Effect of Peripheral Substitution on the Electronic Absorption and Fluorescence Spectra of Metal-Free and Zinc Phthalocyanines

Nagao Kobayashi,*[a] Hiroshi Ogata,[a] Naokazu Nonaka,[b] and Eugene A. Luk'yanets[c]

Abstract: The effect of substituents on the position and intensity of the electronic absorption and fluorescence spectra of phthalocyanines (Pcs) was examined for 35 Pc compounds. When electron-releasing groups are bound to four α-benzo positions of the Pc skeleton, the B and Q bands shift to longer wavelength. Relative to this shift, the effect of introducing the same electron-releasing groups at the other four α positions amounts to about 1.6–2.0. Although the effect is not always clearly seen, introduction of electron-releasing groups in the β-benzo positions of the Pc skeleton generally shifts the Q band to shorter wavelength. The effect of electron-withdrawing groups is exactly the opposite with respect to the α and β positions. These effects can be reasonably explained by considering the magnitude of the atomic orbital coefficients of the carbon atoms derived from molecular orbital (MO) calculations. In addition, the following intriguing phenomena were observed in the experiments, although not all were explained theoretically: 1) the splitting of the Q band of metal-free Pcs decreases with increasing wavelength of the Q band, 2) the ring currents of Pcs with Q bands at longer wavelength are generally smaller, and 3) the absorption coefficients of the Q band of Pc compounds with 16-electron-releasing substituents are larger than those of the corresponding tetra- and octasubstituted Pcs by several tens of percent. 4) Our PPP calculations suggested that the absorption coefficient of the Q band of Pcs with more strongly electron releasing substituents is larger. 5) The second HOMO of the Pcs with the Q band at longer wavelength has b_{1u} symmetry, as opposed to the a_{2u} symmetry of normal Pcs. 6) Pcs showing S1 emission maxima at wavelengths longer than about 740 nm generally have quantum yields of less than 0.1.

Keywords: fluorescence spectroscopy · molecular orbital calculations · phthalocyanines · substituent effects · UV/Vis spectroscopy

Introduction

Phthalocyanines (Pcs) have traditionally found use as dyes and pigments, as catalysts for desulfurization processes in the oil industry, and more recently as photoconducting agents in photocopiers, deodorants, germicides, optical computer read/write disks, and as promotion or retardation films for plant growth in greenhouses, because of their easy synthesis, high stability, and the presence of $\pi-\pi^*$ transitions in the near-UV/visible/near-IR region.[1] In recent decades, there has been renewed interest in the use of Pcs in a variety of high-tech fields, including semiconductor devices,[2] photovoltaic solar cells,[3] electrophotography,[4] rectifying devices,[5] molecular electronics,[6] Langmuir–Blodgett films,[7] electrochromism in display devices,[8] low-dimensional metals,[9] gas sensors,[10] liquid crystals,[11] nonlinear optics,[12] photodynamic reagents for cancer therapy and other medical applications,[13] and electrocatalytic reagents.[14] In a number of these applications, the wavelength of the major $\pi-\pi^*$ transitions in the UV/Vis region is of critical importance. The position and bandwidth of absorption bands of Pcs can be adjusted in two ways. One is by changing size and symmetry of the π-conjugated system of Pcs,[15] and the other is by varying the central metal atom and the type, number, and positions of peripheral substituents.[16] It is known, for example, that the Q band can be shifted with approximate additivity when the same substituents are introduced at the same position of each benzene ring of the Pcs.[17] However, the effect of introducing a plurality of substituents on each benzene unit has not been examined systematically to date, except for our preliminary communication.[18] Here we report regiospecific and nonlinear effects of substituents on both the energy and intensity of the electronic absorption and fluorescence emission spectra of metal-free and zinc Pcs, as well as their effect on the splitting of the Q_{00} band of the metal-free Pcs. We examined 35 Pcs with electron-releasing alkoxyl or alkyl(phenyl)thio groups and electron-withdrawing nitro or sulfonyl groups. Some of

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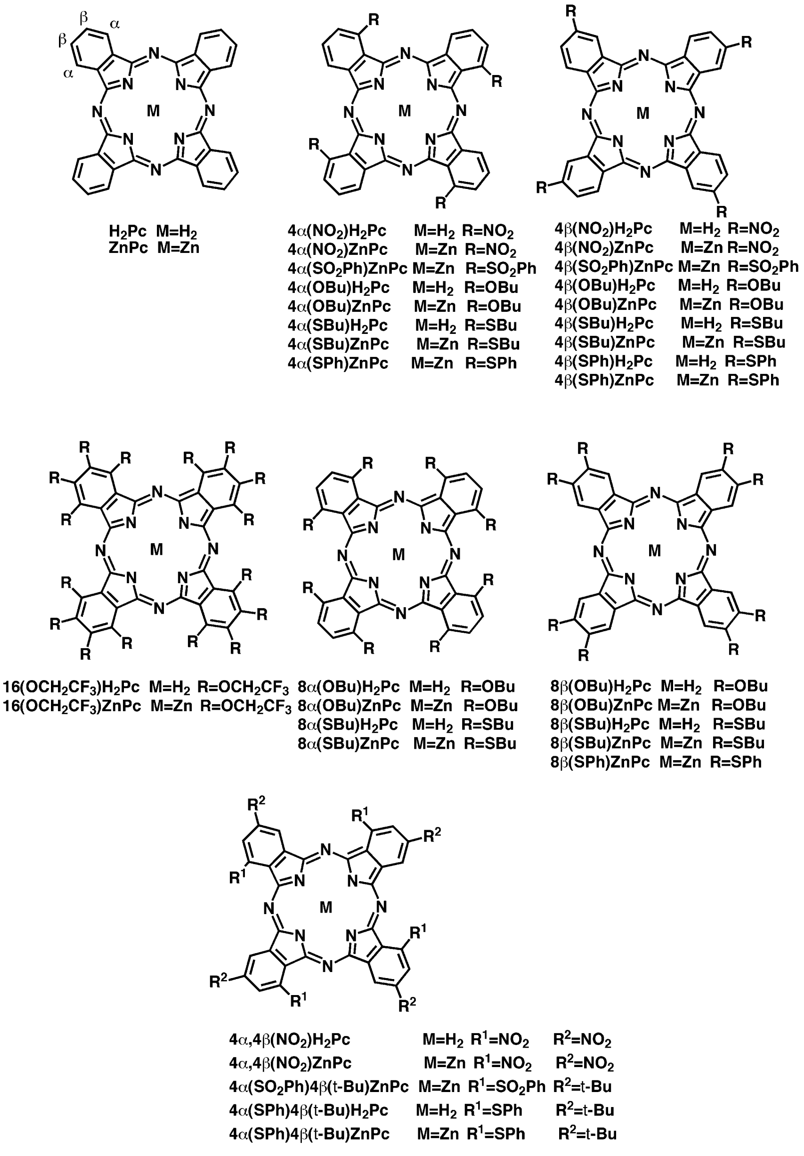
the experimental observations were reproduced by MO calculations within the framework of the Pariser–Parr–Pople (PPP) approximation.

Results and Discussion

The structures and abbreviations of Pcs used in this study are shown in Figure 1. In the abbreviations, the first number indicates the number of substituents introduced on the Pc periphery, α or β indicates their positions, and substituent is identified in parentheses. For example, 4α(SBu)ZnPc denotes a ZnPc with four butylthio groups in the α positions, while $4\alpha,4\beta(NO_2)H_2Pc$ is a metal-free Pc with four nitro groups each in the α and β positions.

Absorption and magnetic circular dichroism spectra: Figure 2 shows the absorption and magnetic circular dichroism (MCD) spectra of alkoxy-substituted H_2Pcs (the B[19] and Q band regions are shown separately so that the peak positions can be clearly seen). As can be seen in the figure, for Pcs with the same number of alkoxyl groups, substitution at the α positions results in a Q band absorption at longer wavelength (lower energy). An increase in the number of substituents from four to eight results in opposite behavior for α and β substitution. Substitution at α positions further shifts the Q band to longer wavelength, and substitution at β positions to shorter wavelength. The latter shift suggests that substitution at the β positions by electron-releasing groups shifts the band to shorter wavelength, although this shift is smaller than the longer wavelength shift due to substitution at the α positions. The shift to shorter wavelength due to β substitution appears real, however, since the Q band of $16(OCH_2CF_3)H_2Pc$ is at shorter wavelength than that of $8\alpha(OBu)H_2Pc$. In accordance with previous studies,[16] the shift in the B band region is not clear, although there is a trend that substitution at the α positions broadens the band.[20, 21] Interestingly, the shapes of the B bands of 4β(OBu)- and $8\beta(OBu)H_2Pc$ are similar, and this also holds true for 4α(OBu)- and $8\alpha(OBu)H_2Pc$. The H_2Pcs substituted at the β positions have three peaks in the B band region, while the α-substituted H_2Pcs have the strongest peaks at 315–330 nm. Comparison of the spectra of 8α(OBu)-, 8β(OBu)-, and $16(OCH_2CF_3)H_2Pc$ further shows that the absorption coefficient of $16(OCH_2CF_3)H_2Pc$ is roughly 1.2 times larger than those of the other two. Furthermore, comparison of the spectra of 4α- and $4\beta(OBu)H_2Pc$ suggests that the intensity of the Q band of the former is slightly higher.

