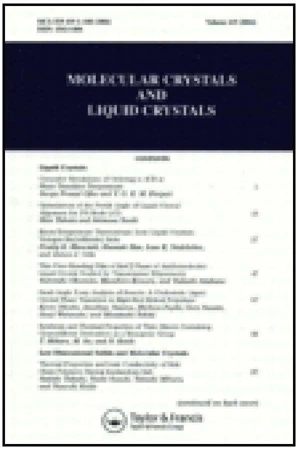

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FAST BURNING OF PERSISTENT SPECRTRAL HOLES IN DONOR-ACCEPTOR ELECTRON TRANSFER SYSTEMS

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Abstract Persistent spectral hole burning (PHB) has been achieved on nano- or subnanosecond time scales in donor-acceptor electron transfer (DA-ET) systems. The characteristics and mechanism of PHB in those systems are discussed with a view to future memory application.

INTRODUCTION

In the past few years there have been many attempts to realize fast PHB. This is because of its potential for future memory applications where a large volume of information is handled at very high speed. PHB on a submicrosecond time scale was reported via the one-photon proton tautomerization (PT) of metal-free phthalocyanine.[1] A high-sensitivity detection scheme is crucial for successful hole-burning in times as short as 100 ns.[1] Subsequently, PHB on a nanosecond time scale was achieved in several DA-ET systems.[2,3] The high quantum yield of these reactions has made it possible to detect spectral holes burnt in such short times by means of conventional transmittance change measurement. The shortcoming of the systems is the longer duration of the gating excitation, which means that the overall burning time becomes as long as hundreds of milliseconds.[2,3] It will be necessary to shorten the burning time if PHB is to be applied to future memory.

Recently we have achieved fast PHB on nano- or subnanosecond time scales in some DA-ET systems where the donor and the acceptor consist of metal-free tetraphenylporphine (TPP) and a variety of organic molecules, respectively (Fig. 1).[4-8] Their solidity at room temperature makes it much easier to prepare stable samples with a desired composition than in other DA-ET systems reported to date where the acceptors are in liquid state at room temperature.[2,3]

