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Violet emission observed from phthalocyanines

Yuji Kaneko [a], Yoshinobu Nishimura [a,1], Nobuaki Takane [a,2], Tatsuo Arai [a],
Hirochika Sakuragi [a], Nagao Kobayashi [b], Daisaku Matsunaga [c], Chyongjin Pac [d],
Katsumi Tokumaru [a,3]

[a] *Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan*
[b] *Graduate School of Science, Tohoku University, Kawauchi, Sendai 980-77, Japan*
[c] *Chemical Research Laboratories, Nippon Kayaku Co. Ltd., Shimo, Kita-ku, Tokyo 115, Japan*
[d] *Kawamura Institute of Chemical Research, Sakado, Sakura, Chiba 285, Japan*

Abstract

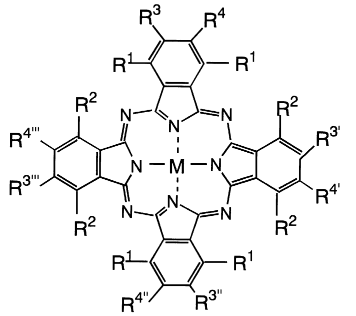
Spectral features of violet emission observed from phthalocyanines in addition to the well-known strong red emission are presented. The origin of the violet emission from the present and reported phthalocyanines is argued based upon the observed and estimated features. © 1997 Elsevier Science S.A.

Keywords: Phthalocyanines; Emission; Two-photon excitation

1. Introduction

Since the first report from Ferraudi's group in 1982 [1], more than twenty phthalocyanines (Fig. 1) [1–10] including several binuclear phthalocyanines [9] have been reported to show an emission in the violet region in addition to the well-known emission in the red to near-IR region from the lowest singlet excited state. The violet emission was assigned to either fluorescence from a higher singlet excited state corresponding to the Soret absorption band based on observation of the excitation spectra of the emission in the region of the Soret absorption band [6], or phosphorescence from a triplet excited state localized in the phthalocyanine ring [1–3,9,10]; however, the origin still seems not very clear.

During the course of an investigation on wavelength-dependent photochemical reactions of several phtahlocyanines [7,8,11], we found that those compounds, that is, unmetallized 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine (hereafter abbreviated as α-$H_2Pc(OBu)_8$), and its copper(II) derivative (α-$CuPc(OBu)_8$), unmetallized 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine (β-$H_2Pc(OBu)_8$), tetrasodium tetrasulfonatozinc(II)- and tetra-



MPc: M = H_2, Mg, Ti, Zn; $R^1 = R^2 = R^3 = R^{3'} = R^{3''} = R^{3'''} = R^4 = R^{4'} = R^{4''} = R^{4'''} = H$
RhPc(MeOH)X: M = (MeOH)RhX [X = Cl, Br, I]; $R^1 = R^2 = R^3 = R^{3'} = R^{3''} = R^{3'''} = R^4 = R^{4'} = R^{4''} = R^{4'''} = H$
$RuPc(py)_2$: M = $Ru(py)_2$ [(py): pyridine]; $R^1 = R^2 = R^3 = R^{3'} = R^{3''} = R^{3'''} = R^4 = R^{4'} = R^{4''} = R^{4'''} = H$
AlPcCl: M = AlCl; $R^1 = R^2 = R^3 = R^{3'} = R^{3''} = R^{3'''} = R^4 = R^{4'} = R^{4''} = R^{4'''} = H$
$ZnPcPh_4(OMe)_4$: M = Zn; R^1 = Ph; $R^{3'} = R^{3'''} = R^{4'} = R^{4'''}$ = OMe; $R^2 = R^3 = R^{3''} = R^4 = R^{4''} = H$
$MPc(neo\text{-}C_5H_{11}O)_4$: M = H_2, Zn; $R^3 = R^{3'} = R^{3''} = R^{3'''} = OCH_2C(CH_3)_3$; $R^1 = R^2 = R^4 = R^{4'} = R^{4''} = R^{4'''} = H$
H_2PcCR: M = H_2; $R^1 = R^2 = H$; $R^3\text{-}R^4 = R^{3'}\text{-}R^{4'} = R^{3''}\text{-}R^{4''} = R^{3'''}\text{-}R^{4'''} = (OCH_2)_4O$
ZnNIL: M = Zn; $R^1 = R^2 = H$; $R^3 = R^4$ = Ph; $R^{3'}\text{-}R^{4'} = R^{3''}\text{-}R^{4''} = R^{3'''}\text{-}R^{4'''} = (OCH_2)_4O$
ZnBz: M = Zn; $R^1 = R^2 = H$; $R^3 - R^4$ = 1,4-diphenylnaphtho[2,3]; $R^{3'}\text{-}R^{4'} = R^{3''}\text{-}R^{4''} = R^{3'''}\text{-}R^{4'''} = (OCH_2)_4O$
ZnNAP: M = Zn; $R^1 = R^2 = H$; $R^3 - R^4$ = 3,6-diphenylbenzo[1,2]; $R^{3'}\text{-}R^{4'} = R^{3''}\text{-}R^{4''} = R^{3'''}\text{-}R^{4'''} = (OCH_2)_4O$
$MPc(SO_3^-)_4$: M = Zn, Cu, Co; $R^3 = R^{3'} = R^{3''} = R^{3'''} = SO_3^-$; $R^1 = R^2 = R^4 = R^{4'} = R^{4''} = R^{4'''} = H$
α-$MPc(OBu)_8$: M = H_2, Cu; $R^1 = R^2 = O(CH_2)_3CH_3$; $R^3 = R^{3'} = R^{3''} = R^{3'''} = R^4 = R^{4'} = R^{4''} = R^{4'''} = H$
β-$H_2Pc(OBu)_8$: M = H_2; $R^1 = R^2 = H$; $R^3 = R^{3'} = R^{3''} = R^{3'''} = R^4 = R^{4'} = R^{4''} = R^{4'''} = O(CH_2)_3CH_3$