The MCD spectra are shown for the three representative species. In the Q band region, 8α(OBu)- and $16(OCH_2CF_3)$-H_2Pc display dispersion-type, Faraday *A*-term-like curves. Since the compounds have D_{2h} symmetry, this is a pseudo-Faraday *A* term produced by superimposition of closely lying Faraday *B* terms of opposite signs.[22] However, careful analysis of this apparent dispersion-type Q band of $8\beta(OBu)H_2Pc$ perhaps experimentally substantiates that the splitting of the Q band of this species is larger than those of 8α(OBu)- and $16(OCH_2CF_3)H_2Pc$. The shape of the B MCD indicates that the main B band of these three species lies at about 330–360 nm.



H_2Pc M=H_2
ZnPc M=Zn

$4\alpha(NO_2)H_2Pc$ M=H_2 R=NO_2
$4\alpha(NO_2)ZnPc$ M=Zn R=NO_2
$4\alpha(SO_2Ph)ZnPc$ M=Zn R=SO_2Ph
$4\alpha(OBu)H_2Pc$ M=H_2 R=OBu
4α(OBu)ZnPc M=Zn R=OBu
$4\alpha(SBu)H_2Pc$ M=H_2 R=SBu
4α(SBu)ZnPc M=Zn R=SBu
4α(SPh)ZnPc M=Zn R=SPh

$4\beta(NO_2)H_2Pc$ M=H_2 R=NO_2
$4\beta(NO_2)ZnPc$ M=Zn R=NO_2
$4\beta(SO_2Ph)ZnPc$ M=Zn R=SO_2Ph
$4\beta(OBu)H_2Pc$ M=H_2 R=OBu
4β(OBu)ZnPc M=Zn R=OBu
$4\beta(SBu)H_2Pc$ M=H_2 R=SBu
4β(SBu)ZnPc M=Zn R=SBu
$4\beta(SPh)H_2Pc$ M=H_2 R=SPh
4β(SPh)ZnPc M=Zn R=SPh

$16(OCH_2CF_3)H_2Pc$ M=H_2 R=OCH_2CF_3
$16(OCH_2CF_3)ZnPc$ M=Zn R=OCH_2CF_3

$8\alpha(OBu)H_2Pc$ M=H_2 R=OBu
8α(OBu)ZnPc M=Zn R=OBu
$8\alpha(SBu)H_2Pc$ M=H_2 R=SBu
8α(SBu)ZnPc M=Zn R=SBu

$8\beta(OBu)H_2Pc$ M=H_2 R=OBu
8β(OBu)ZnPc M=Zn R=OBu
$8\beta(SBu)H_2Pc$ M=H_2 R=SBu
8β(SBu)ZnPc M=Zn R=SBu
8β(SPh)ZnPc M=Zn R=SPh

$4\alpha,4\beta(NO_2)H_2Pc$ M=H_2 R^1=NO_2 R^2=NO_2
$4\alpha,4\beta(NO_2)ZnPc$ M=Zn R^1=NO_2 R^2=NO_2
$4\alpha(SO_2Ph)4\beta$(t-Bu)ZnPc M=Zn R^1=SO_2Ph R^2=t-Bu
$4\alpha(SPh)4\beta(t\text{-}Bu)H_2Pc$ M=H_2 R^1=SPh R^2=t-Bu
$4\alpha(SPh)4\beta$(t-Bu)ZnPc M=Zn R^1=SPh R^2=t-Bu

Figure 1. Structures and abbreviations of phthalocyanines in this study.

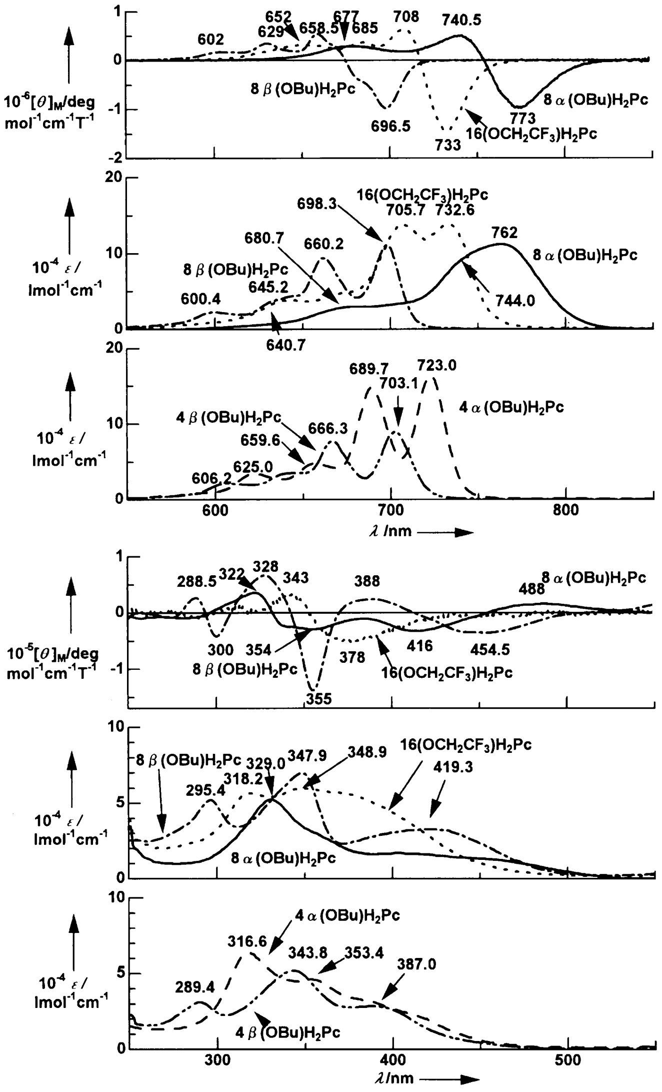


Figure 2. Electronic absorption and MCD spectra of some metal-free Pcs in THF in the Q (top) and B (Soret) band (bottom) regions.

Figure 3 shows the electronic absorption and MCD spectra of three butylthio-substituted ZnPcs as representative spectra of metalated Pcs. As for the metal-free species in Figure 2, the Q band of 4β(SBu)-, 4α(SBu)- and 8α(SBu)ZnPc shifts to longer wavelength, while, conversely, the most intense peak in the B band region of these species shifts to shorter wavelength in this order; this suggests that the configuration interaction between the B and Q states increases in this order (unfortunately, attempts to prepare 16(OCH_2CF_3)ZnPc were unsuccessful).[23] In the MCD spectra, since all compounds have D_{4h} symmetry, at least one Faraday *A* term is expected for the Q and B bands, respectively, of each compound. In the Q band region, all ZnPcs show dipersion-type *A* terms corresponding to the Q_{00} band. In the B band region, the most intense *A* terms of 4α- and 4β(SBu)ZnPc are very clear and appear at 340 and 360 nm, respectively. However, the *A* term of 8α(SBu)ZnPc is small (ca. 290–300 nm region).

While collecting absorption data of H_2Pcs substituted with various groups, we noticed a wavelength-dependent splitting of the Q band. These data are summarized in Figure 4. The splitting generally decreases with increasing wavelength of the Q band, and H_2Pcs (and metal-free naphthalocyanine) with the Q band at around 800 nm do not show apparent splitting.

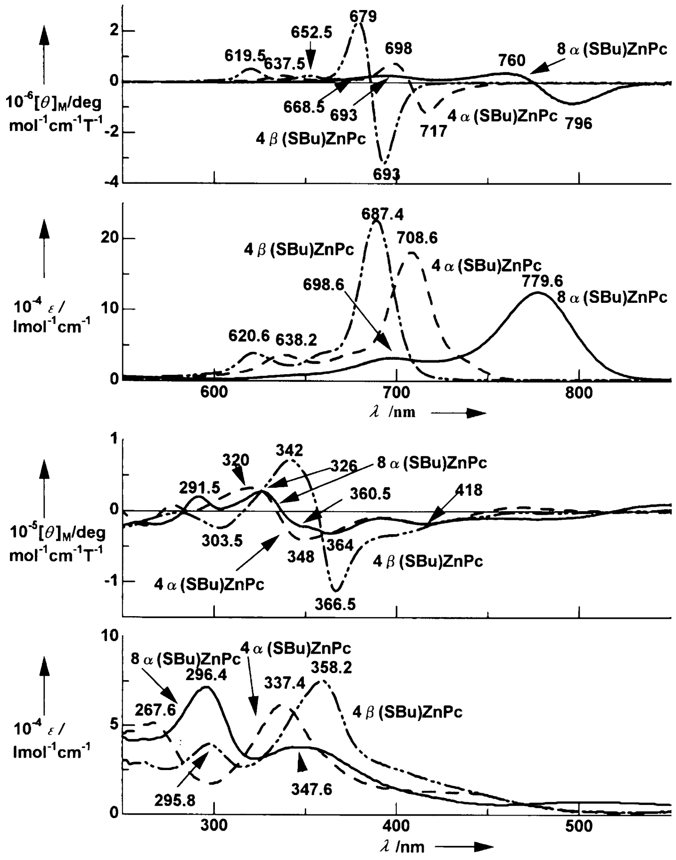


Figure 3. Electronic absorption and MCD spectra of 8α(SBu)ZnPc (solid lines), 4α(SBu)ZnPc (broken lines), and 4β(SBu)ZnPc (dotted broken lines) in THF in the Q (top) and B (Soret) band (bottom) regions.

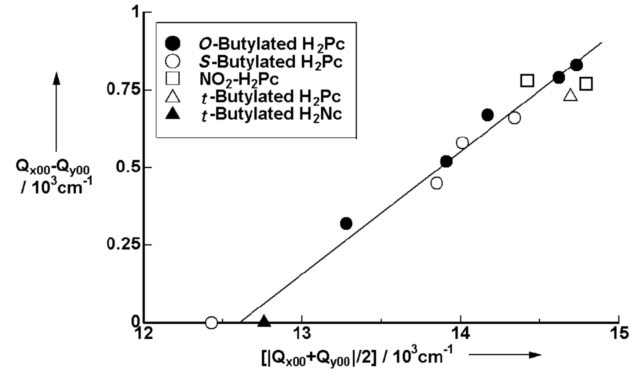


Figure 4. Correlation between the splitting of the Q band, $Q_{x00} - Q_{y00}$, and the mid-energy of the Q band ($(Q_{x00} + Q_{y00})/2$.