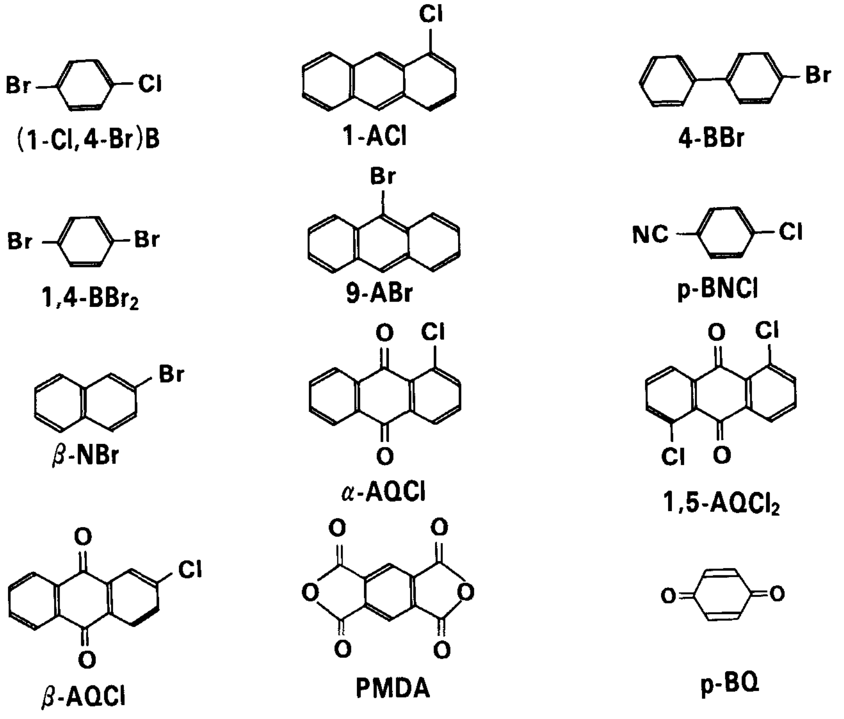

FIGURE 1 Molecular structures of the acceptor molecules. Abbreviations are as follows: (1-Cl, 4-Br)B; 1-Chloro-4-Bromobenzene, 1-ACl; 1-Chloroanthracene, 4-BBr; 4-Bromobiphenyl, 4-BBr2; 4-Dibromobenzene, 9-ABr; 9-Bromoanthracene, β–BNCl; β-Chlorobenzonitrile, β-NBr; β-Bromonaphthalene, α-AQCl; α-Chloroanthraquinone, 1,5-AQCl2; 1,5-Dichloroanthraquinone, β-AQCl; β-Chloroanthraquinone, PMDA; Pyromelittic dianhydride and *p*-BQ; *p*-Benzoquinone.

EFFECTS OF REACTION EXOTHERMICITY ON PHB MECHANISM

We have established that the PHB reaction mechanism in DA-ET systems correlates well with the overall change in the free energy, ΔG, which accompanies the reaction.[9] The ΔG value for a photoinduced ET reaction from a photoexcited donor to a ground state acceptor is given by[9,10]:

One-Photon Type: $\Delta G_{op} = E_{ox}{}^{D} - E_{red}{}^{A} - E_{D}{}^{*}$ (1)

Two-Photon Type: $\Delta G_{tp} = E_{ox}{}^{D} - E_{red}{}^{A} - E_{IM} - E_{gate}$ (2)

where the symbols have their usual meanings.

Table I lists the burning conditions, hole formation mechanism and reduction potential of the acceptors, together with ΔG_{op} and ΔG_{tp} values calculated with eqs. (1) and (2). Hole-burning was achieved via the one-photon process for all the D-A combinations that satisfied the condition, $\Delta G_{op}<0$, and via the two-photon process for those that satisfied the conditions $\Delta G_{op}>0$ and $\Delta G_{tp}<0$.[9] The hole formation mechanism in DA-ET systems can therefore be predicted on the basis of the ΔG value.

TABLE I Reduction potential of the acceptors,[4,7,11] the calculated reaction exothermicity, the hole formation mechanism and the burning conditions in a variety of D-A combinations. The donor is TPP (E_{ox}^{D}=0.95 V vs SCE).[12]

Acceptor	E_{red}^{A} (V vs SCE)	Exothermicity ΔG_{op}	ΔG_{tp}	Mechanism	Burning conditions λ_1	λ_2
					(μW/cm^2, ms)	
(1-Cl, 4-Br)B	-1.96	+	-	TP[a)]	25, 8	43, 33
1-ACl	-1.84	+	-	TP	60, 8	60, 8
4-BBr	-1.73	+	-	TP	60, 8	400, 67
4-BBr$_2$	-1.71	+	-	TP	30, 8	43, 33
9-ABr	-1.68	+	-	TP	60, 8	60, 8
p-BNCl	-1.65	+	-	TP	120, 0.01	80, 3
β-NBr	-1.64	+	-	TP	40, 8	620, 67
α-AQCl	-0.83	-	-	OP[b)]	20, 8	-
1,5-AQCl$_2$	-0.79	-	-	OP	40, 8	-
β-AQCl	-0.78	-	-	OP	40, 8	-
PMDA	-0.55	-	-	OP	80, 0.01	-
p-BQ	-0.51	-	-	OP	65, 8	-

[a)]Two-photon process. [b)]One-photon process.

FAST PHB VIA ONE-PHOTON MECHANISM

We have recently observed, for the first time, subnanosecond (500 ps) PHB in TPP-*p*-BQ/PMMA.[8] It has been confirmed that, apart from the possibility of the PT of TPP, no spectral hole could be detected in TPP/PMMA by the irradiation of only a single 500 ps light pulse with the same burning energy as that used in TPP-*p*-BQ/PMMA (tens of nJ/cm^2). In other DA-ET systems reported to date, the persistence of spectral holes has been attributed to dissociative halogen detachment in the acceptor.[2-7,9,13] This is not the case for this system because *p*-BQ molecules have no halogen substituent. Since *p*-BQ has a higher reduction potential than those of the acceptors used so far, their anions should be more stable than others and enable persistent spectral holes to be burnt. However, the spectral holes disappeared almost completely if the temperature was increased to 20 K (Fig. 2). This is in remarkable contrast to ones burnt in other systems with a PMMA matrix.[14] Since the thermal stability of spectral holes is primarily determined by the nature of the host matrix, the rapid hole filling reflects the fact that thermally activated recombination between the photoproducts (TPP cation radicals and *p*-BQ anion radicals) plays an important role in the hole filling process. Thus the halogen detachment accompanying the DA-ET is important for the achievement of good spectral hole stability.