Fig. 1. Structural formulae of phthalocyanines.

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[1] Present address: Department of Chemical Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan.

[2] Present address: Tsukuba Research Laboratory, Hitachi Chemical Co. Ltd., Wadai, Tsukuba, Ibaraki 300-42, Japan.

[3] Present address: The Foundation for Advancement of International Sciences, 3-9-1 Amakubo, Tsukuba 305, Japan.

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sulfonatocopper(II)-phthalocyanine ($ZnPc(SO_3^-)_4$ and $CuPc(SO_3^-)_4$, respectively) (Fig. 1), show violet emission. We now attempt, though not yet attaining a definite assignment, to explain the origin of the violet emission based upon our findings, particularly that the excitation spectra are often shifted from the Soret absorption band, and estimation of radiative lifetimes, etc. of the emission from the above and hitherto reported phthalocyanines.

2. Experimental details

2.1. Materials

α-$H_2Pc(OBu)_8$ and β-$H_2Pc(OBu)_8$ were prepared by procedures similar to those reported [12,13]. Their elemental analyses and NMR spectra gave satisfactory results. (For example, found: C, 70.07; H, 7.63; N, 10.09 for the α-isomer, and C, 70.14; H, 7.60; N, 10.34 for the β-isomer. Calc. for $C_{64}H_{82}N_8O_8$: C, 70.41, H, 7.57, N, 10.27.) The absorption and emission spectra were unchanged after repeated purification of the samples. α-$CuPc(OBu)_8$ was prepared from 1,4-dibutoxy-2,3-dicyanobenzene and CuCl in butanol in the presence of ammonium molybdate and finally twice recrystallized from hexane. $ZnPc(SO_3^-)_4$ and $CuPc(SO_3^-)_4$ were supplied as previously reported [7].

2.2. Spectroscopy

Absorption and fluorescence spectra were recorded with a JASCO Ubest 55 spectrophotometer and a Hitachi F-4000 spectrofluorometer, respectively.

2.3. Quantum yields of emission

Quantum yields of emission were determined with use of Rhodamine B ($\Phi_f = 0.42$) [14] or Cresyl violet ($\Phi_f = 0.54$) [15] as references on excitation with light in UV or red region.

2.4. Lifetimes of emission

Lifetimes of the emission in violet region were determined for a 1×10^{-5} mol dm^{-3} sample solution under argon with 379 nm laser pulses from a third harmonic generator of a Spectra Physics 3900 Tsunami Ti:sapphire laser pumped by a Spectra Physics 2060 CW argon ion laser. The resulted emission was passed through a Jobin Yvon CP200 grating monochromator and detected with a Hamamatsu C4334 streak scope and transferred to an Apple Macintosh IIfx personal computer and analyzed.

