polymer papers

Photon-gated photochemical hole burning by electron transfer reaction: zinc tetratolyltetrabenzoporphine in poly(chloromethylstyrene)

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(Received 7 October 1993; revised 5 January 1994)

We report a new photon-gated photochemical hole burning system involving a donor–acceptor electron transfer reaction in which the electron acceptor, i.e. a Cl atom, is directly bonded to the matrix polymer chain in each monomer unit, namely zinc tetratolyltetrabenzoporphine (ZnTTBP)/poly(chloromethylstyrene) (PCMS). The simultaneous irradiation by an Ar$^+$ laser in conjunction with a dye laser forms holes 70 times more efficiently than irradiation by the dye laser alone for this ZnTTBP/PCMS system. The irradiation intensity dependence and the annealing temperature dependence of the hole depth for a one-colour hole suggest that the hole formation mechanism for the latter is a non-photochemical process in the PCMS. The quantum efficiency of hole formation by two-colour irradiation and the gating ratio in PCMS are much larger than those found for poly(vinyl chloride).

(Keywords: photochemical hole burning; two-colour irradiation; donor–acceptor electron transfer)

INTRODUCTION

The phenomenon of photochemical hole burning (PHB), where a persistent spectral hole is burnt in the absorption band of a chromophore dispersed in a host matrix at a low temperature, has attracted considerable interest over the past decade. This is partly because PHB is one of the most powerful methods available for studying the dynamical relaxation processes in glassy systems[1], the low energy excitation modes of host matrices[2], and various other aspects of low-temperature solid-state photophysics and photochemistry[3,4]. In addition, PHB has potential applications in the field of frequency-domain high-density optical storage[3].

A number of recent studies on PHB have been devoted to photon-gated systems because these make possible the realization of a non-destructive readout in a practical optical memory. In these photon-gated PHB systems, the spectral holes are formed efficiently only when the guest chromophore is excited by two photons (ideally of different wavelengths) and not so efficiently by irradiation of one colour only[3]. The various photon-gated PHB systems that have been reported can be divided into four types, based on the kinds of hole formation photoreactions that are involved, namely, ionization[5–7], decomposition[8–10], donor–acceptor electron transfer (DA-ET)[11,12], and sensitization[13,14]. Among these, DA-ET has been the most widely studied in investigations of new materials. This is probably because the DA-ET process is one of the most popular types of photochemical reaction, and allows many combinations of donors and acceptors to be considered.

In almost all of the reported photon-gated PHB systems involving DA-ET, porphyrin derivatives are used as the donor chromophores, with halogenated compounds as acceptors. The advantage of using a halogenated compound as an acceptor is that a rapid detachment of a halogen anion takes place after electron transfer, with the stability of this detached anion preventing a reversal of the electron transfer reaction. In these systems, the acceptor must exist in proximity to the donor porphyrin and so the matrix should contain the acceptor in high concentrations, without any phase separation. To achieve this, electron acceptors such as chloroform, which can be a good solvent for the porphyrin and the matrix polymers, has been used in some systems[11,12]. Another way to achieve a high concentration of electron acceptor in the matrix is to use a polymer which has the electron acceptor directly bonded to the polymer chain[15,16].

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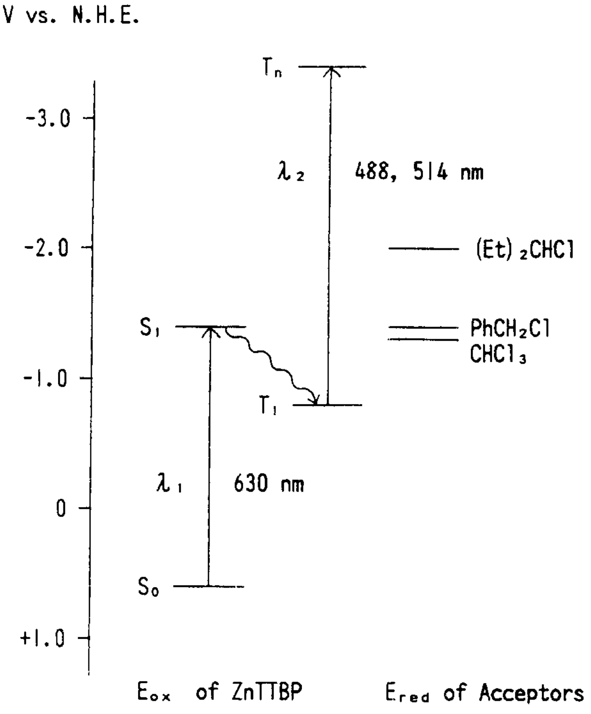

