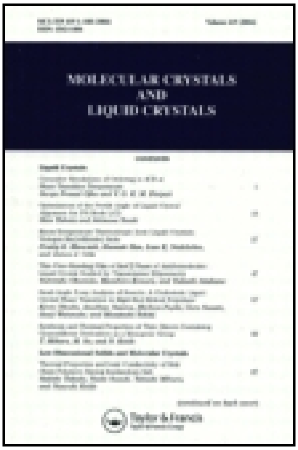

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Photophysical Properties of MESO-Phenyl-Tetra-Benzo-Porphyrins and Photon-Gated Spectral Hole Burning in Mixed Donor-Acceptor Systems at Low Temperature

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PHOTOPHYSICAL PROPERTIES OF *MESO*-PHENYL-TETRA-BENZO-PORPHYRINS AND PHOTON-GATED SPECTRAL HOLE BURNING IN MIXED DONOR-ACCEPTOR SYSTEMS AT LOW TEMPERATURE

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Abstract The photophysical properties of a series of compounds, *meso*-phenyl-tetra-benzoporphyrinato-Zinc (Zn-P_nTBP, n=1-4) were presented. Multiple photon-gated spectral hole burning in the mixed donor-acceptor systems, Zn-P_{1-2}TBP/DCB/PMMA was performed at 4.2 K and the mechanism of the photoinduced donor-acceptor electron transfer reaction at 20 K was elucidated.

INTRODUCTION

Tetrabenzoporphyrin (TBP) and their derivatives (Zn-P_nTBP) are aromatic macrocyclic compounds containing 18 πelectrons in which the 0-0 transition appears in the near IR region beyond 600 nm and have a large molar extinction coefficient ($\log \varepsilon > 4$). These molecules as photosensitizers have excellent light and thermal stabilities, and are of potential importance in the fields of optical memory and processing and nonlinear optics[1,2]. However, studies of the properties and applications of TBP have often been faced with difficulties due to the limitation of synthetic methods[3,4] , in which pure compounds of *meso*-substituted TBP were obtained only with considerable difficulty, so that the photophysical properties of a series *meso*-substituted TBP are incomplete obviously. Herein we report the photophysical studies for a series of pure compounds *meso*-phenyl-tetrabenzoporphyrinato-znic after the procedure of the synthesis has been improved in our laboratory[5], and multiple photon-gated spectral hole burning in the controable mixed donor systems at low temperature. The mechanism of photoinduced donor-acceptor electron transfer in the system of Zn-P_{1-2}TBP/DCB/PMMA during photon-gated spectral hole burning at 20 K is elucidated.

EXPERIMENTAL DETAILS

meso-phenyl-tetrabenzoporphyrinato-zinc, Zn-P_nTBP (n=1-4) were synthesized by an improved procedure[5], and each compound was purified by thin layer chromatography for use as an electron donor. Dicyanobenzene (DCB) was purchased from Aldrich and used as an electron acceptor . Poly(methylmethacrylate) (PMMA), the host matrix was monodisperse with an average molecule weight of $M=10^6$ ($M_w/M_m=1.36$) .

The electron spectroscopies of Zn-P_nTBP were determined by using Hitachi photospectrometers (Models 557, 850 and MPF-4 respectively). The triplet-triplet transient absorption spectra and the lifetimes of the lowest excited triplet state of each compound were determined by nanosecond flash photolysis equipment[6] .

Optical samples were prepared by mixing the chloroform solution containing the donor, the acceptor and the matrix in the appropriate ratios as described previous[7] and the photon-gated spectral hole burning was performed at 4.2 K and 20 K respectively. The conditions of the hole burning at 4.2 K were given as before[7] and the conditions of hole burning at 20 K were given as below: The sample was placed in the optical cryostat (Sumitomo SRD-204), in where the temperature of the sample was controalled at 20 K ± 0.5 K. An argon ion laser pumped ring DCM dye laser (Coherent 699-01) provided a frequency-selective light λ_1 for one photon spectral hole burning. The laser beam was not focused and the beam diameter at the sample was about 20 mm. The gating beam λ_2 was provided by the argon ion laser (NEC,GLG3200) with all lines .The detection of the spectral holes with one - metre grating monochrometer (JASCOCT 100C) was performed by scanning λ_1 and detecting the variation of the sample transmittance. A computer was used to collect and analyze the data for obtaining the hole depth $\Delta T/T_i$ or $\Delta A/A_i$, where the ΔA is the difference between the initial absorbance A_i and the final at the laser frequency.