Lifetimes of the emission in the red region were determined at wavelengths longer than 720 nm through a Toshiba R-72 cut-off glass filter on excitation of a sample solution with UV or red monochromatic light isolated through a grating monochromator from a hydrogen arc lamp on a Horiba NAES 1100 time-resolved spectrofluorometer.

2.5. Two-photon laser excitation

A 10^{-5} mol dm^{-3} sample ethanol solution was irradiated with varying intensity of 723 nm pulses from a Lambda Physik FL-3002 dye laser (10 ns FWHM; Rhodamine 700 as a dye) pumped by a Lambda Physik LPX-100 XeCl excimer laser. The resulting transient spectra were recorded as previously reported [7].

3. Results

3.1. Spectral features

Fig. 2 shows the spectra of α-$H_2Pc(OBu)_8$ as a typical example of the phthalocyanines examined, i.e. the absorption spectrum, the fluorescence spectrum determined on excitation at 360 nm and the excitation spectra monitored at 790 and 450 nm in ethanol. This compound shows weak and broad fluorescence in the violet region in addition to strong fluorescence in the red region.

The red emission is induced by excitation of both the Q band and the Soret band. The excitation spectrum monitored at the red emission (790 nm) shows maxima at 327 and 770 nm along with a shoulder at 740 nm and coincides very well with the absorption spectrum in both the Soret and Q bands. The Stokes shifts determined between the maxima of the red emission and either its excitation spectrum or the Q absorption band remain at 430 cm^{-1}.

However, for the violet emission, the excitation spectrum monitored at 450 nm, which is a mirror image of the violet emission spectrum, shows a maximum at 377 nm and is clearly shifted to longer wavelength than the Soret absorption band with a maximum at 327 nm. This means that the violet emission is induced on excitation at the longer wavelength tail of the Soret band. Moreover, the maximum of the violet

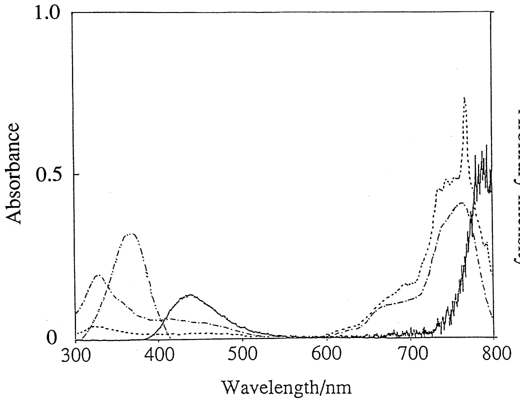

Fig. 2. Absorption (– · –) emission (excited at 360 nm, ——) and excitation spectra monitored at 790 nm (- - -) and at 450 nm (– · · –) of α-$H_2Pc(OBu)_8$ in ethanol.

Table 1
Features of emission from phthalocyanines (Pcs) [a]