Experimental electronic absorption data of H_2Pcs and ZnPcs are summarized in Tables 1 and 2, respectively. Note that the absorption coefficients of unsubstituted H_2Pc and 8α(OBu)ZnPc may be not correct due to low solubility of the former and instability of the latter in solution. By subtracting the Q band energy of unsubstituted Pcs from those of substituted ones, we can calculate the effect of substituents quantitatively (in the case of metal-free species, $(Q_x + Q_y)/2$ indicates the Q band position). For electron-releasing groups,

Table 1. Electronic absorption data of metal-free phthalocyanines in THF.

	Q_x [cm^{-1}] λ [nm]	Q_y [cm^{-1}] λ [nm]	$10^{-4}\varepsilon$ [L mol^{-1}cm^{-1}]	$Q_x - Q_y$ [10^3cm^{-1}]	$0.5(Q_x + Q_y)$ [10^3cm^{-1}]	Δ [10^3cm^{-1}][a]
H_2Pc (reference)	14316.4 698.5	15048.9 664.5	–[b]	0.73	14.68	0
electron-withdrawing substituents						
4α(NO_2)H_2Pc	14409.2 694.0	15174.5 659.0	–[b]	0.77	14.79	0.11
4β(NO_2)H_2Pc	14035.1 712.5	14814.8 675.0	–[b]	0.78	14.42	−0.26
4α,4β(NO_2)H_2Pc	14035.1 712.5	14814.8 675.0	–[b]	0.78	14.42	−0.26
electron-releasing substituents						
4α(OBu)H_2Pc	13831.3 723.0	14499.1 689.7	16.57	0.67	14.17	−0.51
8α(OBu)H_2Pc	13123.4 762.0	13440.8 744.0	11.20	0.32	13.28	−1.40
4β(OBu)H_2Pc	14222.7 703.1	15008.3 666.3	8.90	0.79	14.62	−0.06
8β(OBu)H_2Pc	14320.5 698.3	15146.9 660.2	11.25	0.83	14.73	0.05
16(OCH_2CF_3)H_2Pc	13650.0 732.6	14170.3 705.7	14.35	0.52	13.91	−0.77
4α(SBu)H_2Pc	13633.3 733.5	14084.5 710.0	10.14	0.45	13.85	−0.83
8α(SBu)H_2Pc	12430.1 804.5	12430.1 804.5	13.56	0	12.43	−2.25
4β(SBu)H_2Pc	14015.4 713.5	14673.5 681.5	6.34	0.66	14.34	−0.34
8β(SBu)H_2Pc	13717.4 729.0	14295.9 699.5	4.11	0.58	14.01	−0.67
4β(SPh)H_2Pc	14094.4 709.5	14755.8 677.7	10.66	0.66	14.43	−0.25
4α(SPh)4β(*t*Bu)H_2Pc	13541 738.5	14074.6 710.5	14.35	0.53	13.81	−0.87

[a] Shift relative to the Q band energy of H_2Pc. [b] Reliable data could not be obtained because of low solubility of the compounds.

substitution at the α positions shifts the Q band to longer wavelength. Tetrasubstitution produces Q band shifts of −0.51 and −0.83 kcm^{-1} for 4α(OBu)H_2Pc and 4α(SBu)H_2Pc, respectively, relative to H_2Pc, and shifts of −0.55 and −0.80 kcm^{-1} for 4α(OBu)ZnPc and 4α(SBu)ZnPc, respectively, relative to ZnPc. These increase to −1.40, −2.25, −1.72, and −2.09 kcm^{-1} in 8α(OBu)H_2Pc, 8α(SBu)H_2Pc, 8α(OBu)ZnPc, and 8α(SBu)ZnPc, respectively. These values indicate, for example, that the effect of a thioether group is about 1.45–1.62 times larger than that of the alkoxyl groups, and that the magnitude of the shift due to the second four substituents is about 1.6–2.0 times larger than that owing to the first four substituents. According to symmetry-adapted perturbation theory,[15] which is a first-order perturbation theory, the shifts in the Q band produced by increasing the number of substituent groups from zero to four and from four to eight are expected to be the same. The value of 1.6–2.0 therefore suggests the presence of a higher order perturbation in the second tetrasubstitution at the α positions.

The substituent effect at the β positions is much smaller than that in the α positions, and appears different for alkoxyl and thioether groups. In the case of alkoxyl groups, the shift in the Q band of 4β(OBu)H_2Pc and 8β(OBu)H_2Pc relative to the Q band of H_2Pc is less than ±0.06 kcm^{-1}, while those of 4β(SBu)H_2Pc and 8β(SBu)H_2Pc are −0.34 and −0.67 kcm^{-1}, respectively. Thus, substitution by thioalkyl groups slightly shifts the Q band to longer wavelength, and the size of the shift approximately pararells the number of substituent groups. Since the position of the Q band of 8α(OBu)-, 16(OCH_2CF_3)-, and 8β(OBu)H_2Pc changes from longer to shorter wavelength, we suggest that substitution by electron-releasing groups at the β positions essentially moves the Q band to shorter wavelength. The slight longer wavelength shift due to alkylthio groups may reflect the increase of the size of effective π system, since the 3p orbital of sulfur is known to mix well with the π orbital of tetraazaporphyrins.[24]

The effect of electron-withdrawing groups is the opposite of that of electron-releasing groups. As can be seen in the comparison of 4α(NO_2)- and 4β(NO_2)H_2Pcs and -ZnPcs, substitution at α or β positions shifts the Q band to shorter or longer wavelength, respectively. However, the magnitude of the shift for substitution at β positions is not necessarily small compared with that at α positions [cf., for example, the data of 4α- (0.15 kcm^{-1}) and 4β(SO_2Ph)ZnPc (−0.14 kcm^{-1})], in contrast to the above cases of electron-releasing groups.

Fluorescence emission and ring-current strength: Like other metal-free and ZnPcs,[25] all compounds in this study show fluorescence emission from the S1 state. Figure 5 displays the correlation between the wavenumber of fluorescence maximum and quantum yield of 35 Pcs. The following facts emerge from this figure: 1) Pcs showing emission peaks at

Table 2. Electronic absorption data of zinc phthalocyanines in THF.

	$Q_{0\text{-}0}$ [cm^{-1}] λ [nm]	$10^{-4}\varepsilon$ [L mol^{-1} cm^{-1}] at Q_x	Δ [10^3cm^{-1}][a]
ZnPc (reference)	14914.2 670.5	28.00	0
	electron-withdrawing substituents		
4α(NO_2)ZnPc	14943.2 669.2	14.41	0.03
4β(NO_2)ZnPc	14903.1 671.0	–[b]	– 0.01
4α,4β(NO_2)ZnPc	14836.7 674.0	–[b]	– 0.08
4α(SO_2Ph)ZnPc	15060.2 664.0	9.48	0.15
4β(SO_2Ph)ZnPc	14777.6 676.7	17.86	– 0.14
4α(SO_2Ph)4β(*t*Bu)ZnPc	14961.1 668.4	22.22	0.05
	electron-releasing substituents		
4α(OBu)ZnPc	14370.0 696.0	17.26	– 0.55
8α(OBu)ZnPc[c]	13190.0 758.0	17.58	– 1.72
4β(OBu)ZnPc	14830.0 674.5	13.35	– 0.09
8β(OBu)ZnPc	14830.0 674.5	20.42	– 0.09
16(OCH_2CF_3)ZnPc	14144.3 707.0	15.26	– 0.77
4α(SBu)ZnPc	14112.3 708.6	18.30	– 0.80
8α(SBu)ZnPc	12827.1 779.6	12.45	– 2.09
4β(SBu)ZnPc	14547.6 687.4	22.88	– 0.37
8β(SBu)ZnPc	14144.3 707.0	13.91	– 0.77
4α(SPh)ZnPc	14150.3 706.7	25.81	– 0.76
4β(SPh)ZnPc	14609.2 684.5	29.21	– 0.31
8β(SPh)ZnPc	14128.3 707.8	24.88	– 0.79
4α(SPh)4β(*t*Bu)ZnPc	14094.4 709.5	24.20	– 0.82

[a] Shift relative to the Q band energy of H_2Pc. [b] Reliable data could not be obtained because of low solubility of the compounds. [c] Because of instability of the solution in THF, spectrum was recorded in pyridine.

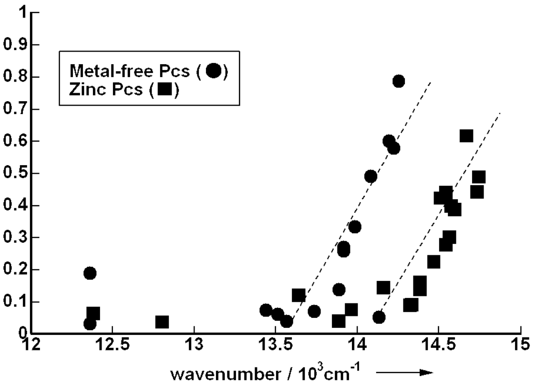


Figure 5. Correlation between wavenumber of fluorescence peak maximum and quantum yield Φ_F of S1 fluorescence.

shorter wavelength have higher quantum yields; 2) the quantum yields of metal-free Pcs are generally higher, even though their emission maxima appear at lower energy than those of the corresponding ZnPcs; and 3) Pcs showing S1 emission maxima at wavelengths longer than about 740 nm generally have quantum yields of less than 0.1. Point 1) suggests that nonradiative decay becomes more difficult as the energy gap increases between the HOMO and the LUMO, and 2) is due to the heavy-atom effect of zinc. A relation such as that in point 3) has not been reported to date. The data for S1 emissions of H_2- and ZnPcs are summarized in Tables 3 and 4.