RESULTS AND DISCUSSION

Photophysical Properties of *meso*-Phenyl-tetra-benzoporphyrinato-zinc.

There have been only scarttered spectral data of Zn-P_nTBP for each single compound reported in literature[8,9]. Table I shows the spectral data for each compound of Zn-P_nTBP (n=1 – 4), in ground state (S_0), the lowest excited singlet state (S_1) and the lowest excited triplet state (T_1) in chloroform at room temperature, respectively.

TABLE I Photophysical parameters for *meso*-phenyl-tetrabenzoporphyrinato-zinc in choloform at room temperature

ZnP$_n$TBP	S_0 Q(0.0)		S_1		T_1	
	λ max/nm	E_0/kJ · mol^{-1}	λ max/nm	E_S/kJ · mol^{-1}	λ max/nm	E_T/kJ · mol^{-1}
Zn-P_1TBP	630.0	189.9	634.0	188.6	804.0	148.8
ZnP_2TBP	635.0	188.4	638.0	187.5	805.0	148.6
Zn-P_3TBP	640.0	182.9	649.0	184.3	810.0	147.7
Zn-P_4TBP	654.0	182.9	659.7	181.3	817.0	146.4

The data in the table reveal that the maximum absorption peaks for the Q band and the corresponding emmissions for both fluorescence and phosphorescence have red shifts depending on the increasing in number of substituents on the meso-position of TBP, in which the corresponding energies decrease. Obviously, both the red shift of the spectra and the decrease of the transition energy are attributed to the substitution of phenyl on the *meso*-position of TBP. In addition, these molecules may effectively absorb the near infrared irradiation due to the large molar extinction coefficient ($\log \varepsilon > 4$) beyond 600 nm, which make molecules populate easily on the excited states. However, the fluorescence quantum yields of the lowest excited singlet state for a series of compounds, Zn-P_nTBP have a less values determined ($\Phi_f < 0.2$), while the intersystem crossing quantum yield (Φ_{isc}) as high as 0.8 was reported[10], hence providing a possibility for utilizing the properties of the lowest excited triplet state in the condition of photon-gating spectral hole burning. The triplet—triplet transient absorption spectra of each compounds of ZnP_nTBP in deaerated chloroform at room temperature are shown in Figure 1.

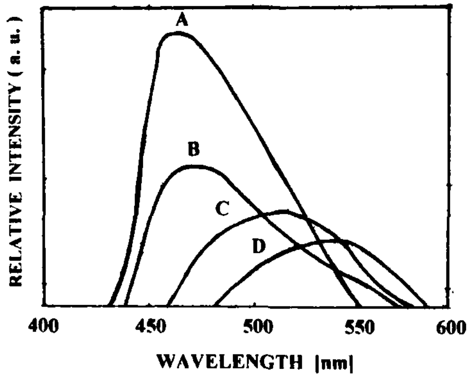

FIGURE 1 Triplet-triplet transient absorption spectra of Zn-P_nTBP in solution A, Zn-P_1TBP (in chloroform); B, Zn-P_2TBP (in chloroform); C, Zn-P_3TBP (in benzene); and D, Zn-P_4TBP (in benzene).

The T – T absorptions have red-shifts and intensity dropping with the increase in number of the substituents on *meso*-position of TBP, in which λ max are 460 (n=1), 480 (n=2), 506 (n=3), 525 (n=4) nm with the corresponding energies of 260.1 (n=1), 249.2 (n=2), 236.4 (n=3) and 227.9 (n=4) kJ/mol, respectively. Especially, at room temperature the T – T absorptions of Zn-P_nTBP are acquired, indicating that there are enough population of the molecules in the lowest excited triplet state, which provides a convenient condition for determining the lifetime of the lowest excited triplet state at room temperature. Table II lists the data of the lifetimes for several species of Zn-P_nTBP, including the free base of H_2-P_2TBP in chloroform at room temperature by laser flash photolysis.