Pc	Solvent [b]	Violet emission							Red emission			Ref.
		λ_{max} (nm)	Φ_f	τ (ns)	Exc. λ_{max} (nm)	Sor. λ_{max} (nm)	τ^0 (μs) [c]	ϵ_{max} (mmol^{-1} cm^2) for violet emission [c]	λ_{max} (nm)	Φ_f	τ (ns)	
H_2Pc	C	436	9×10^{-4}			340			692	0.55	6.5	[6]
MgPc	E	424	3×10^{-4}		355	344			668			[6]
TiPc	C	428	9×10^{-4}		360	356			690			[6]
ZnPc	E	420	2×10^{-4}			340			664	0.30	3.5	[6]
RhPc(MeOH)Cl	A	420	1.4×10^{-3}	3.8(18.4) [f]	335	290	2.7 [g]	40 [g]				[3]
RhPc(MeOH)Br	A	420	1.2×10^{-3}	3.4(21.2) [f]	340	290	2.8 [g]	40 [g]				[3]
RhPc(MeOH)I	A	420	1.4×10^{-3}	4.0(19.1) [f]	345	270	2.9 [g]	30 [g]				[3]
$RuPc(py)_2$	E–M		7.7×10^{-4}									[3]
AlPcCl	E–M		5×10^{-4}									[3]
$ZnPcPh_4(OMe)_4$	C	397	1.4×10^{-2}		343	350		780	717	0.034		[5]
$H_2Pc(OCH_2CMe_3)_4$	C	413	5.6×10^{-4}	13.0(3.5) [f]	352		0.23 [g]	4.3 [g]	713	0.24	7.3	[9]
$ZnPc(OCH_2CMe_3)_4$	C		1.5×10^{-3}	12.5(1.6) [f]		349	8.3 [g]	12 [g]		0.25	3.9	[9]
H_2PcCR	C	428	1.0×10^{-2}		348	347		420	704	0.070		[4]
ZnNIL	C	442	8.9×10^{-3}	19.4(5.9) [f]	338	353	2.2 [g]	50 [g]	698	0.09	2.2	[10]
ZnBZ	C	439	6.6×10^{-3}	25.5(6.5) [f]	336	353	3.9 [g]	30 [g]	692	0.16	3.1	[10]
ZnNAP	C	448	8.5×10^{-3}	26.2(3.3) [f]	332	351	3.1 [g]	40 [g]	709	0.09	3.5	[10]
$CoPc(SO_3^-)_4$	E		5×10^{-4}									[3]
$CuPc(SO3^-)_4$	E	445	3.5×10^{-5}									[3]
$CuPc(SO_3^-)_4$	A–W	470	7.2×10^{-2}	3.0	360	343	0.04	3080				[7], [g]
$ZnPc(SO_3^-)_4$	A–W	450	3.8×10^{-2}	5.4	390	345	0.14	1570	680	0.31	4.0	[7], [g]
α-$H_2Pc(OBu)_8$	E	440	1.3×10^{-2}	4.6	377	327	0.36	490	788	0.19 [f]	4.2	[8], [g]
α-$CuPc(OBu)_8$	E	438	9.2×10^{-3}	5.1	360	327	0.55	330				[8], [g]
β-$H_2Pc(OBu)_8$	T	461	1.1×10^{-2}	2.2	344	354	0.20	440	703	0.96		[g]

[a] Emission maxima, λ_{max}, quantum yields, Φ_f and lifetimes, τ, for violet and red emission. λ_{max} values of excitation spectra (Exc.) and the Soret absorption bands (Sor.), estimated natural radiative lifetimes, τ^o, estimated molar absorption coefficients, ϵ_{max}, at the λ_{max} of the excitation spectra for violet emission.

[b] A:acetonitrile, A–W: 1:1 acetonitrile–water, C:chloroform, E:ethanol, E–M:ethanol–methanol (9:1), T:toluene.

[c] Estimated according to procedures described in Section 4.

[d] In two-component decay, those of lower contribution are in parentheses.

[e] Only those for higher contributed components of τ are indicated.

[f] In THF [16].

[g] The present work.

emission band shifts in 3800 cm^{-1} from the maximum of the excitation band, and is further shifted by as much as 7850 cm^{-1} from the maximum of the Soret absorption band.

The quantum yield (Φ_f) for the violet emission is 1.3×10^{-2} at 370 nm excitation in ethanol. Concerning the red emission (Φ_f: 0.19 in THF [16]), the apparent intensity was reduced to one quarter at 360 nm excitation instead of 640 nm excitation.

The lifetime (τ_S) of the violet emission is 4.6 ns, which is much longer than those generally expected for higher excited states.

Other phthalocyanines examined show similar spectral features for the violet emission to the above compound as summarized in Table 1 in which are also included mononuclear phthalocyanines hitherto reported for violet emission [3–10]. For most of the phthalocyanines examined now, the excitation spectrum of the violet emission is clearly shifted to longer wavelength from the Soret absorption band except β-$H_2Pc(OBu)_8$, for which the excitation spectrum of the violet emission considerably overlaps with the Soret absorption band as seen in Fig. 3. The lifetimes of these phthalocyanines for the violet emission are 2–5 ns.