Figure 6 shows the relationship between the position of the Q_{00} band and pyrrole proton signals of alkoxy- and alkylthio-substituted H_2Pcs in the ^{1}H NMR spectra. In compounds such as porphyrins and Pcs, pyrrole protons appear with negative chemical shifts due to the ring current of the macrocycle.

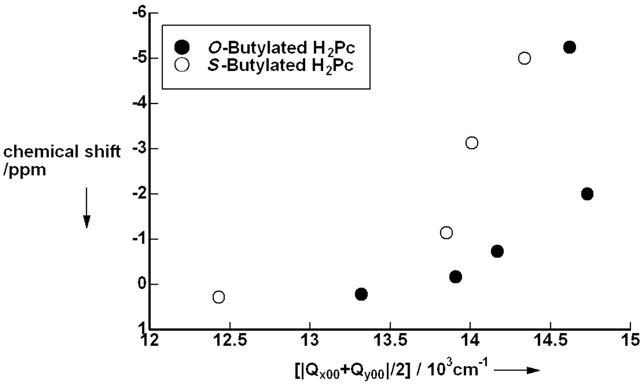


Figure 6. Correlation between chemical shift [ppm] of the pyrrole proton and the mid-energy of the Q band ($Q_{x00}+Q_{y00}$)/2 [cm^{-1}] of metal-free Pcs.

Table 3. S1 fluorescence emission data of metal-free phthalocyanines in THF.

	Excitation wavelength λ [nm]	Fluorescence peak maximum λ[nm]	Fluorescence lifetime [ns]	Φ	Excitation peak maximum λ [nm]	Stokes shift [10^3cm^{-1}]
H_2Pc (reference)	640	704.5		0.600		
		electron-withdrawing substituents				
4α(NO_2)H_2Pc	640	701.5	7.36	0.787	696	0.11
4β(NO_2)H_2Pc	640	718.5	5.72	0.270	715	0.07
4α,4β(NO_2)H_2Pc	640	718.5	5.62	0.258	715.5	0.06
4α(OBu)H_2Pc	633	729.2	4.85	0.070	722.6	0.13
8α(OBu)H_2Pc	700	809	3.80	0.189	741	1.13
4β(OBu)H_2Pc	625	710	7.78	0.490	704.5	0.11
8β(OBu)H_2Pc	633	703	8.83	0.579	699.5	0.07
		electron-releasing substituents				
16(OCH_2CF_3)H_2Pc	633	740	10.8	0.0607	733.8	0.11
4α(SBu)H_2Pc	630	737	4.54	0.038	736.5	0.01
8α(SBu)H_2Pc	722.5	809	1.31	0.032	738	1.19
4β(SBu)H_2Pc	630	720	6.30	0.138	718	0.04
8β(SBu)H_2Pc	630	733.4	4.34	0.052	726.8	0.12
4β(SPh)H_2Pc	640	715	6.44	0.334	714	0.02
4α(SPh)4β(*t*Bu)H_2Pc	640	744	4.79	0.073	740.8	0.06

Table 4. S1 fluorescence emission data of zinc phthalocyanines in THF.

	Excitation wavelength λ [nm]	Fluorescence peak maximum λ [nm]	Fluorescence lifetime [ns]	Φ	Excitation peak maximum λ [nm]	Stokes shift [$10^3 cm^{-1}$]
ZnPc (reference)	620	686.5	4.36	0.300		
electron-withdrawing substituents						
$4\alpha(NO_2)$ZnPc	608	678	4.63	0.488	672.5	0.12
$4\beta(NO_2)$ZnPc	612.5	695	3.83	0.159	691	0.08
$4\alpha,4\beta(NO_2)$ZnPc	612.5	698	3.36	0.088	691	0.15
$4\alpha(SO_2Ph)$ZnPc	608	720	4.69	0.038	714.5	0.11
$4\beta(SO_2Ph)$ZnPc	608	686	4.35	0.397	684.5	0.03
$4\alpha(SO_2Ph)4\beta(t$Bu)ZnPc	608	678.5	3.98	0.441	672.5	0.13
4α(OBu)ZnPc	633	706	3.05(81 %) 4.53 (19 %)	0.143	696	0.20
8α(OBu)ZnPc	675	807.5	0.57	0.062	739	1.15
electron-releasing substituents						
4β(OBu)ZnPc	633	689	5.31 (88 %) 1.51 (12 %)	0.422	687.6	0.03
8β(OBu)ZnPc	633	681.5	4.39	0.616	676.4	0.11
$16(OCH_2CF_3)$ZnPc	633	716	3.93	0.0745	713	0.06
4α(SBu)ZnPc	630	718.2	2.63	0.137	708	0.20
8α(SBu)ZnPc	700	781	1.58	0.036	712.5	1.23
4β(SBu)ZnPc	630	685	3.93	0.386	683.5	0.03
8β(SBu)ZnPc	630	733	3.18	0.119	700	0.64
4α(SPh)ZnPc	620	687.5	2.65	0.276	686.5	0.02
4β(SPh)ZnPc	620	687.5	3.93	0.439	684	0.08
8β(SPh)ZnPc	620	721.2	3.35	0.090	713.2	0.16
$4\alpha(SPh)4\beta(t$Bu)ZnPc	620	727.4	3.05	0.224	721.8	0.11

Interestingly, as seen in this figure, H_2Pcs having Q bands at longer wavelength show lower ring currents. This type of relationship has not been reported to date.

Molecular orbital calculations: To enhance our understanding on the effect of substituents, we carried out molecular orbital (MO) calculations on several alkylthio- and alkoxy-substituted (pyrrole-proton-deprotonated) H_2Pc species within the framework of the Pariser–Parr–Pople (PPP) approximations.[26] The calculated electronic absorption spectra are shown in Figure 7, and transition energies, oscillator strengths *f*, and configurations are summarized in Table 5. The experimental order of the wavelengths of the Q band according to the type of substituents is well reproduced by the calculation; the Q band shifts to longer wavelength in the order of unsubstituted, 8β(O-alkyl)-, 8β(S-alkyl)-, 16(O-alkyl)-, 16(S-alkyl)-, 8α(O-alkyl)-, and 8α(S-alkyl)-Pcs. For these species, the estimated wavelengths were 662, 685, 694, 738, 744, 770, and 799 nm, while the experimental values of zinc Pcs in THF were, 671, 675, 707, 707, [no datum], 758, and 780 nm. In all cases the Q band shifts to longer wavelength on introduction of electron-releasing groups. A comparison of the corresponding alkoxy- and alkylthio-substituted species shows that the Q band of the latter appears at longer wavelength, and its intensity is higher than that of the former. In addition, the intensities of the Q band of hexadecasubstituted species were calculated to be about 30–50 % stronger than those of the octasubstituted species. Among the octasubstituted species, the intensity of those substituted at α positions is stronger by several tens of percent than those substituted at β positions.

It is empirically known that the B band of Pcs is about twice as strong as the Q band.[27] This feature is reproduced for unsubstituted and octaalkoxy β-substituted Pcs. However, Pcs having the Q band at longer wavelength, such as 8α- and 16(O- or S-alkyl)Pcs, were calculated to have split and broad B bands. In particular, this trend is more evident for alkylthio-substituted species, for which one of the split components is expected to appear midway between the Q and B bands, as is indeed observed for 8α(SBu)ZnPc at about 500 nm. Another important point is that the most intense B band of 8α(S-alkyl)Pc is expected to lie at the shortest wavelength among alkoxy- and alkylthio-substituted Pcs. Indeed, as seen in the absorption spectra in Figure 3, the most intense B band of 8α(SBu)ZnPc lies at wavelength shorter than 300 nm. Thus, Pcs which have the Q band at longer wavelengths generally have the B band at shorter wavelengths, and this indicates that the configuration interaction in these Pcs is stronger than that in Pcs which have the Q band at shorter wavelengths. This type of relationship was recently substantiated for ZnPc, ZnNc, and their intermediate compounds.[28]

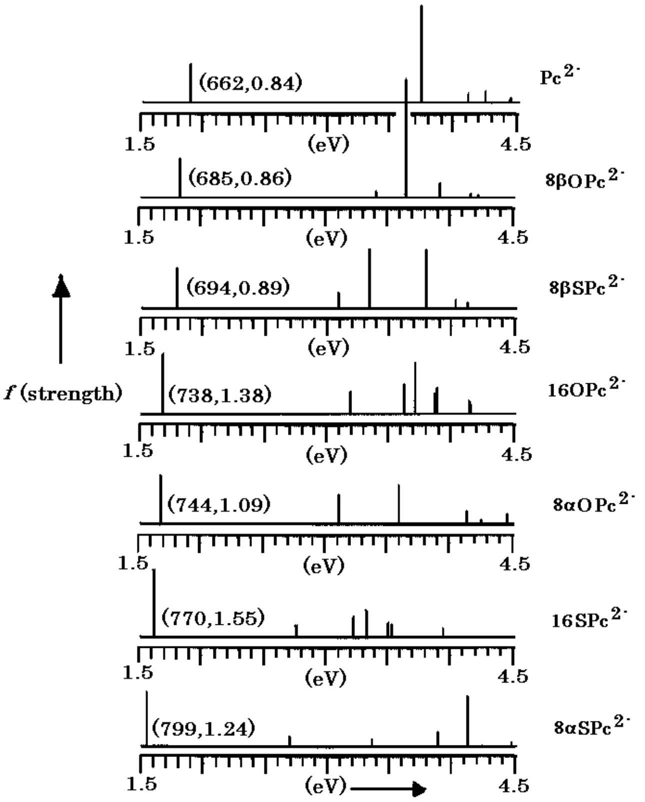


Figure 7. Calculated transition energies and oscillator strengths *f* for pyrrole-proton-deprotonated Pcs (Pc^{2-}). Numbers indicate the values of the Q band.