Figure 1 Schematic representation of the DA-ET reaction, showing the E_{ox} of ZnTTBP in its S_0, S_1, T_1, and T_n states, and E_{red} of Et_2CHCl, $PhCH_2Cl$, and $CHCl_3$

In this paper, we report a new, efficient system for photon-gated PHB via a DA-ET reaction, in which the matrix polymer contains a chlorine acceptor in its monomer repeat unit. The system consists of a zinc porphyrin derivative, zinc[9,18,27,36-tetra(4-tolyl)tetrabenzoporphine] (ZnTTBP) as the donor chromophore, and poly(chloromethylstyrene) (PCMS) as the matrix polymer containing the acceptor groups. The quantum efficiency of hole formation of ZnTTBP for one- and two-colour excitations and the gating ratio have been measured in PCMS and compared to the values obtained in poly(vinyl chloride) (PVC)[14] and poly(methyl methacrylate) (PMMA) with chloroform[11,12].

Figure 1 shows a schematic representation and relevant parameters for the photon-gated PHB process via a DA-ET reaction for ZnTTBP/PCMS and related systems. The relevant parameters are the oxidation potential, E_{ox}, of ZnTTBP[17] in its S_0, S_1, T_1, and T_n states, i.e. $E_{ox}(S_0)$, $E_{ox}(S_1)$, $E_{ox}(T_1)$, and $E_{ox}(T_n)$, respectively, and the reduction potential, E_{red}, of the various electron acceptors containing chlorine, namely, 3-chloropentane (Et_2CHCl), benzylchloride ($PhCH_2Cl$), and chloroform ($CHCl_3$)[18]: Et_2CHCl and $PhCH_2Cl$ are considered to have similar reduction potentials to PVC and PCMS, respectively. The E_{red} of $PhCH_2Cl$ is close to that of $CHCl_3$ and also $E_{ox}(S_1)$ of ZnTTBP, but is lower than the E_{red} of Et_2CHCl.

In PCMS, the quantum efficiency of hole formation for two-colour excitation is 70 times larger than that for one-colour excitation. The irradiation intensity dependence of the hole depth of a one-colour hole and the results from annealing experiments has suggested that the one-colour hole is created by a non-photochemical process in PCMS. The hole formation efficiency for two-colour excitation and the gating ratio in PCMS are slightly smaller than those found in PMMA with chloroform, and are much larger than those in PVC. The effects of the concentration and the reduction potential of the acceptor on the hole formation efficiency, and on the gating ratio, are also discussed.

EXPERIMENTAL

The ZnTTBP compound was synthesized by the method reported previously[19] and was purified by extraction and column chromatography. The PCMS was prepared from distilled chloromethylstyrene (mixture of *p*- and *m*-isomers, Tokyo Kasei) by a radical polymerization reaction using 2,2′-azobisisobutyronitrile (Tokyo Kasei) as the initiator. The PMMA was prepared from distilled methyl methacrylate (Wako Pure Chemical). The PCMS and PMMA, plus PVC (Wako Pure Chemical) were used after reprecipitation from benzene/methanol. Sample films, containing $\sim 1 \times 10^{-4}$ mol kg^{-1} of ZnTTBP, were prepared by a film casting method, using tetrahydrofuran as the solvent.

