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New persistent photon-gated spectral hole burning systems: metal–tetrabenzoporphyrin derivatives/p-hydroxybenzaldhyde/PMMA

Baozhu Luo, Mingzhen Tian, Wenlian Li, Shihua Huang and Jiaqi Yu
Changchun Institute of Physics, Academia Sinica, 1 Yan-an Road, Changchun 130021, China

In this paper, the authors report persistent spectral hole burning in new donor–acceptor electron transfer (DA-ET) systems composed of metal–tetrabenzoporphyrin (MTBP) derivatives as the donors and p-hydroxybenzaldhyde (PHBA) as the acceptor, which is solid at room temperature, in poly-methylmethacrylate (PMMA) films. A range, from −3.51 to −1.5 eV, of reduction potential of electron acceptor for MTBP as a donor was given. In the Zn–tetraphenylbenzoporphyrin (ZnTPBP)/PHBA/PMMA system the inhomogeneous line width (FWHM, Γ_i) was 7.0×10^2 cm^{-1}. At 4.2 K, a narrow hole with Γ_{hole} = 8 GHz was obtained, and a high ratio, $\Gamma_i/\Gamma_{hole} = 2.6\times10^3$, was obtained. The hole could be filled efficiently by heating or irradiation with 532 nm laser light. It indicates that the holes can be erased spot by spot.

1. Introduction

As the potential of persistent spectral hole burning has enabled us to expect a 10^3 to 10^4 fold increase in storage density over conventional optical storage systems, the interest in persistent spectral hole burning materials with high Γ_i/Γ_{hole} ratio and erasability is growing. Some organic materials were investigated and a few mechanisms were put forward [1]. A representative system was TZT/$CHCl_3$/PMMA undergoing donor–acceptor electron transfer (DA-ET) which was perhaps the best mechanism for persistent spectral hole burning in organic systems [2]. However, there was an insurmountable problem in the system because the electron acceptor, $CHCl_3$, is a volatile liquid at room temperature. The problem made preparation and conservation of samples difficult.

In this paper, a range of reduction potential of electron acceptor was given according to the condition of electron transfer. PHBA was selected as a solid electron acceptor to overcome the above mentioned disadvantage. The solid electron acceptor could easily be doped in a polymer film in which its concentration could be modified precisely. Five kinds of porphyrin derivatives (MTBP) were synthesized and five MTBP/PHBA/PMMA polymer films were prepared. The ratio Γ_i/Γ_{hole} of ZnTPBP/PHBA/PMMA system reached 2.6×10^3 at 4.2 K which was the highest one so far to the best of our knowledge. The erasability of the hole was also investigated. It indicated that the hole could be erased efficiently by heating or irradiation of 532 nm laser with low power which did not bring about heating effect.

Correspondence to: Dr. B. Luo, Changchun Institute of Physics, Academia Sinica, 1 Yan-an Road, Changchun 130021, China.

2. Experimental

Five kinds of MTBP, Zn-tetrabenzoporphyrin, Zn-tetraphenylbenzoporphyrin, Mg-tetraphenylbenzoporphyrin, Zn-tetranaphthalenebenzoporphrin and Zn-tetratolylbenzoporphyrin were synthesized, and PHBA was obtained commercially. 0.5×10^{-6} mol MTBP, 1×10^{-3} mol PHBA and 0.5 g PMMA were dissolved in $CHCl_3$, the homogeneous solution evaporated naturally

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in the air and the polymer films that we expected were obtained more than ten hours later. MTBP/PMMA polymer films were also prepared to show the function of acceptor.

A hole formation experiment was performed at 4.2 and 20 K. A ring dye laser (dye was RB) pumped by an Ar^+ laser or He–Ne laser (632.8 nm) was used as the frequency selecting light. And Ar^+ laser (514.5 nm) or Nd:YAG (SHG, 532 nm) was used as the gating light. Hole detection was performed by probing the transmission of a beam of white light passing through the sample.

Laser-induced hole filling experiments were done with irradiation of 532 nm laser. The thermal hole filling was performed in a helium gas closed-cycling cryostat system. Experiments were done for each sample, but our discussion will focus on the representative ZnTPBP/PHBA/PMMA system.

3. Results and discussions

3.1. Selection of electron acceptor

In a donor–acceptor electron transfer system, ΔG, the equilibrium free energy release during electron transfer reaction, can be expressed by the following relation [3]:

$$\Delta G = F(E_{OX}^{D} - E_{red}^{A}) - E_{00} - e^2/R_c\varepsilon, \qquad (1)$$

where F is the Faraday constant, E_{OX}^{D} is the oxidation potential of the donor, E_{red}^{A} is the reduction potential of the acceptor, E_{00} is the electronic energy deposited in the donor by the photoexcitation, e is the electronic charge, R_c is the separation distance of the ion pair, and ε is the dielectric constant of the medium.