Table 5. Calculated transition energies, oscillator strengths *f*, and configurations.[a]

Energy [nm]	*f*	Configurations
Pc^{2-}		
662	0.84	21 → 22(87 %) 20 → 23(12 %)
662	0.84	21 → 23(87 %) 20 → 22(12 %)
332	2.19	20 → 23(67 %) 13 → 23(12 %) 21 → 22(11 %)
332	2.19	20 → 22(67 %) 13 → 22(12 %) 21 → 23(11 %)
302	0.25	16 → 22(23 %) 21 → 27(20 %) 13 → 22(15 %) 16 → 23(14 %) 21 → 26(12 %)
302	0.25	16 → 23(23 %) 21 → 26(20 %) 13 → 23(15 %) 16 → 22(14 %) 21 → 27(12 %)
$8\beta OPc^{2-}$		
685	0.86	29 → 30(87 %)
685	0.86	29 → 31(87 %)
366	0.16	25 → 31(47 %) 28 → 31(20 %) 24 → 31(20 %)
366	0.16	25 → 30(47 %) 28 → 30(20 %) 24 → 30(20 %)
342	2.65	28 → 30(57 %) 25 → 30(14 %)
342	2.65	28 → 31(57 %) 25 → 31(14 %)
318	0.34	24 → 30(54 %) 21 → 31(19 %) 25 → 30(18 %)
318	0.34	24 → 31(54 %) 21 → 30(19 %) 25 → 31(18 %)
$8\beta SPc^{2-}$		
694	0.89	29 → 31(87 %)
694	0.89	29 → 30(87 %)
402	0.38	25 → 31(35 %) 28 → 31(31 %)
402	0.38	25 → 30(35 %) 28 → 30(31 %)
371	1.35	28 → 30(50 %) 25 → 30(41 %)
371	1.35	28 → 31(50 %) 25 → 31(41 %)
327	1.32	24 → 31(58 %) 21 → 30(29 %)
327	1.32	24 → 30(58 %) 21 → 31(29 %)
308	0.21	21 → 31(49 %) 24 → 30(20 %)
308	0.21	21 → 30(49 %) 24 → 31(20 %)
$16OPc^{2-}$		
738	1.38	37 → 38(94 %)
738	1.38	37 → 39(94 %)
389	0.53	36 → 39(88 %)
389	0.27	36 → 38(92 %)
342	0.70	33 → 38(45 %) 32 → 38(31 %)
335	1.15	33 → 39(69 %) 32 → 39(15 %)
320	0.48	32 → 39(78 %) 33 → 39(18 %)
320	0.60	32 → 58(59 %) 33 → 38(38 %)
$8\alpha OPc^{2-}$		
744	1.09	29 → 30(76 %) 29 → 31(14 %)
744	1.09	29 → 31(76 %) 29 → 30(14 %)
399	0.67	28 → 30(70 %) 28 → 31(12 %)
399	0.67	28 → 31(70 %) 28 → 30(12 %)
345	0.93	25 → 30(53 %) 24 → 31(21 %) 28 → 30(10 %)
345	0.93	25 → 31(53 %) 24 → 30(21 %) 28 → 31(10 %)
301	0.35	24 → 30(40 %) 24 → 31(20 %) 25 → 31(10 %)
301	0.35	24 → 31(40 %) 24 → 30(20 %) 25 → 30(10 %)
$16SPc^{2-}$		
770	1.55	37 → 38(95 %)
770	1.55	37 → 39(95 %)
449	0.30	36 → 39(92 %)
449	0.15	36 → 38(94 %)
386	0.52	33 → 38(47 %) 32 → 38(39 %)
373	0.62	33 → 39(59 %) 32 → 39(34 %)
354	0.38	32 → 39(63 %) 33 → 39(35 %)
351	0.32	32 → 38(55 %) 33 → 38(44 %)
315	0.26	37 → 42(93 %)
315	0.23	37 → 43(94 %)
$8\alpha SPc^{2}$		
799	1.24	29 → 30(92 %)
799	1.24	29 → 31(92 %)
460	0.26	28 → 30(91 %)
460	0.26	29 → 31(91 %)
369	0.19	25 → 30(67 %) 24 → 31(24 %)
369	0.19	25 → 31(67 %) 24 → 30(24 %)
319	0.35	29 → 34(21 %) 29 → 35(20 %) 24 → 30(16 %) 24 → 31(16 %)
319	0.35	29 → 35(21 %) 29 → 34(20 %) 24 → 31(16 %) 24 → 30(16 %)
301	1.18	29 → 34(22 %) 24 → 31(17 %) 23 → 31(16 %) 29 → 35(12 %)
301	1.18	29 → 35(22 %) 24 → 30(17 %) 23 → 30(16 %) 29 → 34(12 %)

[a] Excited states with energy less than about 3.9 eV and *f* greater than 0.15 are shown.

The numbers of configurations in Table 5 further suggest that the purity of the Q band increases for species having the Q band at longer wavelengths.

Figure 8 shows some frontier orbitals of representative species. As previously reported,[27] the HOMO and next HOMO of general Pcs have a_{1u} and a_{2u} symmetry, respectively, in the D_{4h} point group. However, one of the most important features in this figure is that the next HOMO of Pcs having the Q band at longer wavelength, such as 8α(O- or S-alkyl)- and 16(O- or S-alkyl)Pcs, has b_{1u} symmetry, which is generally the 4th or lower HOMO in Pcs having the Q band at shorter wavelength (see also Figure 9). Data in Table 5 and Figure 8 therefore suggest that the second lowest transition for 8α(O- or S-alkyl)- and 16(O- or S-alkyl)Pcs is a transition from this b_{1u} orbital to the LUMO or LUMO + 1. In accord with this assignment, a Faraday *A* term is seen for the 500 nm band of 8α(SBu)ZnPc (Figure 3).

Figure 9 displays a partial molecular orbital energy diagram for some Pcs substituted with O- or S-alkyl groups. The following points emerge from the inspection of this figure: 1) substitution at the β positions raises the energy of all frontier orbitals; 2) this effect is slightly more pronounced for the HOMO than for the LUMO; 3) this effect is more pronounced for S-alkyl- than for O-alkyl-substituted Pcs; 4) compared with substitution at β positions, that at α positions results in larger destabilization of the HOMO and slight destabilization of the LUMO; 5) substitution at the α positions lifts a low-lying b_{1u} orbital (the 4th HOMO in unsubstituted Pc) significantly, so that it becomes the HOMO – 1; and 6) the energy gap between the HOMO and LUMO decreases in the following order: unsubstituted Pc ≈ 8β(O-alkyl)