Regarding red emission observed from metal-free and zinc phthalocyanines, the Φ_f values are reduced on excitation around 350 nm instead of excitation of the Q-band. Thus, in β-$H_2Pc(OBu)_8$, the Φ_f for the red emission (λ_{max}: 702 nm) is lowered from 0.96 on 650 nm excitation to less than the half, 0.36, on 370 nm excitation in toluene. Likewise, the Φ_f for $ZnPc(SO_3^-)_4$, 0.31, on 680 nm excitation is reduced to nearly one third, 0.11, on 390 nm excitation.

3.2. *Violet emission resulted from two red photon excitation*

An attempt was made to populate the violet emissive state by two red photon excitation under high flux red laser irradiation. Fig. 4 illustrates time-resolved transient spectra observed on excitation of α-$CuPc(OBu)_8$ with a 723 nm laser of a power of 7.1 mJ per pulse in ethanol. Immediately after the excitation, the emission appeared around 450 nm and

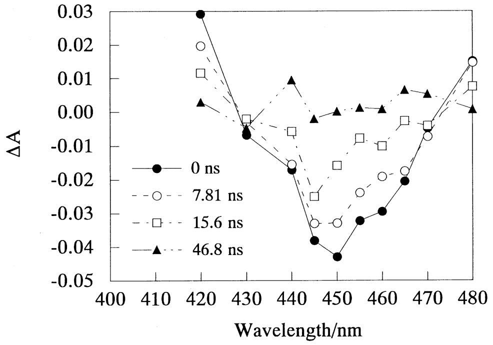

Fig. 3. Absorption spectrum (upper figure). Emission spectrum (excited at 370 nm, ——) and excitation spectrum (monitored at 702 nm, ···) of β-$H_2Pc(OBu)_8$ in toluene. Insets: enlarged violet emission spectrum (excited at 370 nm, ——) and excitation spectrum (monitored at 450 nm, ···) (lower figure).

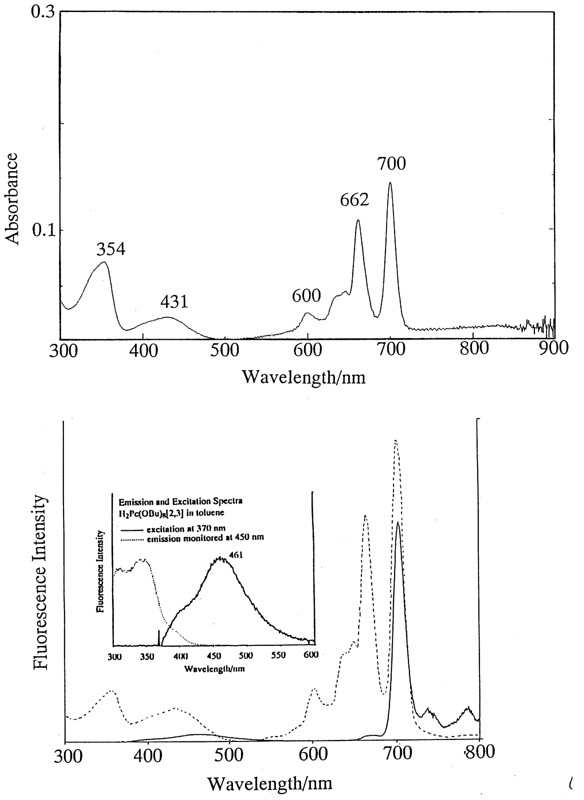

Fig. 4. Time-resolved transient spectra on excitation of α-$CuPc(OBu)_8$ with a 723 nm pulsed laser in ethanol with a flux of 7.1 mJ per pulse.

quickly decayed. Decrease of the laser intensity for the excitation reduced the intensity of the resulting emission. Fig. 5 plots the maximum intensity of the resulted emission against the square of the incident laser power. This indicates that the emission intensity increases almost linearly with the square of the laser power as in typical two photon excitation processes. These findings indicate that excitation with 723 nm laser pulses induces two photon absorption of the compound to populate the violet emissive state.

On the other hand, two photon excitation of α-$H_2Pc(OBu)_8$ did not give a clear result possibly due to the presence of a strong, broad and long-lived (the lifetime as long as hundreds μs) absorption of the lowest triplet state, T_1, in 450–650 nm ($\lambda_{max} = 610$ nm).