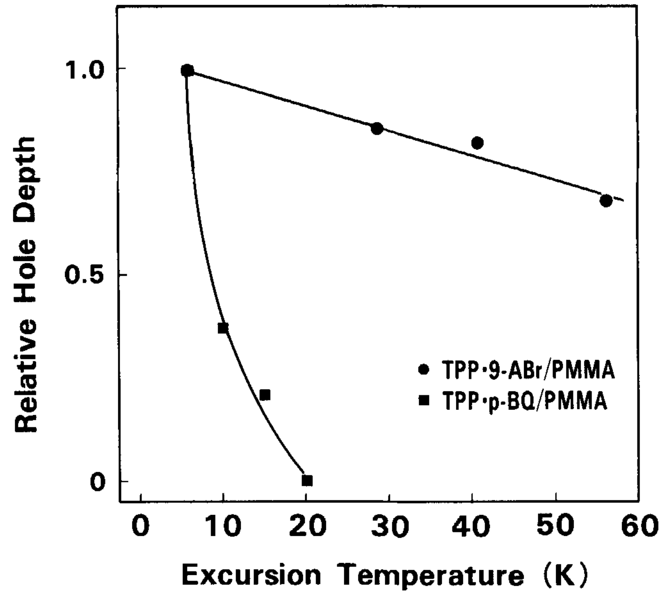

FIGURE 2 The thermal stability of a spectral hole in TPP-*p*-BQ/PMMA and TPP-9-ABr/PMMA measured by a temperature cycling experiment. Note that *p*-BQ has no halogen substituent while 9-ABr has a halogen substituent.

FAST PHB VIA PHOTON-GATED TWO-PHOTON MECHANISM

Photon-gated two-photon PHB was observed in TPP-AX (X=Cl or Br) systems.[4-7] Spectral holes were burnt by the irradiation of both frequency selective (λ_1; duration: 2.5 ns) and gating (λ_2; duration: 67 ms, wavelength: 514.5 nm) excitations. The possibility of PHB via the PT of TPP is excluded due to the triplet bottleneck effect.[1] A photon-gated spectral hole can be burnt even with a focused laser beam irradiation of 200 μmϕ.

The hole formation yield η strongly depends on the polymer matrix, the acceptor concentration and the gating light wavelength. The first two types of dependence reflect the fact that the η value is a function of the D-A average separation. In fact, the η value increased by up to one order with a 100-fold increase in the acceptor concentration up to 5×10^{-2} M. A further increase in acceptor concentration up to about 10^{-1} M has recently been achieved by branching the acceptor into a host polymer side-chain via copolymerization.[15] The η value in PE is larger than that in PMMA because the D-A average separation in PE is shorter than that in PMMA. It is reported that the guest molecules in a semicrystalline PE matrix are situated in the amorphous parts of the matrix.[16] The thermal stability of spectral holes, investigated with a temperature cycling experiment, indicates that although the trend of the irreversible hole broadening is the same as that for the PT in both polymer matrices,[14] its magnitude for TPP-AX systems is smaller than that for the PT in the respective matrix. It should be noted that the holewidth after temperature cycling up to about 80 K was still narrower than 30 GHz in a PMMA matrix. Very recently we have found that the stability of spectral holes in DA-ET systems increases by branching the acceptor into a host polymer side-chain.[15]

The action spectrum of the photon gating for λ_2 indicates that unlike the DA-ET systems reported so far, the intermediate state of the two-photon PHB reaction is not the triplet state of the donor (Fig. 3). The persistence of spectral holes is realized by the dissociative halogen detachment of the acceptor as also observed earlier.[2-7,9,13]

