnCl(Ph_8PcH)]$ in CH_2Cl_2 agree with those obtained by absorption titration experiments (red line in Figure 2a,b), which clearly indicates that the protonated Ph_8Pcs are stable even in a non-acidic solution owing to the large formation constants of the protonated species (Figure S7 in the Supporting Information).

In the case of planar free-base phthalocyanines, the protonation of the *meso*-position is energetically more favorable;^[4] however, inner protonation ($-9.5 \text{ kcal mol}^{-1}$) is more stable than outer protonation ($-4.5 \text{ kcal mol}^{-1}$) for the saddle-distorted H_2Ph_8Pc , as suggested by DFT calculations (Figure S8 in the Supporting Information).^[13] This energy reversal can be explained by the compensation for destabilization arising from the structural distortion by stabilization of hydrogen bond formation among N–H protons of the isoindole rings and bromide ions, as seen in the crystal structure.

In the 1H NMR spectrum of the single crystals of $[H_4Ph_8Pc]Br_2$ in $CDCl_3$, a singlet signal at $\delta = 6.4$ ppm was assigned to the isoindole N–H, since the peak disappeared

upon addition of a drop of D₂O (Figure S9a in the Supporting Information). The ¹H NMR spectrum of [ZnCl(Ph₈PcH)] shows more complex signals than that of [ZnPh₈Pc], probably owing to the lowering symmetry induced by the proton at the *meso*-nitrogen atom (Figure S9b in the Supporting Information). This situation was confirmed by the observation of an exchangeable proton with a signal at $\delta = 12.3$ ppm, which was assigned to the proton bound to the *meso*-nitrogen atom. The coordination of the chloride ion to the zinc center of [ZnCl(Ph₈PcH)] in solution was confirmed by electrospray ionization mass spectrometry (ESI-MS), which detected a peak cluster arising from [ZnCl(Ph₈Pc)][−] (*m/z* 1222.4) in its deprotonated form in the negative detection mode (Figure S10 in Supporting Information).

We measured the magnetic circular dichroism (MCD) spectra of protonated Ph₈Pcs in CH₂Cl₂ to reveal the electronic structures of both inner- and outer-protonated Ph₈Pcs (Figure 3).^[14] [H₄Ph₈Pc]Br₂ adopts *D*_{2d} symmetry owing to saddle deformation of the ligand caused by steric congestion at the ligand periphery. The spectral features are similar to those of a *D*_{4h} metallophthalocyanine derivative, because a four-fold axis of symmetry is retained in the central part of the core and the lowest unoccupied molecular orbital (LUMO) therefore remains doubly degenerate.^[15] An intensification of the lower-energy Q band was observed in the MCD spectrum relative to the absorption spectrum, owing to the larger orbital angular momentum change associated with the Q transition.^[16] Only the A₁ term arising from the Q band

of [H₄Ph₈Pc]Br₂ can be readily identified owing to extensive configurational interaction between the B1 and higher-energy $\pi\pi^*$ states.^[7b] The presence of an axial ligand and a protonated *meso*-nitrogen atom lowers the symmetry of [ZnCl(Ph₈PcH)] to *C*₁. Therefore, the Q band shifts to longer wavelength (845 nm) relative to the corresponding *D*_{2d} [ZnPh₈Pc] complex (786 nm).^[7b] A trough of MCD intensity (846 nm) corresponds almost exactly to the absorption maximum of the Q band (845 nm), thus confirming the presence of well-separated Faraday **B**₀ terms, as would normally be anticipated when there is a large zero-field splitting of the Q and B1 $\pi\pi^*$ states owing to the absence of a *C*₃ or higher axis of symmetry.^[16] A minus-to-plus pattern is consistently observed in ascending energy terms in the Q-band region of each MCD spectra. The orbital angular momentum properties of the excited states and hence the sign sequences observed in the MCD spectrum are determined by the relative magnitudes of the splitting of the two occupied and the two unoccupied Gouterman orbitals (i.e. the MOs derived from the 1a_{1u}, 1a_{2u}, and 1e_g^{*} MOs of the parent *D*_{4h}-symmetry metal-Pc complex).^[15,17] The minus-to-plus pattern is consistent with a greater splitting of the occupied MOs than would be anticipated for [H₄Ph₈Pc]Br₂ based on the *D*_{2d} symmetry of the chromophores and for [ZnCl(Ph₈PcH)] based on the results of molecular orbital calculations (Figure S12 in the Supporting Information).^[18] From electrochemical measurements in CH₂Cl₂, we could observe large positive shifts of the reduction potentials for [H₄Ph₈Pc]Br₂ (+0.58 V) and [ZnCl(Ph₈PcH)] (+0.38 V), which correspond to the energetic stabilization of the LUMO upon protonation (Figure S13 and Table 1 in the Supporting Information).^[4,6]