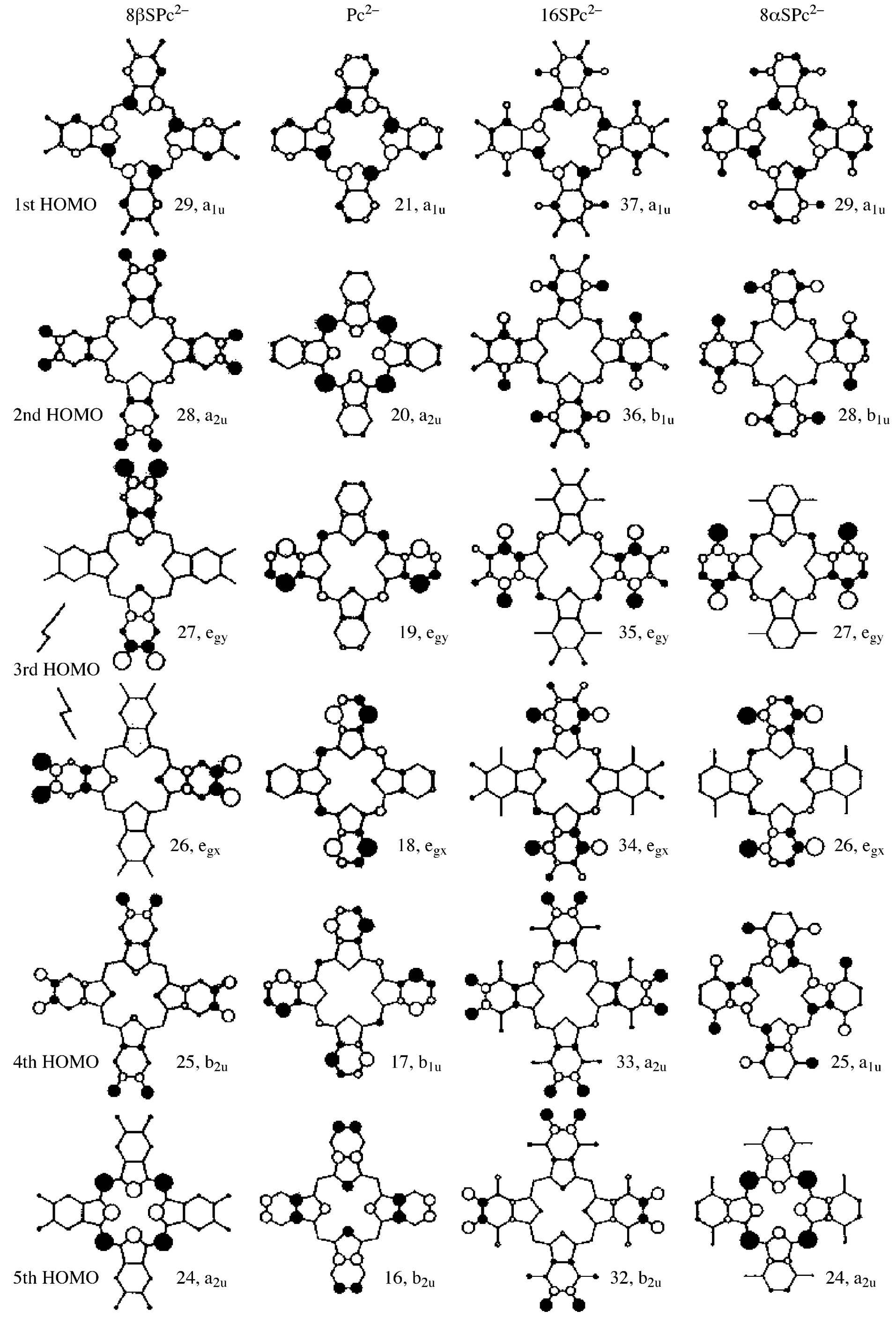


Figure 8. Some frontier orbitals of pyrrole-proton-deprotonated $8\beta SPc^{2-}$, Pc^{2-}, $16SPc^{2-}$, and $8\alpha SPc^{2-}$.

$> 8\beta$(S-alkyl) $>$ 16(O-alkyl) $\approx 8\alpha$(O-alkyl) $>$ 16(S-alkyl) $\approx 8\alpha$-(S-alkyl). Of these, points 3) and 4) are consistent with experiments, since the Q band is nearly described as a single transition from the HOMO to LUMO.

Conclusion

The effect of substituents on the position and intensity of the electronic absorption and fluorescence spectra of phthalocyanines has been examined for 35 Pc compounds. These compounds differ from each other in the number, position, and electrostatic effect of the substituents. As electron-releasing groups, mostly alkoxyl and alkyl(phenyl)thio groups were used, while as electron-withdrawing groups, nitro and phenylsulfonyl groups were employed. When electron-releasing groups are bound to four α-benzo positions of the Pc skeleton, the B and Q bands shift to longer wavelength. Relative to this shift, the effect of introducing the same electron-releasing groups at the other four α positions amounts to about 1.6–2.0. Although the effect is not always clearly seen, introduction of electron-releasing groups in the β-benzo positions of the Pc skeleton generally shifts the Q band to shorter wavelength. The effect of electron-withdrawing groups is exactly the opposite, that is, four such groups in α or β positions shift the Q band to shorter and longer wavelength, respectively. These effects can be reasonably explained by taking into account the size of the carbon atomic orbital coefficients derived from the molecular orbital calculations. Specifically, since the coefficients of α carbon atoms are larger than those of the β carbon atoms in the HOMO, the extent of destabilization of this orbital by introducing electron-releasing groups is larger when they are linked to the α positions, which makes the HOMO–LUMO gap smaller. As a result, the Q band, which is composed mainly of the HOMO–LUMO transition, shifts to longer wavelength, particularly when the electron-releasing groups are introduced at the α positions. The following intriguing phenomena were observed in the experiments:

1) The splitting of the Q band of metal-free species decreases with increasing wavelength of the Q band.
2) Judging from the pyrrole proton signals in the ^{1}H NMR spectra, the ring current of Pcs which have the Q band at longer wavelength have smaller ring currents.
3) The absorption coefficients of the Q bands of Pcs with 16 electron-releasing substituents are larger than those of the

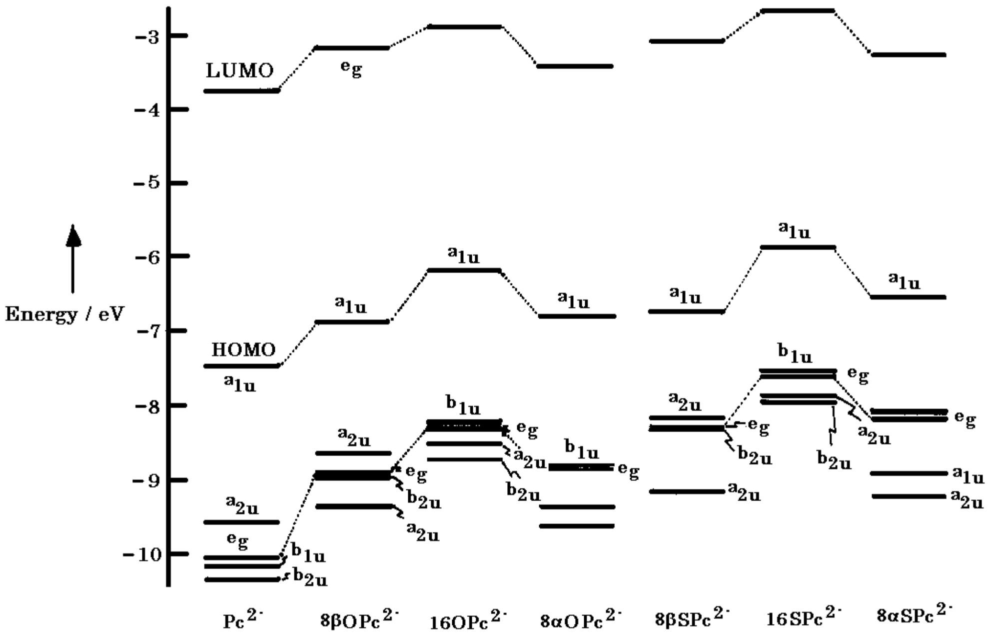


Figure 9. Partial energy diagram obtained by PPP calculations for the pyrrole-proton-deprotonated Pcs (Pc^{2-}).

corresponding tetra- and octasubstituted Pcs by several tens of percent.

4) Pcs showing S1 emission maxima at wavelengths longer than about 740 nm generally have quantum yields of less than 0.1.

Molecular orbital calculations within the framework of the PPP approximations reproduced observations in points 1) and 3) and furthermore suggest that the absorption coefficient of the Q band of Pcs substituted by more strongly electron releasing substituents is larger. The second HOMO of Pcs showing the Q band at longer wavelength has b_{1u} symmetry, in contrast to the a_{2u} symmetry of normal Pcs.

Experimental Section

Measurements: Electronic spectra were measured with a Hitachi U-3410 spectrophotometer. Magnetic circular dichroism (MCD) measurements were made with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields of up to 1.09 T with parallel and antiparallel fields. Its magnitude was expressed in terms of molar ellipticity per tesla $[\theta]_M/10^4$ deg mol^{-1} dm^3 cm^{-1} T^{-1}. The 400 MHz ^{1}H NMR spectra were recorded in $CDCl_3$ on a JEOL GSX-400 spectrometer.

Method of calculation: The Pc structures were constructed from standard phthalocyanine X-ray structural data[29] and by making the ring perfectly planar and adopting D_{4h} symmetry. Molecular orbital (MO) calculations were performed for the pyrrole proton-deprotonated dianionic species within the framework of the Pariser–Parr–Pople (PPP) approximation[30] with employment of recently published semiempirical parameters.[31] These are atomic valence state ionization potentials of 11.16 (carbon), 20.21 (central nitrogen), and 14.21 eV (imino nitrogen), together with atomic valence affinities of 0.03 (carbon), 5.32 (central nitrogen), and 1.78 eV (imino nitrogen). The central nitrogen atoms were assumed to be equivalent, supplying 1.5 electrons each to the π system. In addition, σ polarizability was taken into account according to Hammond.[32a] Resonance integrals were taken to be -2.48 (β_{CN}) and -2.42 (β_{CC}).[31] Two-center repulsion integrals were calculated by the method of Mataga and Nishimoto.[32b] The choice of configuration was based on energetic considerations, and all singly excited configurations up to 56458 cm^{-1} were included.

Chemicals: THF was distilled from sodium. DMF, *n*-pentanol, *n*-butanol, and 1-hexanol were dried over activated 4 Å molecular shieves. Pyridine was dried over KOH and distilled. All other commercially available reagents and solvent were used without further treatment.

The following phthalonitrile (1,2-dicyanobenzene) starting materials were synthesized according to published procedures: 3,6-[33a] and 4,5-dibutyloxy-,[33b] 4-butylthio-,[33c] 4,5-dibutylthio-,[33d] 3- and 4-phenylthio-,[33e] 3-*tert*-butyl-5-phenylthio- and 3-*tert*-butyl-5-phenylsulfonyl-,[33f] and 3,4,5,6-tetrakis(2′,2′,2′-trifluoroethoxy)-1,2-dicyanobenzene.[33g] 3-*n*-Butyloxy-1,2-dicyanobenzene, 3-*n*-butylthio-1,2-dicyanobenzene, and 4-*n*-butylthio-1,2-dicyanobenzene were prepared by a minor modification of the procedure of Leznoff et al.[34] for the preparation of alkoxy- and alkylthio-substituted phthalonitriles. Phthalocyanines not listed below were reported in earlier work.[33e–g]

3-*n*-Butyloxy-1,2-dicyanobenzene: The crude product was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:1) as eluant to give a 47.3 % yield of a white solid of 3-butyloxy-1,2-dicyanobenzene. M.p. 131–132 °C; elemental analysis (%) calcd for $C_{12}H_{12}N_2O$ (200.24): C 71.98, H 6.04, N 13.99; found: C 72.07, H 6.11, N 14.19; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.58-2.07$ (m, 7H; $CH_2CH_2CH_3$), 3.75–4.38 (m, 2H; OCH_2), 6.85–7.75 ppm (m, 3H; Ar-H).