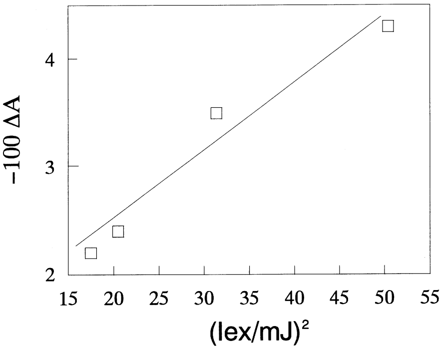

Fig. 5. Plots of the largest intensity of the emission ($-\Delta A$) observed during irradiation of α-$CuPc(OBu)_8$ with high flux of 723 nm laser of varying power against square of the irradiating laser power (I_{ex}) in mJ per pulse.

4. Discussion

4.1. Features of violet emission

As Table 1 indicates, the excitation spectra of the violet emission of the phthalocyanines examined mostly do not coincide with the Soret absorption bands except for β-$H_2Pc(OBu)_8$ (Fig. 3), but located in their longer wavelength slopes and often correspond to shoulder of the Soret absorption bands as seen in Fig. 2 for α-$H_2Pc(OBu)_8$.

Reexamination of spectral figures of violet emission from phthalocyanines previously reported reveals that the λ_{max} values of the excitation spectra of $RhPc(CH_3OH)X$ around 340 nm correspond to shoulders located in the longer wavelength region of the Soret absorption bands (λ_{max}: ca. 290 nm) [3]; and the λ_{max} of the excitation spectrum of titanium(II) phthalocyanine around 360 nm is slightly shifted to longer wavelength than that of the Soret absorption band at ca. 340 nm [6]. On the other hand, the maximum of the excitation spectrum is situated at slightly shorter wavelength of the maximum of the Soret absorption band for ZnNIL, ZnBZ and ZnNAP [10] as for β-$H_2Pc(OBu)_8$.

Population of the violet emitting species by high flux red laser (723 nm) excitation of α-$CuPc(OBu)_8$ is reasonably attributed, based on the result of Fig. 5, to successive excitation of the lowest singlet excited state, S_1, initially produced by the first photon absorption, as previously reported by Kossanyi et al. for metal-free, magnesium(II), titanium(II) and zinc(II) phthalocyanines [6]. They observed violet emission by high flux red (695 nm) laser excitation of carefully purified samples of those phthalocyanines in ethanol. They showed that this process was neither due to annihilation between the lowest triplet state, T_1, produced by intersystem crossing of S_1 nor to excitation of the resulted T_1 into a higher triplet state followed by intersystem crossing to a higher singlet excited state, because the violet emissive state was supposed to live for a much shorter time than the T_1, and the T_1

did not absorb 723 nm light. Therefore, these facts suggest that the violet emissive state is intrinsic to the phthalocyanine examined which has the lowest singlet excited state produced by the red photon absorption.

The observed Φ_f values for the violet emission from most of the present phthalocyanines of the order of either 10^{-2} or 10^{-3} are comparable with those reported for H_2PcCR (1.0×10^{-2}) [4], $ZnPc(OMe)_4Ph_4$ (1.4×10^{-2}) [5] or those for $ZnPc(OCH_2CMe_3)_3$ (1.5×10^{-3}) [9], ZnNIL, ZnBZ, ZnNAP (($(7–9)\times10^{-3}$) [10], $RhPc(CH_3OH)X$ (X: Cl, Br, and I) (1×10^{-3}) [3] and $RhPc(py)_2$ (8×10^{-4}) [3]. However, these values are higher than those reported for unmetallized and metallized unsubstituted phthalocyanines [6], AlPcCl, $CoPc(SO_3^-)_4$ (10^{-4}) [3] and $CuPc(SO_3^-)_4$ (10^{-5} in ethanol) [3].

The observed lifetimes of the violet emissive states of several nanoseconds are comparable with those for shorter lifetime components, 3–7 ns, of the violet emission from rhodium phthalocyanines, $RhPc(CH_3OH)X$ (X: Cl, Br and I) [3], $ZnPc(OCH_2CMe_3)_3$, $H_2Pc(OCH_2CMe_3)_3$ [9], ZnNIL, ZnBZ and ZnNAP [10] and shorter than those for longer lifetime components of these phthalocyanines, 12–26 ns. Generally, when a higher singlet excited state lies in much higher energy than the lowest singlet excited state, it can emit intrinsic fluorescence in addition to the emission from the latter state as observed in zinc(II) tetraphenylporphyrin [17] and azulene [18]. The above lifetimes of 3–7 ns are much longer than that of fluorescence from the second singlet excited state (S_2 state) of zinc(II) tetraphenylporphyrin (3.5 ps [17]), but are of the same order as that from the S_2 state of azulene (nearly 1 ns, which is much longer than the lifetime of the S_1 state, 8 ps [18]).