In summary, we have determined the first crystal structures of phthalocyanines protonated at the *meso*- and isoindole nitrogen atoms by using saddle-distorted phthalocyanines. The saddle distortion of Ph₈Pc facilitates the protonation of the phthalocyanine ring. The outer protonation of [ZnPh₈Pc] affords the stable monoprotonated form with small structural change, while the inner-diprotonated [H₄Ph₈Pc]Br₂ shows a significantly deformed structure. The presence of two possible sites for protonation differentiates phthalocyanine from porphyrin in terms of protonation pattern and resultant characteristics. The saddle-distorted structure of H₂Ph₈Pc enables the inner protonation by virtue of the hydrogen bonding among isoindole protons and the counteranion, as is also true for saddle-distorted porphyrins.^[6b] These results describe two types of protonated phthalocyanines in terms of their structures and their spectroscopic and electrochemical properties. The protonation of phthalocyanines should affect their electronic structure, thus providing them with novel properties and functionality.

Experimental Section

Synthesis of [H₄Ph₈Pc]Br₂: Red crystals of [H₄Ph₈Pc]Br₂ were obtained by two-layered recrystallization with addition of acetonitrile on the top of the toluene solution (2 mL) of H₂Ph₈Pc (50 mg, 0.045 mmol) in the presence of excess hydrobromic acid. The obtained crystals (36 mg, 63 % yield) were dried in vacuo. ¹H NMR

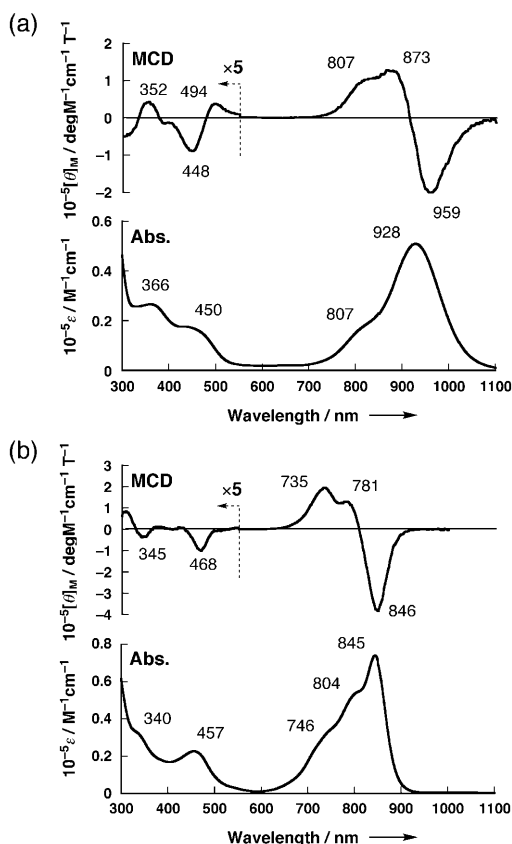


Figure 3. Absorption (lower) and MCD (upper) spectra of a) [H₄Ph₈Pc]Br₂ and b) [ZnCl(Ph₈Pc)] in CH₂Cl₂.

(300 MHz, CDCl_3 , 298 K): δ = 7.71 (8H, s), 7.34–7.46 (40H, m), 6.43 ppm (4H, s). Elemental analysis (%) calcd for $\text{C}_{80}\text{H}_{52}\text{Br}_2\text{N}_8$: C 74.77, H 4.08, N 8.72; found: C 75.21, H 4.13, N 8.44. Absorption maxima (CH_2Cl_2 , λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)): 366 (2.6×10^4), 450 (1.7×10^4), 807 (1.7×10^4), 928 (5.1×10^4).

Synthesis of $[\text{ZnCl}(\text{Ph}_8\text{PcH})]$: A mixture of $[\text{ZnPh}_8\text{Pc}]$ (50 mg, 0.042 mmol) in CH_2Cl_2 (2 mL) and excess hydrochloric acid was washed with water in a separating funnel, and the organic phase was collected. Volatile components were removed in vacuo from the resulting red solution to give $[\text{ZnCl}(\text{Ph}_8\text{PcH})]$ quantitatively as a red-brown powder. A single crystal suitable for X-ray crystallography was obtained by the two-layered recrystallization from CH_2Cl_2 /methanol. Elemental analysis (%) calcd for $\text{C}_{80}\text{H}_{49}\text{ClN}_8\text{Zn}$: C 78.56, H 4.04, N 9.16; found: C 78.29, H 4.25, N 9.22. ESI-MS (in CHCl_3): m/z calcd for $\text{C}_{80}\text{H}_{49}\text{N}_8\text{Zn}$: 1187.7; found: 1187.6 $[\text{M}-\text{Cl}]^+$ in the positive detection mode; m/z calcd for $\text{C}_{80}\text{H}_{48}\text{N}_8\text{ZnCl}$: 1222.2; found: 1222.4 $[\text{M}-\text{H}]^+$ in the negative detection mode. Absorption maxima (CH_2Cl_2 , λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)): 457 (2.2×10^4), 746 (sh) (3.2×10^4), 804 (sh) (5.3×10^4), 845 (7.4×10^4).