TABLE II The lifetimes of the lowest excited triplet states of Zn-P_nTBP at room temperature

Compound	Solvent	$\tau_1/\mu s$	$\tau_2/\mu s$	x^2	$\tau/\mu s$
Zn-P_1TBP	$CHCl_3$	0.82(11.2%)	3.73(88.8%)	1.54	3.40
Zn-P_3TBP	C_6H_6	1.21(16.6%)	4.16(83.4%)	1.08	3.67
Zn-P_4TBP	C_6H_6	1.56(61.5%)	9.79(38.5%)	1.86	4.72
H_2-P_2TBP	$CHCl_3$	1.32(28.1%)	6.14(71.9%)	1.20	4.79

The experimental results are simulated by the double exponential deconvoluting method and there are two processes for the decay of the lowest excited triplet state of molecules populating on the T_1 level, which includes the shorter life (τ_1) and the longer life (τ_2) species. The average lifetime is about 3 – 5 μs which can be prolonged to 40 ms at liquid helium temperature[11].

Photon-Gated Spectral Hole Burning In Mixed Donor-Acceptor Systems.

The expanding of absorption bandwidth of the 0-0 transition of photoresponsive molecule in matrix is one of the effective means for increasing the density of the information storage in the frequency domain optical storage[12]. One of the way for expanding the absorption bandwidth is that the substitutions of phenyl on *meso*-position of TBP have also made a contribution to the broaden of the absorption bandwidth, furthermore, due to the red-shift of the 0-0 transition with substituents increasing for each compound, the end of the long wavelength of one component is able to overlap the end with the short wavelength of others in the mixed systems containing several donors, so that the absorption bandwidth has been expanded effectively.

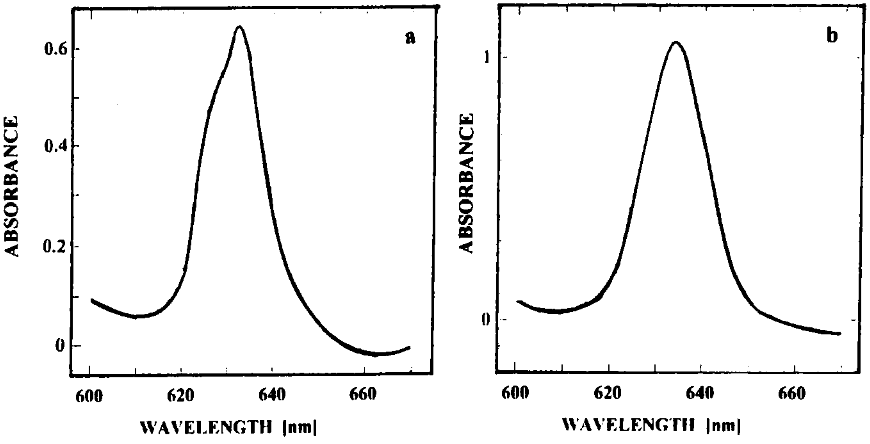

FIGURE 2 Comparison of the absorption spectra at 20 K between (a) Zn-P_2TBP/DCB/PMMA and (b) Zn-$P_{1\text{-}3}$TBP/CB/PMMA

Figure 2 shows the comparison of the absorption spectra at 20 K between Zn-P_2TBP/DCB/PMMA system with the full width at half maximum (FWHM) of

407 cm^{-1} at λ max 632 nm (Figure 2(a)) which has the contracting about 29cm^{-1} than that of in chlorofom at room temperature and Zn-P_{1-3}TBP/DCB/PMMA system with the broadened FWHM of 488 cm^{-1} at λ_{max} 634 nm (Figure 2(b)), in which Zn-P_2TBP is a predominent composition in the mixture of the donors of containing proper amount of Zn-P_1TBP and Zn-P_3TBP. Obviously, this means is convenient and effective for extending the absorption bandwidth of the 0-0 transition of the donor in the mixed system. While due to less thermal and light stabilities of Zn-P_4TBP in the photon-gated process, preferable to the low substitutions of phenyl on *meso*-position of TBP are chosen to consist of the mixed donor systems.