The sample films were placed in a cryostat attached to a cryogenic refrigerator (Sumitomo, SRD204), and were irradiated at 20 K with an Ar^+-laser (Coherent, Innova70) pumped single mode CW DCM dye laser (Coherent, 699-01) as the site-selecting light (λ_1) and with an Ar^+ laser (NEC, GLG3200) as the gating light (λ_2). The holes were detected through the change in transmittance using a 1 m monochromator (Jasco, CT100C), a photomultiplier (Hamamatsu, R943-02), and a lock-in amplifier (Jasco, LA126W). Details of the apparatus used have been given previously[20].

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectrum of ZnTTBP/PCMS at room temperature. The site-selecting light (λ_1) is irradiated at the lowest *Q* band of ZnTTBP, at $\sim$ 630 nm. The ZnTTBP, excited to the S_1 state, undergoes intersystem crossing with a high efficiency (>0.7) to T_1[11,12]. The T_1 state of ZnTTBP can then be excited to a highly excited triplet state, T_n, by the gating light (λ_2) at 488 and 514 nm, because the wavelength of λ_2 is close to the maximum absorption of the T–T transition of

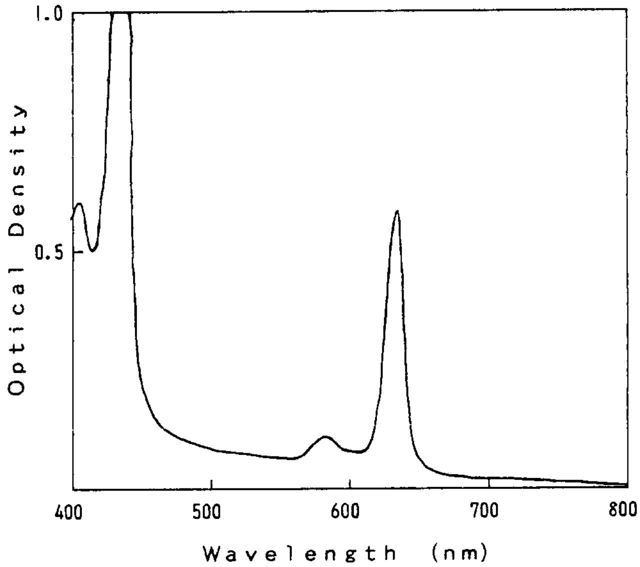

Figure 2 Absorption spectrum of ZnTTBP/PCMS, measured at room temperature

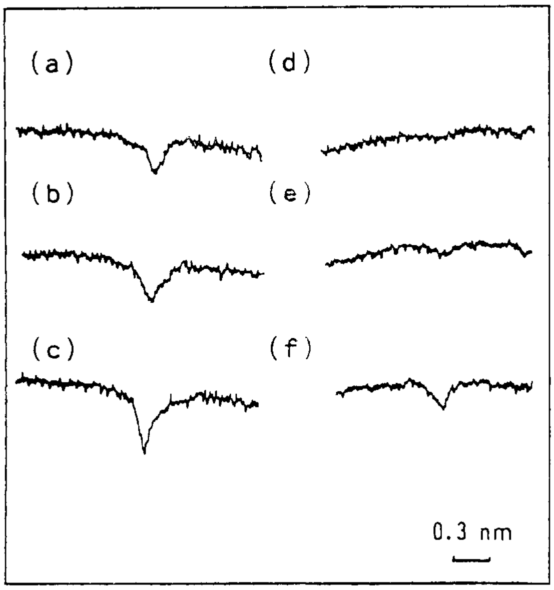

Figure 3 Typical hole profiles obtained for the ZnTTBP/PCMS system. Traces (a), (b), and (c) show the growth of a two-colour hole at 627.8 nm, burnt by 1, 2, and 4 min irradiations, respectively, using 10 μW cm^{-2} of λ_1 and 1 mW cm^{-2} of λ_2. Traces (d), (e), and (f) show the growth of a one-colour hole at 629.8 nm. Trace (d) is produced by 4 min irradiation of 10 μW cm^{-2} of λ_1, and traces (e) and (f) are the resulting hole spectra after additional irradiations by λ_1 on sample (d): (e) 40 μW cm^{-2}, 2 min; (f) 400 μW cm^{-2}, 1 min

ZnTTBP and the ground-state ZnTTBP has only a small absorption cross section in the λ_2 region. The excitation of ZnTTBP to T_n in the same wavelength regions of λ_1 and λ_2 has also been reported for the ZnTTBP–CHCl$_3$/PMMA[11,12] and ZnTTBP/glycidyl azide polymer (GAP)[13,14] systems.