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- [8] a) Crystallographic data for $[\text{H}_4\text{Ph}_8\text{Pc}]\text{Br}_2$: single crystals of $[\text{H}_4\text{Ph}_8\text{Pc}]\text{Br}_2$ containing toluene and acetonitrile were obtained by recrystallization from toluene/acetonitrile. $\text{C}_{93}\text{H}_{69}\text{Br}_2\text{N}_{11}$, monoclinic, space group $P2_1/a$ (no. 14), $a = 14.0324(8)$, $b = 36.5296(18)$, $c = 14.5273(8)$ Å, $\beta = 100.6810(9)^\circ$, $V = 7317.6(7)$ Å³, $Z = 4$. Intensity data were collected at 123 K on a Rigaku Mercury CCD area detector with graphite monochromated $\text{MoK}\alpha$ radiation. The structure was solved by direct methods and expanded using Fourier techniques. A total of 56659 reflections were measured, of which 12312 were independent. Final $R_1 = 0.0710$, $R_w = 0.1735$ ($I > 2\sigma(I)$); b) Crystallographic data for $[\text{ZnCl}(\text{Ph}_8\text{PcH})]$: single crystals of $[\text{ZnCl}(\text{Ph}_8\text{PcH})]$ containing methanol were obtained by recrystallization from CH_2Cl_2 /methanol. $\text{C}_{82}\text{H}_{55}\text{ClN}_8\text{O}_2\text{Zn}$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.365(3)$, $b = 15.687(3)$, $c = 16.428(3)$ Å, $\alpha = 70.471(10)$, $\beta = 67.454(10)$, $\gamma = 61.182(9)^\circ$, $V = 3148.9(9)$ Å³, $Z = 2$, $T = 123$ K. A total of 22898 reflections were measured of which 12370 were independent. Final $R_1 = 0.0719$, $R_w = 0.1850$ ($I > 2\sigma(I)$). CCDC 795321 ($\text{C}_{93}\text{H}_{69}\text{Br}_2\text{N}_{11}$) and 795322 ($\text{C}_{82}\text{H}_{55}\text{ClN}_8\text{O}_2\text{Zn}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [9] ΔR_{MS} values of unprotonated phthalocyanines were calculated using the crystal structure reported in Ref. [7].
- [10] We could not determine the exact position of the additional proton, since the C–N bonds and the C–N–C angles are virtually the same (1.33–1.34 Å and 123–124°, respectively), and we concluded that one proton is disordered over the four meso-nitrogen atoms.
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- [12] We could not determine the equilibrium constant of the monoprotection of $[\text{ZnPh}_8\text{Pc}]$ in CH_2Cl_2 because it proceeds quantitatively. The equilibrium constant of the second protonation in CH_2Cl_2 , K_2 , was determined to be $1.7 \times 10^3 \text{ M}^{-1}$. The protonation of phthalocyanines includes the formation of a complex of phthalocyanine with a counteranion of the corresponding acid (see Scheme 1), as seen with porphyrin.^[6] The formation of the complex was confirmed by the crystal structure determination and ESI-MS measurements. From this point of view, the difference in the formation constants between PhCN and CH_2Cl_2 solution is consistent with the fact that the anion-bound complex is more stable in less polar solvents.
- [13] DFT calculations were performed with B3LYP/6-311+G-(2d,2p)//B3LYP/6-31G(d) level of theory.^[18] The stability energy (ΔE) of each monoprotected phthalocyanine ($[\text{H}_3\text{Ph}_8\text{Pc}]\text{Br}$) was calculated by subtracting the sum of total energy of $\text{H}_2\text{Ph}_8\text{Pc}$ and HBr from the total energy of $[\text{H}_3\text{Ph}_8\text{Pc}]\text{Br}$.
- [14] The MCD spectrum of $[\text{ZnPh}_8\text{Pc}]$ has been reported and the effects of structural deformation on the spectroscopic and electrochemical properties were discussed.^[7b] We also measured the MCD spectra of diprotated H_2DPP , $[\text{H}_4\text{DPP}]\text{Cl}_2$ (Figure S11 in the Supporting Information). The saddling of the ligand and the substituent effect caused by the phenyl groups modifies the energies of the key frontier π MOs. The B (or Soret) and Q bands, which are associated with the $\Delta M_L = \pm 1$ and ± 9 transitions in Gouterman's four-orbital model, appear at longer wavelengths than those of planar metallophthalocyanines.^[15] The first-derivative-shaped MCD bands corresponding to the main peaks in the absorption spectrum of $[\text{H}_4\text{DPP}]\text{Cl}_2$ are consistent with the presence of A_1 terms arising from the Zeeman splitting of orbitally degenerate $\pi\pi^*$ excited states.^[16] The trend predicted for the HOMO–LUMO band decreases in the order $[\text{H}_4\text{DPP}]\text{Cl}_2 > \text{ZnCl}(\text{Ph}_8\text{PcH}) > [\text{H}_4\text{Ph}_8\text{Pc}]\text{Br}_2$ and is consistent with the observed Q-band wavelengths.
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