Figure 3 gives the experimential result of the multiple photon-gated spectral hole burning in the mixed system of Zn-P_{1-2}TBP/DCB/PMMA at 4.2 K, in which fifty holes have been burnt with 0.3 A hole width and > 50% hole depth ($\Delta T/\Delta T_i$) in the region of 8.5 nm between 627.5-636.0 nm (Figure 3(a)) starting from the end of the short wavelength with 10 seconds interval, using P_1=102 μ W/cm^2, P_2=10 mW/cm^2 for continued hole burning .

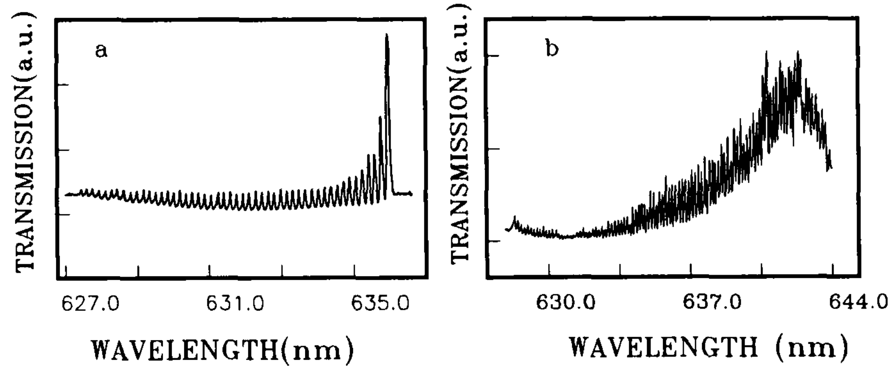

FIGURE 3 Multiple photon-gated spectral hole burning in mixed system of Zn-P_{1-2}TBP/DCB/PMMA between 627.5-636.0 nm (a), and 627.0-644.0 nm (b), with P_1=102 μ W/cm^2, P_2=10 mW/cm^2 for continued hole burning at 4.2 K.

Similarly, one hundred holes are also burnt among the expanded absorption bandwidth between 627.0-644.0 nm (Figure 3(b)). It implys that the density of the information storage on one recording spot could be increased about 100 times in the selected mixed donor system matching proper acceptor for the frequency domain optical storage.

Mechanism Of Spectral Hole Burning In Zn-P_nTBP/DCB/PMMA System At Low Temperature

The driving force for a donor-acceptor electron transfer system in thermodynamics can be evaluated by Rhem-Weller equation:

$$\triangle G = E_{ox} - E_{red} - E_{0,0} - C$$

Here E_{ox} is the oxidation potential of the donor, E_{red} is the reduction potential of the acceptor, $E_{0,0}$ is the electronic energy (eV) deposited in the donor by the photoexcitation, which includes both energies of the frequency-selective irradiation λ_1 and the gating irradiation λ_2 in the photon-gating process. The feasibility of photoinduced electron transfer in the solvents can be predicted, when the free energy change, $\triangle G < 0$, which can be calculated from the redox potentials and the excitation energy, the process is an exothermic and the electron transfer can proceed at thermodynamics. Table III presents the calculated results of $\triangle G$ values for Zn-P_2TBP as the electron donor in the presence of different electron acceptors.

TABLE III Free energy change ($\triangle G$) of Zn-P_2TBP in the presence of the electron acceptors.

Acceptor	E_{red} /V E/2 vs. SCE(CH_3CN)	$\triangle G(S_0)$ /eV	$\triangle G(S_1)$ /eV	$\triangle G(T_n)$ /eV
9,10-DCA	-0.89	1.42	-0.54	-2.70
9-CA	-1.39	1.92	-0.04	-2.20
DCB	-1.60	2.13	0.17	-1.99
CBZ	-1.76	2.29	0.33	-1.83
1-CN	-1.98	2.51	0.55	-1.61
$CHCl_3$	-1.70	2.23	0.27	-1.89

9,10-DCA:dicyanoanthracene,9-CA:9-cyanoanthracene,DCB:1,4-dicyanobenzene,CBZ:methyl-p-cyano-bezoate, 1-CN:1-cyanonaphthalene. $E_{ox}=0.53^{10}$, $E_S=1.96$ eV, $E_{T_1}=1.54$ eV, $E_{T_n}=2.58$ eV .