The lifetimes of the violet emission from α-$CuPc(OBu)_8$ and $Cu(SO_3^-)_4$, 3 and 5 ns, also seem very long for copper compounds, because the presence of a copper atom in a molecule generally accelerates the deactivation.

The observed reduction of Φ_f for the red emission by changing the excitation light from red to UV light can be attributable to the following two possibilities. In the first, the violet emissive state can dissipate by violet emission and nonradiative processes competing with the deactivation to the S_1 which subsequently emits red fluorescence. Excitation of the Q band efficiently populates its excited state leading to a high Φ_f for the red emission; on the other hand, excitation around 360 nm region first populates the violet emissive state, which partially gives the excited state of the Q band owing to the dissipation by competing processes, therefore, resulting in lower Φ_f for the red emission. In the second possibility, an impurity eventually present could be excited and the resulted excited state could sensitize the phthalocyanines resulting in red emission.

4.2. Estimation of natural radiative lifetimes and molar absorption coefficients of absorptions responsible for violet emission

From the observed values of Φ_f and τ_S, the natural radiative lifetime of the emission, τ^0, can be obtained by Eq. (1).

$$\tau^0=\tau_S/\Phi_f \qquad (1)$$

The τ^0 values obtained for various phthalocyanines are mostly of the order of μs and 10^{-1} μs as listed in Table 1. (A few τ_S values of lower contribution give τ^0 of the order of 10 μs, though these are not indicated in Table 1.)

Subsequently molar absorption coefficients at the maximum (ϵ_{max}) of the corresponding absorption could be estimated from the well known Eq. (2) by assuming the absorption band as a symmetrical one, where $\Delta\nu_{1/2}$ means the FWHM of a symmetrical absorption band and ν stands for the wavenumber of the 0–0 transition [19].

$$\varepsilon_{max}=3.4\times10^8/\nu^2\,\Delta\nu_{1/2}\tau^0 \qquad (2)$$

On application of Eq. (2), the FWHM of a nearly symmetrical excitation spectrum of the violet emission is taken as $\Delta\nu_{1/2}$, and the wavenumber at which both the excitation and the emission spectra cross is taken as ν.

The estimated ϵ_{max} values of the absorption responsible for the violet emission from various phthalocyanines are included in Table 1. These are of the order of 10^2 $mmol^{-1}$ cm^2 for α-$H_2Pc(OBu)_8$, β-$H_2Pc(OBu)_8$, α-$CuPc(OBu)_8$, $ZnPc(OMe)_2Ph_2$ and H_2PcCR, and of the order of 10^3 $mmol^{-1}$ cm^2 for $ZnPc(SO_3^-)4$ and CuPc-$(SO_3^-)_4$, respectively. Those for $RhPc(CH_3OH)X$ (X= Cl, Br and I), $ZnPc(OCH_2CMe_3)_4$, ZnNIL, ZnBZ and ZnNAP are of the order of 10 $mmol^{-1}$ cm^2. As described before, the excitation spectra for the violet emission from these phthalocyanines are more or less shifted from the Soret absorption band. The above estimated values are much smaller than not only the apparent ϵ_{max} values of the Soret absorption bands but also the apparent ϵ values in the absorption band at the λ_{max} values of the excitation spectra.