Typical hole profiles for the ZnTTBP/PCMS system are shown in *Figure 3*. Traces (a), (b), and (c) show the growth of a two-colour hole at 627.8 nm, burnt by irradiations of 1 min, 2 min, and 4 min, respectively, of a 10 μW cm^{-2} dye laser and a 1 mW cm^{-2} Ar$^+$ laser. Trace (d) is the transmission spectrum obtained after 4 min irradiation by 10 μW cm^{-2} of λ_1 at 629.8 nm. Further irradiations (one-colour) at 629.8 nm on the sample in (d) produced traces (e) and (f) (conditions: (e) 40 μW cm^{-2}, 2 min; (f) 400 μW cm^{-2}, 1 min). It is apparent that λ_2 enhances the hole formation because the total irradiated energy of λ_1, for the trace (f), for example, is 52 times larger than that for the trace (a), in which a similar depth of hole to that in trace (f) has been burnt. The two-colour hole burning for ZnTTBP/PCMS is attributed to the DA-ET reaction from the T_n of ZnTTBP to the chlorine atom in PCMS, as the strong irradiation of the two-colour treatment reduces the area of the absorption band of ZnTTBP.

The quantum efficiency for hole formation, based on λ_1 and Φ, was measured at the peak of the inhomogeneous line and was calculated by using the following equation[20,21]:

$$\Phi = -[\mathrm{d}(A/A_0)\,\mathrm{d}t]_{t=0}A_0/[10^3 I_0(1-10^{-A_0})\varepsilon R] \qquad (1)$$

where A is a time-varying absorbance at the laser frequency, A_0 is the absorbance before irradiation, I_0 is the incident laser intensity given in einstein cm^{-2} s^{-1}, ε is the molar extinction coefficient for the peak absorption at room temperature, and $R(=\Gamma_i/\Gamma_h)$ is the reciprocal initial ratio of a hole width, Γ_h, to an inhomogeneous width, Γ_i. In PCMS, values for Φ in the presence of λ_2, i.e. Φ_2, and for the case without λ_2, i.e. Φ_1, are 6.1×10^{-4} and 8.7×10^{-6}, respectively. So the gating ratio, $G(=\Phi_2/\Phi_1)$, becomes 70 for this ZnTTBP/PCMS system.

It is necessary to clarify the hole formation mechanism of the one-colour holes in the photon-gated PHB systems for achieving the high gating ratio. *Figure 4* shows the irradiation intensity dependence of the relative hole depth of the one-colour hole in PCMS. The one-colour holes were burnt with different intensities of λ_1 for a fixed irradiation time of 4 min. In *Figure 4* the hole depth varies as an almost linear function of the intensity in the low-intensity region, but becomes saturated when the intensity is more than 0.5 mW cm^{-2}. This fact indicates that the absorption of ZnTTBP becomes saturated as a result of a 'bottleneck' effect of the T_1 state, when the excitation intensity of λ_1 is more than 0.5 mW cm^{-2}, and that the hole formation under one-colour irradiation is a one-photon process. This is reasonable because the critical intensity of λ_1, i.e. I_{1c}, which induces absorption saturation, is estimated to be ~0.2 mW cm^{-2}, according to the following equations[14]:

$$I_{1c} = hc/(\sigma\Phi_{\mathrm{ISC}}\tau_{T_1}\lambda_1) \qquad (2)$$

$$\sigma = 10^3\varepsilon\Gamma_i/(N_A \log_e \Gamma_h) \qquad (3)$$

where σ is the absorption cross section of a ZnTTBP molecule, Φ_{ISC} is the quantum yield of the intersystem crossing, τ_{T_1} is the lifetime of T_1, h is the Planck constant, c is the velocity of light, and N_A is the Avogadro constant. Values of $\Phi_{\mathrm{ISC}}=0.9$, $\tau_{T_1}=20$ ms, $\varepsilon=10^5$ l mol^{-1} cm^{-1}, and $(\Gamma_i/\Gamma_h)=300$ were used for the estimation of I_{1c}. The one-photon hole formation process under one-colour irradiation in PCMS is in contrast to the one-colour process for the ZnTTBP/GAP system[14], in which the hole is burnt via a two-photon sensitization mechanism.

Figure 5 shows changes in the hole spectra for one- and two-colour holes in the ZnTTBP/PCMS system during cyclic annealing to 35 K. Trace (a) shows the spectrum at 20 K before annealing. In this trace the left hole (at 631.1 nm) is burnt by two-colour irradiation ($\lambda_1=40$ μW cm^{-2}, $\lambda_2=1$ mW cm^{-2}) for 3 min, while the right hole (at 632.6 nm) is burnt by one-colour irradiation (400 μW cm^{-2}, for 10 min). Trace (b) shows the spectrum

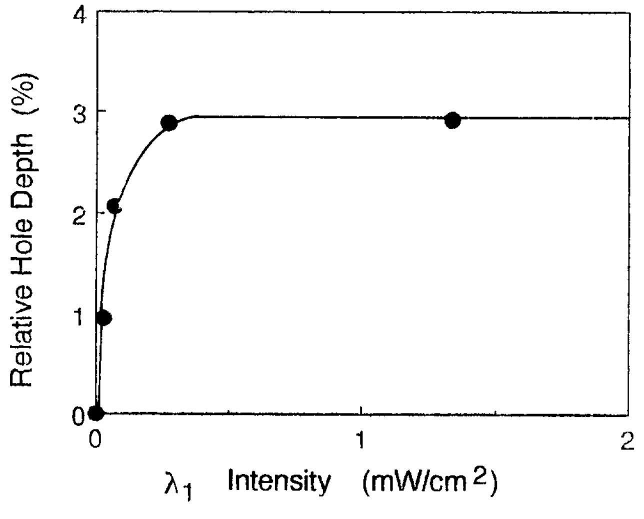

Figure 4 Irradiation intensity dependence of the relative hole depth of the one-colour holes for the ZnTTBP/PCMS system; the one-colour holes are burnt by different intensities of λ_1 for set periods of 4 min

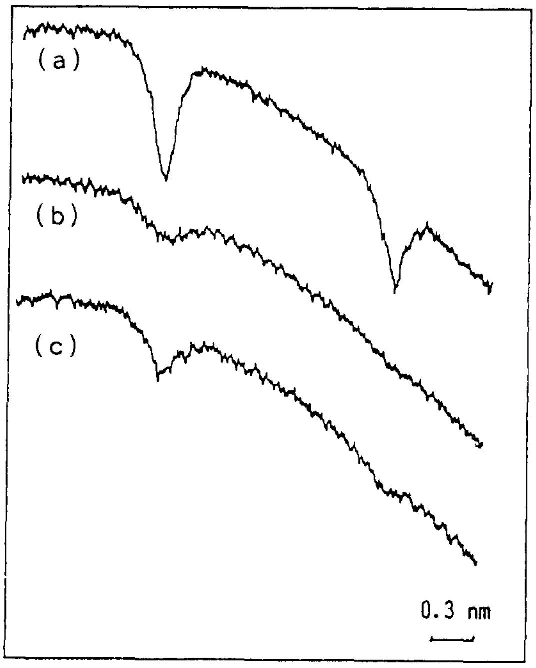

Figure 5 Hole profiles of the one- (left) and two- (right) colour holes for the ZnTTBP/PCMS system during cyclic annealing to 35 K: (a), before annealing, at 20 K; (b) during annealing; (c) after annealing, at 20 K. The two-colour hole at 631.1 nm is burnt by 3 min irradiation ($\lambda_1 = 40\,\mu\mathrm{W\,cm^{-2}}$, $\lambda_2 = 1\,\mathrm{mW\,cm^{-2}}$), and the one-colour hole at 632.6 nm is formed by 10 min irradiation ($400\,\mu\mathrm{W\,cm^{-2}}$)