The data show that the electron transfer is forbidden in the ground states for the systems because of $\Delta G(S_0)>0$, in which the systems have quite good thermic stability and $\Delta G(s_1)$ has a dependence on the acceptors in the excited singlet states, for example, the electron transfer could occur for 9,10-DCA or 9-CA as an acceptor ($\Delta G(S_1)<0$), and the electron transfer is forbidden for others ($\Delta G(S_1)>0$) in the single photon processes, which is an important condition for choosing a satisfying photon-gating spectral hole burning system. In contrast for the two-photon excitation, the probabilities for the electron transfer have greatly enhanced in the upper excited triplet states, $\Delta G(T_n)$ in the last column are all negative for all acceptors, which implies that the electron transfer reactions are all allowed in the thermodynamics for the systems designed in the photon-gating process. Considering the back electron transfer which induced a hole filling[13] for the holes burnt in advance, it is still important to choose a matching donor-acceptor system, for example, the system of Zn-P_2TBP/ DCB is a good match, which has an enough driving force for photon-gating spectral hole burning and a high efficiency and stability for the holes burnt in advance.

Figure 4 shows the variation of the absorption spectra of the 0-0 transition (Q band) of Zn-P_2TBP/DCB/PMMA system before and after the photon-gated spectral hole burning at 20 K with P_1= 38 mW/cm^2, P_2= 75 mW/cm^2 for 60 min..

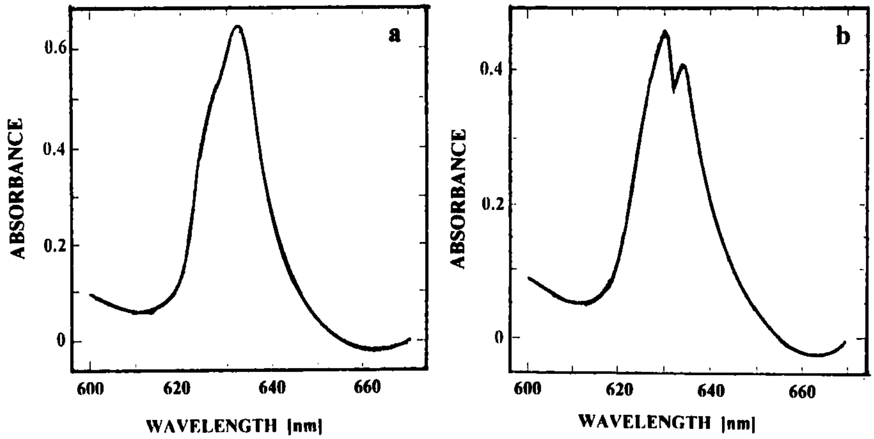

FIGURE 4. Comparison of the absorption spectra of the 0-0 transition of Zn-P_2TBP/DCB/PMMA before (a) and after (b) the photon-gated spectral hole burning at 20 K with P_1=38 mW /cm^2, P_2=75 mW/cm^2,for 60min.

Figure (4a) gives the profile of the Q band before hole burning at 20 K, in which the maximum absorption peak appears at 632 nm with the absorbance of 0.64 and FWHM of 14.7 nm, which has 3 nm blue shift of absorption peak and a decrease of FWHM by about 14%, respectively compared with that of the values determined at room temperature[12]. Figure 4(b) gives the profile variation of the Q band after hole burning at λ_l= 632 nm using more powerful power density P_l=38 mW/cm^2 and P_2=75 mW/cm^2 for 60min. So that the typical photon-gated spectral deep hole at λ_l= 632nm is formed due to the absorbance decreasing greatly and the corresponding photoproduct spectrum could also be detected in the absorption band of Zn-P_2TBP.

Figure 5 shows the differential absorption spectra after the hole burning under the condition as mentioned above.