3-*n*-Butylthio-1,2-dicyanobenzene: The crude product was recrystallized from ethanol to give a 95 % yield of white needles. M.p. 70–71 °C; elemental analysis (%) calcd for $C_{12}H_{12}N_2S$ (216.31): C 66.63, H 5.59, N 12.95, S, 14.82; found: C 66.49, H 5.62, N 12.93, S 14.52; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.61$ (t, 3H; CH_3), 1.49 (tq, 2H; $S(CH_2)_2CH_2$), 1.69 (tt, 2H; SCH_2CH_2), 3.05 (t, 2H; SCH_2), 7.51–7.62 ppm (m, 3H; Ar-H).

4-*n*-Butylthio-1,2-dicyanobenzene: After recrystallization from ethanol, this compound was obtained as off-white needles in 93 % yield. M.p. 62–63 °C; elemental analysis (%) calcd for $C_{12}H_{12}N_2S$ (216.31): C 66.63, H 5.59, N 12.95, S, 14.82; found: C 66.43, H 5.55, N 12.78, S 14.82; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.97$ (t, 3H; CH_3), 1.50 (tq, 2H; $S(CH_2)_2CH_2$), 1.70 (tt, 2H; SCH_2CH_2), 3.01 (t, 2H; SCH_2), 7.48 (d, 1H; Ar-H, C6), 7.54 (s, 1H; Ar-H, C2), 7.63 ppm (d, 1H; Ar-H, C5).

1,2-Dicyano-3,6-bis(trifluorosulfonyl)benzene: Triethylamine (5.0 mL, 36 mmol), CH_2Cl_2 (25 mL), and dimethylaminopyridine (0.20 g, 1.6 mmol) were added to 2,3-dicyanohydroquinone (2.4 g, 15 mmol) under nitrogen while maintaining the temperature of the reaction mixture below −70 °C, and the mixture was stirred for 24 h. Trifluoromethanesulfonic anhydride (6.0 mL, 37 mmol) was added dropwise, and the mixture stirred for 24 h. The reaction mixture was poured into CH_2Cl_2 (200 mL), 0.5 N HCl (5 mL) added, and the organic layer separated and evaporated under reduced pressure. The residue was subjected to chromatography on a silica gel column with $CHCl_3$ as eluent to give in 85 % yield 5.4 g of white needles. M.p. 106 – 107 °C; elemental analysis (%) calcd for $C_{10}F_6H_2N_6O_6S_2$ (424.26): C 28.31, H 0.48, N 6.60, S 15.12; found: C 28.02, H 0.82, N 7.77, S 15.24; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.87$ ppm (s, 2H; Ar-H).

1,2-Dicyano-3,6-dibutylthiobenzene: 1,2-Dicyano-3,6-bis(trifluorosulfonyl)benzene (3.0 g, 7.0 mmol) was added to a dry DMF (10 mL) solution containing K_2CO_3 (1.2 g, 8.8 mmol) and butylmercaptan (1.4 g, 15 mmol), and the solution was stirred at room temperature with slight bubbling of nitrogen for 5 h, after which K_2CO_3 (1.2 g, 8.8 mmol) was added again, and stirring continued for further 48 h. The reaction mixture was poured into water (200 mL), and the solid collected by filtration and washed with water. After recrystallization of the solid from ethanol, 0.40 g (19 % yield) of the desired dinitrile was obtained as pale yellowish needles. M.p. 85 – 86 °C; elemental analysis (%) calcd for $C_{16}H_{20}N_2S_2$ (304.48): C 63.12, H 6.62, N 9.20, S 21.06; found: C 62.86, H 6.64, N 9.03, S 20.91; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.94$ (t, 6H; CH_3), 1.48 (tq, 4H; $S(CH_2)_2CH_2$), 1.66 (tt, 4H; SCH_2CH_2), 3.02 (t, 4H; SCH_2), 7.50 ppm (m, 2H; Ar-H).

1,2-Dicyano-4,5-diphenylthiobenzene: A mixture of 1,2-dicyano-4,5-diiodobenzene[35] (195 mg, 1 mmol), thiophenol (660 mg, 6 mmol), and K_2CO_3 (2.36 g, 32 mmol) in dry DMSO (2 mL) was heated at 90 °C for 30 min.[36] After cooling, ice was added, and the precipitated yellow solid was filtered off, and subjected to chromatography on silica with hexane/CH_2Cl_2 (3:10) to give a 61 % yield (211 mg) of the desired dinitrile as a while solid. M.p. 197 – 199 °C; elemental analysis (%) calcd for $C_{20}H_{12}N_2S_2$ (344.47): C 69.74, H 3.51, N 8.13, S 18.62; found: C 69.47, H 3.70, N 7.90, S 18.46. ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 6.99$ (s, 2H; Ar-H), 7.26 – 7.57 ppm (m, 10H; Ar-H).

4α(OBu)H$_2$Pc (mixture of regioisomers): A mixture of lithium (30 mg, 4.32 mmol) and 3-*n*-butyloxy-1,2-dicyanobenzene (500 mg, 2.5 mmol) in dry *n*-pentanol (3 mL) was refluxed for 3 h, the solvent was evaporated to about half-volume under reduced pressure, and the solution was refluxed for a further 40 min. After removing the solvent under vacuum, the residue was subjected to chromatography on a silica gel column with CH_2Cl_2 as eluent to give a 25.9 % yield (130 mg) of a blue solid. Elemental analysis (%) calcd for $C_{48}H_{50}N_8O_4$(802.98): C 71.80, H 6.28, N 13.95; found: C 70.78, H 6.44, N 13.69; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = -0.73$ (m, 2H; pyrrole), 1.13 – 1.40 (m, 12H; CH_3), 1.70 – 2.15 (m, 8H; CH_2), 2.22 – 2.47 (m, 8H; CH_2), 4.40 – 5.00 (m, 8H; OCH_2), 7.20 – 8.10 (m, 8H; Ar-H), 8.30 – 9.00 ppm (m, 4H; Ar-H).

4β(OBu)H$_2$Pc (mixture of regioisomers): This compound was prepared by the procedure described for 4α(OBu)H$_2$Pc, but with 4-*n*-butyloxy-1,2-dicyanobenzene (500 mg, 2.5 mmol) in place of 3-*n*-butyloxy-1,2-dicyanobenzene. Yield: 120 mg (23.9 %); elemental analysis (%) calcd for $C_{48}H_{50}N_8O_4$(802.98): C 71.80, H 6.28, N 13.95; found: C 69.70, H 6.21, N 13.12. ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = -5.24$ (s, 2H; pyrrole), 1.18 – 1.27 (t, 12H; CH_3), 1.68 – 1.79 (m, 8H; CH_2), 1.93 – 2.04 (m, 8H; CH_2), 3.90 – 4.15 (t, 8H; OCH_2), 6.60 – 8.00 ppm (m, 12H; Ar-H).

4α(OBu)ZnPc and 4β(OBu)ZnPc (mixtures of regioisomers): 4α(OBu)H$_2$Pc or 4β(OBu)H$_2$Pc (50 mg, 0.062 mmol) and an approximately equal volume of Zn(OAc)$_2$ were refluxed in a mixture of 1,2-dichloroethane (3 mL) and ethanol (3 mL) for 18 h in the dark. After evaporation of the solvent, the residue was subjected to chromatography on an alumina column with CH_2Cl_2 as eluent. The green-blue fraction was recrystallized from CH_2Cl_2/hexane to yield 16 mg (4α(OBu)ZnPc) or 18 mg (4β(OBu)ZnPc) of a blue-green powder (29.7 and 33.4 %, respectively). Elemental analysis (%) calcd for $C_{48}H_{48}N_8O_4Zn$ (866.34): C 66.55, H 5.58, N 12.93; found for 4α(OBu)ZnPc: C 66.94, H 6.11, N 12.00; found for 4β(OBu)ZnPc: C 67.40, H 6.01, N 12.30.

8α- and 8β(OBu)H$_2$Pc: These compounds were obtained from 3,6- and 4,5-dibutyloxy-1,2-dicyanobenzene, respectively, by a method reported in the literature.[33a, b] Elemental analysis (%) calcd for $C_{64}H_{82}N_8O_8$ (1091.41): C 70.43, H 7.57, N 10.27; found for 8α(OBu)H$_2$Pc: C 70.07, H 7.63, N 10.09; found for 8β(OBu)H$_2$Pc: C 70.14, H 7.60, N 10.34. In the case of 8α(OBu)H$_2$Pc, prolonged heating in *n*-pentanol causes substitution of some of butoxyl groups by pentyl groups so that reaction in *n*-butyl alchohol appears safer.

8α- and 8β(OBu)ZnPc: These compounds were obtained as for 4α(OBu)ZnPc and 4β(OBu)ZnPc by zinc insertion into 8α- and 8β(OBu)H$_2$Pc in 15.5 and ca. 30 % yield, respectively. Elemental analysis (%) calcd for $C_{64}H_{80}N_8O_8Zn$ (1154.77): C 66.57, H 6.98, N 9.70; found for 8α(OBu)ZnPc: C 67.44, H 7.37, N 9.68; found for 8β(OBu)ZnPc: C 67.31, H 7.51, N 8.93. 8α(OBu)ZnPc is unstable in solution and in air.