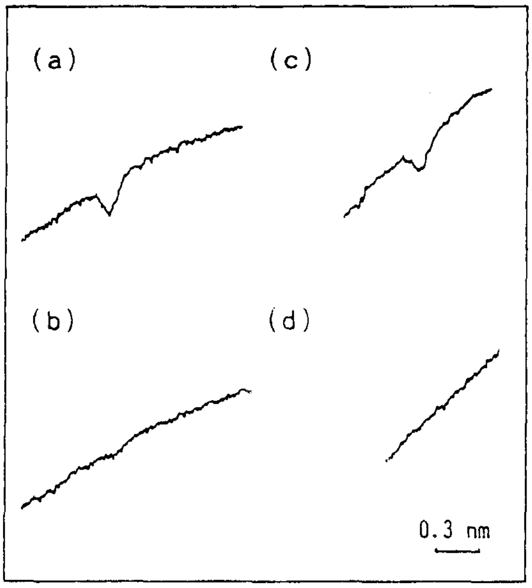

Figure 6 Hole profiles of the one- (c, d) and two- (a, b) colour holes for the ZnTTBP/PVC system at 20 K before (a, c) and after (b, d) annealing to 35 K. The holes are burnt by 8 min irradiation of λ_1 (630.4 nm, $40\,\mu\mathrm{W\,cm^{-2}}$) and λ_2 ($1\,\mathrm{mW\,cm^{-2}}$) (a), or 8 min irradiation of λ_1 (631.4 nm, $40\,\mu\mathrm{W\,cm^{-2}}$) (c)

Table 1 Experimental values obtained for Φ_1, Φ_2, and G at 20 K for ZnTTBP in PCMS, PVC, PMMA with $CHCl_3$, and GAP[11,12]

Parameter	PCMS	PVC	PMMA–$CHCl_3$	GAP
Φ_1	8.7×10^{-6}	1.4×10^{-5}	3.7×10^{-5}	4.0×10^{-7}
Φ_2	6.1×10^{-4}	2.2×10^{-5}	2.3×10^{-3}	9.8×10^{-4}
G	70	1.6	62	2450

of sample (a) during annealing at 35 K, while trace (c) shows the spectrum of the sample cooled to 20 K after annealing treatment. In these two traces the degree of thermally induced hole filling for the two-colour hole is smaller than that of the one-colour hole. Therefore, the two-colour hole and the one-colour hole in PCMS should be produced by different mechanisms. Better thermal stability of the two-colour hole is also observed for zinc tetrabenzoporphine in phenoxy resin with crotonic acid[22] and for ZnTTBP in poly(vinyl hydrogenphthalate)[23]. In general, the photochemical hole is barely filled by annealing below 40 K[24], whereas the hole area (from a non-photochemical origin) is much reduced by such annealing treatment[25]. We conclude, therefore, that the one-colour hole in ZnTTBP/PCMS is created by a non-photochemical mechanism. The one-colour hole burning in ZnTTBP–$CHCl_3$/PMMA is also attributed to a non-photochemical mechanism, as deduced from the difference in the temperature dependence of Φ_1 and Φ_2[11,12].