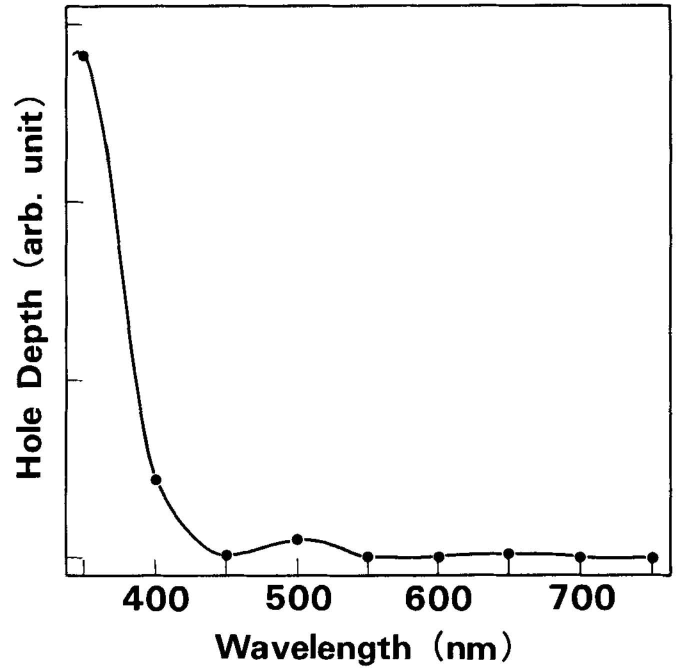

FIGURE 3 Photon-gated action spectrum for λ_2 in TPP-1-ACl/PE.

CONCLUSIONS

The PHB materials based on the DA-ET reaction discussed above exhibit promising characteristics for future memory application. Allowing for the wide variety of D-A combinations, we hope to be able to find optimum D-A combinations by continuing efforts in this direction with the aid of a material design guideline based on ΔG.

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REFERENCES

1. M. Romagnoli, W. E. Moerner, F. M. Schellenberg, M. D. Levenson and G. C. Bjorklund, J. Opt. Soc. Am. B, 1, 341 (1984).
2. W. E. Moerner, T. P. Carter and C. Braeuchle, Appl. Phys. Lett., 50, 430 (1987).
3. T. P. Carter, C. Braeuchle, V. Y. Lee, M. Manavi, and W. E. Moerner, J. Phys. Chem., 91, 3998 (1987).
4. H. Suzuki, T. Shimada, T. Nishi, and H. Hiratsuka, Jpn. J. Appl. Phys., 29, L1146 (1990).
5. H. Suzuki, Nonlinear Optics, in press.
6. H. Suzuki, Solid State Physics, 36, 51 (1991) [in Japanese].
7. H. Suzuki, T. Shimada and H. Hiratsuka, J. Appl. Phys., in press.
8. H. Suzuki and T. Shimada, Appl. Phys. Lett., to be published.
9. H. Suzuki, T. Shimada and H. Hiratsuka, Chem. Phys. Lett., in press.
10. M. Julliard, in Photoinduced Electron Transfer, Part B, edited by M. A. Fox and M. Chanon (Elsevier, Amsterdam, 1988), p. 216.
11. L. Meites and P. Zuman, CRC Handbook Series in Organic Electrochemistry, Vol. 1 (CRC Press, Cleveland, 1976).
12. R. H. Felton, in The Porphyrins, edited by D. Dolphin, Vol. V (Academic Press, New York, 1978) p. 127.
13. T. P. Carter, C. Braeuchle, V. Y. Lee, M. Manavi, and W. E. Moerner, Opt. Lett., 12, 370 (1987).
14. T. Nishi, H. Suzuki, T. Shimada and H. Hiratsuka, in Polymers for Microelectronics, Science and Technology, edited by Y. Tabata, I. Mita, S. Nonogaki, K. Horie and S. Tagawa, (VCH, Weinheim, 1990), p. 497.
15. H. Suzuki, T. Nishi, T. Shimada and H. Hiratsuka, J. Lumin., to be published.
16. Th. Sesselmann, W. Richter and D. Haarer, Phys. Rev. B, 36, 7601 (1987).