16(OCH$_2$CF$_3$)H$_2$Pc and 16(OCH$_2$CF$_3$)ZnPc: These were reported in our earlier study.[33g]

4α(SBu)H$_2$Pc (mixture of regioisomers): 3-*n*-Butylthio-1,2-dicyanobenzene (1.0 g, 4.6 mmol) was added to lithium (20 mg, 2.88 mmol) dissolved in dry *n*-pentanol (6 mL), and the solution was refluxed for 1 h. After cooling, the solution was poured into methanol (200 mL) containing 3 drops of concentrated HCl, and the resulting precipitate was collected by filtration and purified on a silica gel column with pyridine as eluent. The front-running green portion was recrystallized from CH_2Cl_2/methanol to give a 59 % yield (0.59 g) of the desired compound as a green powder. Elemental analysis (%) calcd for $C_{48}H_{50}N_8S_4$ (867.25): C 64.48, H 5.81, N 12.92, S 14.79; found: C 64.17, H 5.98, N 12.27, S 13.77; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = -1.14$ (s, 2H; pyrrole), 1.1 – 1.3 (m, 12H; CH_3), 1.6 – 1.9 (m, 8H; $S(CH_2)_2CH_2$), 1.90 – 2.20 (m, 4H; SCH_2CH_2), 3.41 (br, 8H; SCH_2), 7.4 – 8.1 (m, 8H; Ar-H), 8.65 – 9.15 ppm (m, 4H; Ar-H).

4α(SBu)ZnPc (mixture of regioisomers): A mixture of 1-hexanol (5 mL), Zn(OAc)$_2$, and 4α(SBu)H$_2$Pc (0.2 g, 0.23 mmol) was refluxed for 1 h and then poured into methanol (200 mL), and the resulting precipitate was filtered off and subjected to chromatography on a silica gel column with $CHCl_3$ as eluent. The front-running blue-green portion was collected and recrystallized from $CHCl_3$/methanol to give a 47 % yield (0.10 g) of a green solid. Elemental analysis (%) calcd for $C_{48}H_{48}N_8S_4Zn$ (930.64): C 61.95, H 5.20, N 12.04, S 13.78; found: C 60.49, H 5.03, N 11.04, S 13.64; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.90 – 1.22$ (m, 3H; CH_3), 1.64 – 2.10 (m, 4H; $S(CH_2)_2CH_2$ and SCH_2CH_2), 3.77 – 3.90 (br, 2H; SCH_2), 7.04 – 7.75 (m, 3H; Ar-H), 8.65 – 9.15 ppm (m, 4H; Ar-H).

4β(SBu)H$_2$Pc (mixture of regioisomers): As for the preparation of 4α(SBu)H$_2$Pc, this compound was synthesized from 4-*n*-butylthio-1,2-dicyanobenzene (1.0 g, 4.6 mmol) in 29 % yield (0.29 g). Elemental analysis (%) calcd for $C_{48}H_{50}N_8S_4$ (867.25): C 64.48, H 5.81, N 12.92, S 14.79; found: C 66.02, H 5.58, N 12.79, S 14.70; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = -5.00$ (s, 2H; pyrrole), 1.18 (m, 12H; CH_3), 1.74 (m, 8H; $S(CH_2)_2CH_2$), 1.94 (m, 4H; SCH_2CH_2), 3.16 (br, 8H; SCH_2), 7.00 – 7.75 ppm (m, 12H; Ar-H).

4β(SBu)ZnPc (mixture of regioisomers): As for the preparation of 4α(SBu)ZnPc from 4α(SBu)H$_2$Pc, zinc was inserted into 4β(SBu)H$_2$Pc (0.2 g, 0.23 mmol) to give 0.20 g (93 %) of the desired compound. Elemental analysis (%) calcd for $C_{48}H_{48}N_8S_4Zn$ (930.64): C 61.95, H 5.20, N 12.04, S 13.78; found: C 59.88, H 4.74, N 11.12, S 12.87; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.93$ (m, 12H; CH_3), 1.27 – 1.67 (m, 16H; $S(CH_2)_2CH_2$ and SCH_2CH_2), 2.60 (t, 8H; SCH_2), 6.50 – 7.80 ppm (m, 12H; Ar-H).

8β(SBu)H$_2$Pc: 3,6-Dibutylthio-1,2-dicyanobenzene (0.4 g, 1.3 mmol) was added to lithium (20 mg, 2.9 mmol) dissolved in dry *n*-pentanol (6 mL), and the solution was refluxed for 1 h. After cooling, the solution was poured into methanol (100 mL) containing 3 drops of concentrated HCl, and the resulting precipitate was collected by filtration and purified on a silica gel column with $CHCl_3$ as eluent. The dull green portion was recrystallized from $CHCl_3$/methanol to give a 38 % yield (0.15 g) of a green solid. Elemental analysis (%) calcd for $C_{64}H_{82}N_8S_8$ (1219.95): C 63.01, H 6.78, N 9.19, S 21.03; found: C 62.32, H 6.84, N 8.74, S 21.01; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.28$ (s, 2H; pyrrole), 1.04 (t, 24H; CH_3), 1.65 (tq, 16H; $S(CH_2)_2CH_2$), 1.91 (tt, 16H; SCH_2CH_2), 3.23 (br, 16H; SCH_2), 7.69 ppm (br, 8H; Ar-H).

8α(SBu)ZnPc: A mixture of 1-hexanol (4.5 mL), pyridine (1.5 mL), 8α(SBu)H$_2$Pc (40 mg, 0.033 mmol), and Zn(OAc)$_2$ was refluxed for 1 h, after which the reaction mixture was poured into methanol (80 mL), and the precipitate formed was filtered off and subjected to chromatography on a silica gel column with $CHCl_3$ as eluent. The front-running colored portion was collected and recrystallized from CH_2Cl_2/methanol to give a 93 % yield (39 mg) of a green solid. Elemental analysis (%) calcd for $C_{64}H_{80}N_8S_8Zn$ (1283.34): C 59.90, H 6.28, N 8.73, S 19.99; found: C 59.60, H 6.67, N 8.06, S 18.55; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.97$ (t, 24H; CH_3), 1.63 (br, 16H; $S(CH_2)_2CH_2$), 1.56 (br, 16H; SCH_2CH_2), 2.89 (br, 16H; SCH_2), 7.38 ppm (br, 8H; Ar-H).

8β(SPh)ZnPc: 1,2-Dicyano-4,5-diphenylthiobenzene (172 mg, 0.5 mmol) was added to lithium (2 mg, 0.29 mmol) dissolved in dry *n*-pentanol (1 mL), and the solution was refluxed for 2 h. Then dried $Zn(OAc)_2$ (92 mg) was added and refluxing was continued for 2 h in the dark. After cooling, the solution was poured into methanol (20 mL) containing 1 drop of concentrated HCl, and the resulting precipitate was collected by filtration and purified on an alumina column with CH_2Cl_2/pyridine as eluent. The first-eluted green portion was collected and recrystallized from pyridine/methanol to give a 19.4% yield (35 mg) of green-blue powder. Elemental analysis (%) calcd for $C_{80}H_{48}N_8S_8Zn$ (1443.27): C 66.58, H 3.35, N 7.76, S 17.77; found: C 65.92, H 3.59, N 7.33, S 17.12; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.42-7.48$ (m, 24H; Ar-*H*), 7.62–7.64 (d, 16H; Ar-*H*), 9.06 ppm (s, 8H; Ar-*H*).

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[19] The term "Soret band (region)" has long been used. This is now often referred to as "the B band (region)" (see for example ref. [27]).

[20] In addition to $\pi-\pi^*$ transitions, an $n-\pi^*$ transition of the ether oxygen atom lies at the longer wavelength tail of the B band,[21] which makes the analysis more difficult.

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[23] Our aim was to collect as accurate absorption coefficients as possible for a series of ZnPcs. However, some ZnPcs were unstable in solution. For example, since 8α(OBu)ZnPc was unstable, we could not have confidence in the comparison of the absorption coefficients among 4α-, 4β-, 8α-, and 8β-(OBu)ZnPc and 16(OCH_2CF_3)ZnPc. On the other hand, although 4α-, 4β-, 8α-, and 8β(SBu)ZnPc were stable, we could not obtain 16(SCH_2CF_3)ZnPc, depite many attempts.

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[26] We also calculated MOs of tetranitro- and tetrasulfonyl-substituted, pyrrole-proton-deprotonated species. However, calculations were not definitive. For example, a single Q band was not obtained, although the Q band was calculated at higher energy for tetrasubstitution at α positions. Accordingly, discussion of Pcs substituted by electron-withdrawing groups were not included in this section. The results of the PPP calculations on planar porphyrin oligomers have been reported recently (H. S. Cho, D. H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda, A. Osuka, *J. Am. Chem. Soc.* **2002**, *124*, 14642–14654). Although MO calculations using the ZINDO/S and DFT Hamiltonians have been used for simple, high-symmetry systems such as porphyrins and Pcs with D_{4h} symmetry, and the results are often good, these newer methods do not necessarily produce better results than the older PPP method. For example, in the case of these porphyrin oligomers, the HOMO is an a_{1u}-based molecular orbital when calculated with the ZINDO/S and DFT Hamiltonians, so that the transitions at the longest wavelength become symmetrically forbidden and are not at all consistent with the experimental results (the experimental results are reproduced when the HOMO is an a_{2u}-based orbital). Furthermore, to date MO calculations using the ZINDO/S Hamiltonian on the same π system but with different type, number, and position of substituents have not been carried out, so that the fact that the ZINDO/S calculations do not reproduce sufficiently the experimental order of even the longest-wavelength band among these species has not been reported.

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