In *Figure 6*, the results are shown for one- and two-colour hole burnings, plus those of the cyclic annealing treatment, for the ZnTTBP/PVC system. Trace (a) shows the two-colour hole at 630.4 nm ($\lambda_1 = 40\,\mu\mathrm{W\,cm^{-2}}$, $\lambda_2 = 1\,\mathrm{mW\,cm^{-2}}$, 8 min) at 20 K. In trace (b), the hole profile of the sample (a) at 20 K, after annealing to 35 K, is shown. Traces (c) and (d) are the spectra of the one-colour hole at 631.4 nm, burnt and measured by the same conditions as in traces (a) and (b), respectively, but without λ_2. In contrast to the ZnTTBP/PCMS system, the use of λ_2 hardly enhances hole formation at all in PVC, as can be seen from traces (a) and (c). Traces (b) and (d) show that almost all of the one- and two-colour holes are filled by annealing to 35 K, suggesting that both holes are formed mainly by a non-photochemical process. In trace (b), however, a portion of the two-colour hole remains. This part is probably burnt by the DA-ET reaction.

Values of Φ_1, Φ_2, and G for ZnTTBP in PCMS, PVC, and PMMA with $CHCl_3$, measured by using our experimental apparatus, are shown in *Table 1*. The results obtained for the ZnTTBP/GAP system[14], in which the hole is formed by a two-photon sensitized photoreaction, are also shown in this table for comparison. The Φ_2 in PCMS is ~4 times smaller than that in PMMA with $CHCl_3$, and is ~30 times larger than that in PVC. This indicates that the rate constant of the DA-ET reaction from the T_n of ZnTTBP in PCMS is slightly smaller than that in PMMA with $CHCl_3$, but is much larger than that in PVC. Moerner and coworkers, who have reported photon-gated PHB for the ZnTTBP–$CHCl_3$/PMMA[11,12] and ZnTTBP/PVC[14] systems, have attributed the low value of Φ_2 in PVC to the low concentration of acceptor sites (chlorine atoms) in PVC[14]. However, in spite of the fact that the concentration of the chlorine atoms in PCMS is ~2.5 times lower than that in PVC, the Φ_2 in PCMS is ~30 times larger than that in PVC, as shown in *Table 1*. No dependence of the acceptor concentration on Φ_2 in the case where the acceptor is directly bonded to the matrix polymer is found[15]. So we conclude that the main parameter for the photon-gated PHB system via a DA-ET reaction which determines the Φ_2 is not the concentration of the acceptor, as long as this concentration has a high enough value. Takahashi *et al.*[26] report the dependence of ΔG, the release of free energy in the DA–ET reaction, on Φ_1 and Φ_2 for several photon-gated PHB systems. According to their results and discussions, Φ_2 becomes higher as ΔG increases, a conclusion which is consistent with our results for the ZnTTBP/PCMS and ZnTTBP/PVC systems. Therefore, we attribute the difference in Φ_2 for PCMS and PVC to the difference in ΔG or E_{red} of the two matrices. The difference in Φ_2 between the ZnTTBP/PCMS and ZnTTBP–$CHCl_3$/PMMA systems may be due to the difference in E_{red} of the two matrices, or in the acceptor concentrations. (In our work, we used a ZnTTBP–$CHCl_3$ sample containing more than 10 mol kg^{-1} of $CHCl_3$.)

It can be seen in *Table 1* that the Φ_1 values do not differ from each other as much as the Φ_2 values do, except in the case of the ZnTTBP/GAP system which shows a low Φ_1, which results in a high gating ratio. The hole formation mechanism for the one-colour hole in PCMS, PVC, and PMMA with $CHCl_3$ is a non-photochemical process. On the other hand, the one-colour hole in GAP is burnt by a two-photon photochemical reaction[14]. Therefore, suppression of the non-photochemical hole burning process should be a good way of identifying PHB systems with high gating ratios.

In conclusion, we have presented a new photon-gated PHB system via a DA-ET reaction, namely ZnTTBP/PCMS, in which the electron acceptor is directly bonded to the matrix polymer chain in each monomer unit. The one-colour hole burning process for the ZnTTBP/PCMS system is attributed to a non-photochemical process. The Φ_2 and G values for this system are much larger than those obtained for the ZnTTBP/PVC system.

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