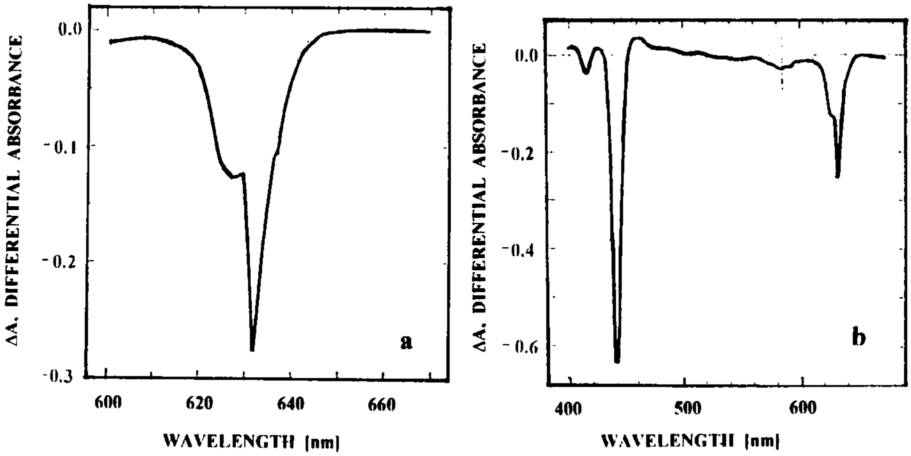

FIGURE 5 The differential absorption spectra of the photoproduct between 600 – 670 nm (a) and 400 – 670 nm (b) after the hole burning for Zn-P_2TBP/DCB/PMMA with P_l=38 mW/cm^2, P_2=75 mW/cm^2 for 60 min at 20 K

Figure 5(a) is the differential absorption spectrum of the Q band between 600 – 670 nm, in which the absorbance has obvious negative variation with the decrease of differential absorbance by 0.27, where a deep hole with $\Delta T/T_l$=42%, hole width of 5 nm around frequency-selective wavelength λ_l=632 nm is formed, which superimposes on the Q band partially broad-band blenched. It indicates that the reaction has been occurred with high conversion yield during the photon-gated process, which should accompany a formation of the photoproduct. Figure5(b) shows the spectrum of the photoproduct between 400 - 670 nm by the differential spectral method, in which an observable positive absorption in the region of 400 - 500 nm is observed, which is a difference absorbance between the negative value of Soret band of the reacted molecules of Zn-P$_2$TBP and the positive value of the photoproduct due to both superimposing each other in this region. From Figure 5(b), the differential absorbance of - 0.6 (the absorbance is 2.4 for Soret band of this sample before hole burning) is obtained , which corresponds to about 25% of the reactant to be converted to form the photoprpduct. However, the conversion of 42% in reactant has been calculated from the variation of - 0.27 of the differential absorbance of the Q band, resulting in a deviation of 17% due to the formation of the photoproduct, from which the absorbance of 0.4 can be calculated conveniently for the photoproduct formed during the photon-gated process. Besides, according to the distribution of the spectral shape in Figure 5(b), the maximum absorption of the photoproduct can be deduced about on the position of 440 nm, which is of a radical cation's (Zn-P$_2$TBP$^{\dot{+}}$) characteristics of the donor, which is similar to the result reported for similar system[1]. This is a direct evidence for the mechanism of donor-acceptor electron transfer during photon-gated spectral hole burning at 20 K for Zn-P$_2$TBP/DCB/PMMA system .

CONCLUSIONS

The photophysical properties of Zn-P$_n$TBP (n=1 - 4) were presented, in which the data of the electronic spectroscopies both the steady and the transient states for a series of pure compound in solutions were determined systematically, it provides a series of basic data for selecting proper donor-acceptor electron transfer systems for photon-gating spectral hole burning. A multiple photon-gated spectral hole burning was performed preferably in the mixed system with low substitution of phenyl on *meso*-position of TBP, Zn-P$_{1\text{-}2}$TBP/DCB/PMMA at 4.2K and the absorption spectrum of the radical cation (Zn-P$_2$TBP$^{\dot{+}}$) of the photoproduct was obtained by differential spectroscopic method. This is a direct evidence for the mechamism of donor-accepter electron transfer reaction during photon-gated spectral hole burning at 20 K for Zn-P_2TBP/DCB/PMMA system .

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