4.3. An attempt at assignment of the violet emitting state

To summarize the above facts, the violet emission observed from the present and reexamined phthalocyanines show the following features. (1) The excitation spectra of the violet emission do not completely coincide with the Soret absorption band but are often situated at longer and sometimes at shorter wavelength tail of the Soret band, being in contrast with the excitation spectra of the red emission, which, if emitted, coincide with the Q band. (2) The lifetimes of several nanoseconds are of the same order as that from the S_2 state of azulene [18], but those of tens of nanoseconds reported for longer components seem very long, when the emission arises from higher singlet excited states. Even copper phthalocyanines show emission with similar lifetimes. (3) Two red photon excitation of α-$CuPc(OBu)_8$ and unsubstituted metal-free and metallophthalocyanines [6] leads to the violet emission, the intensity of which increases with the square of the incident laser intensity. (4) The natural radiative lifetimes of the emission (τ^0) are mostly of the order of μs–10^{-1} μs. The molar absorption coefficients (ϵ_{max}) of the responsible absorption for the violet emission are mostly of the order of 10^1–10^2 and at most 10^3 mmol^{-1} cm^2 in a few cases.

Among the above facts (1)–(4), the results of two photon excitation (3) suggest that the violet emission is intrinsic to the phthalocyanines. The observed lifetimes and the observation of the violet emission even in copper phthalocyanines (2) suggest that the emission would result from a state not facilely undergoing deactivation to lower excited states. Also, at present, one cannot completely eliminate a possibility that the emission would not be intrinsic to the phthalocyanines and would result from contaminated matter, which is hard to be eliminated during purification or gradually produced on standing, although the samples employed showed satisfactory results of elemental analyses and their spectral features were unchanged by repeated purification.

The results of incomplete matching of the excitation spectra with the Soret absorption bands (1) and τ^0 mostly of the order of μs–10^{-1} μs as well as $\epsilon_{\max}$ values mostly of the order of 10^1–10^2 mmol^{-1} cm^2 (4) suggest that the emitting state has a relatively small transition moment with the ground state. This state would result from excitation of either a relatively weak absorption band located in the region of the broad Soret band or unidentifiable contaminants which have such an absorption property. In the former case, the excited state of the weak absorption band should be very inefficient or forbidden in deactivating to lower excited states as indicated by Gouterman's group for the existence of such excited states in phthalocyanines [20]. The observed lifetimes of several nanoseconds (2) and the estimated τ^0 values (4) are of the same magnitudes as those from the S_2 state of azulene (τ^0: 0.07 μs), whereas the estimated $\epsilon_{\max}$ values (4) are much smaller than that of the order of 10^4 mmol^{-1} cm^2 for the $S_0 \rightarrow S_2$ absorption of azulene [18].

Regarding the violet emission from RhPc(CH_3OH)X and related phthalocyanines, Ferraudi et al. proposed that the emissive state would not be n, π^* excited state but π, π^* state localized in the phthalocyanine ring probably in the triplet state [1–3]. It is reported that the n, π^* absorption of phthalocyanines is of very weak intensity for planar phthalocyanines [20], and around 600 nm for zinc(II) phthalocyanine [21].

However, previous assignment of the violet emitting species to triplet states [1–3] seems not applicable for the various phthalocyanines, because the τ^0 values obtained, μs–10^{-1} μs, are much smaller than those usually observed for the triplet states, which are at least 0.1 ms for highly emissive n, π^* triplet states but are generally much longer than ms for π, π^* triplet states carrying no heavy atom [22]. Also, the $\epsilon_{\max}$ estimated above are too much higher than those commonly observed for triplet states. The absorption of ground states directly to triplet states, S → T absorption, is spin-forbidden, and generally has very small ϵ (much lower than unity).

Therefore, at the moment, states responsible for the violet emission cannot be definitely assigned. As discussed above, a probable candidate is a higher singlet excited state which very inefficiently deactivates to lower excited states as the S_2 state of azulene [18], whereas a possibility of contaminants in phthalocyanines cannot yet be completely excluded.

5. Conclusion

Although more than twenty phthalocyanines were reported to show violet emission in addition to red or near-IR emission, examination of the present phthalocyanines for the first time revealed the following facts. Thus, the most of the excitation spectra of the violet emission of the present phthalocyanines are located at the longer wavelength region of the Soret absorption bands. Excitation of these phthalocyanines at the region of the above excitation spectra reduces the Φ_f values for the red emission compared with the excitation at the Q band, indicating that the violet emissive state does not very efficiently give the S_1 state. The natural radiative lifetimes of the violet emission of the present and reported phthalocyanines estimated from the lifetimes and the Φ_f values show that the excited state giving violet emission is populated from the ground state with $\epsilon_{\max}$ values mostly of the order of 10^1–10^2 mmol^{-1} cm^2.

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