The condition that an electron transfer reaction occurs is $\Delta G < 0$. Photon-gated spectral hole burning requests: $\Delta G > 0$ (no hole is formed) when only frequency selecting light (λ_1) pumps the sample; $\Delta G < 0$ (hole can be formed) when frequency selecting light and gating light (λ_2) pump the sample simultaneously. In our experiment, frequency selecting light was at $\lambda_1 = 632.8$ nm and gating light at $\lambda_2 = 532$ nm. Ignoring the

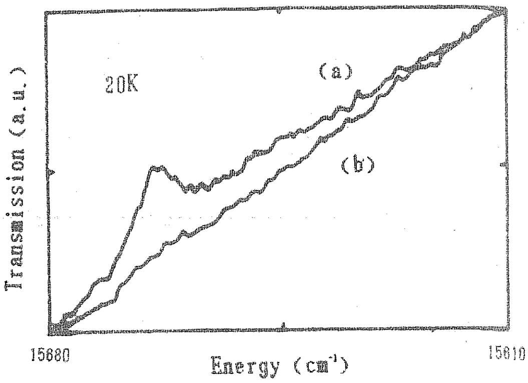

Fig. 1. Gating effect of gating light in the ZnTPBP/PHBA/PMMA system at 20 K. (a) hole burnt simultaneously with two photons at $\lambda_1 = 632.8$ nm and $\lambda_2 = 532$ nm; (b) transmissions after irradiations of $\lambda_1 = 632.8$ nm for 15 s.

final terms in eq. (1) for simplicity and using $E_{OX}^{D} = 0.36$ eV for ZnTBP [4], one can get a selection rule of electron acceptor potential, from -3.51 to -1.6 eV, when electron transfer reaction occurs.

According to the selection rule, the authors chose PHBA ($E_{red}^{A} = -1.68$ eV) as an electron acceptor, and prepared five donor–acceptor PMMA polymer films. Hole-burning experiments showed that all the samples were photon-gated spectral hole-burning systems, as shown in fig. 1. P-aminoacetophenone (PAAP, $E_{red}^{A} = -2.23$ eV) played the same role in ZnTPBP/PAAP/PMMA systems. Two-photon spectral hole-burning experiments for ZnTPBP/PMMA and ZnTPBP/PHBA/PMMA were done. The experimental conditions were the same as that in fig. 1(a). It was found that no detectable hole was formed in the former system in which most probably no electron acceptor existed. On the contrary, there was a clear burnt hole in the latter. The result indicates that the hole-burning mechanism in our system might be donor–acceptor electron transfer.

3.2. Properties of hole burning

Figure 1 shows the gating effect of the second photon, λ_2. Trace (a) shows a hole with depth

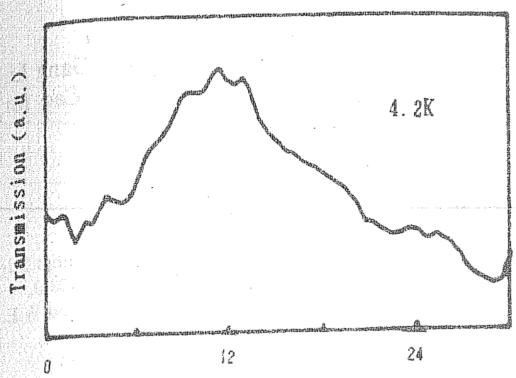

Fig. 2. Photon-gated PHB in the ZnTPBP/PHBA/PMMA system at 4.2 K.

$\Delta\alpha/\alpha = 1.6\%$ and width $\Gamma_{hole} = 6\ cm^{-1}$ burnt by simultaneously irradiating with both $\lambda_1 = 632.8$ nm, power $P_1 = 100\ \mu W$ and $\lambda_2 = 532$ nm, power $P_2 = 26$ mW for 15 s. Trace (b) gives the transmission after 15 s irradiation with only $\lambda_1 = 632.8$ nm, $P_1 = 100\ \mu W$, where no hole was formed. The experimental result indicates that our sample consisted of photon-gated spectral hole-burning material.

The absorption spectra of ZnTPBP/PHBA/PMMA were measured at room temperature, 20 K, and 4.2 K. They show that the inhomogeneous line width of the $S_0 \leftarrow S_1$ transition is not temperature dependent, $\Gamma_i = 7.0 \times 10^2\ cm^{-1}$.

A hole was burnt at 4.2 K (fig. 2) with $\lambda_1 = 630$ nm, $P_1 = 32\ \mu W$ and $\lambda_2 = 514.5$ nm, $P_2 = 8$ mW, the diameter of the laser spot was about 5 mm and the irradiation time $t = 100$ s. The full width at half maximum of the hole (Γ_{hole}) was 8 GHz. The hole depth ($\Delta\alpha/\alpha$) was 2.5%. Thus one could get $\Gamma_i/\Gamma_{hole} = 2.6 \times 10^3$ at 4.2 K which is the highest ratio among organic materials yet reported to the best of our knowledge.

3.3. *Hole filling*

In a donor–acceptor electron transfer mechanism, the electron is transferred from a donor to an acceptor in producing hole burning; whence the hole filling process is a back reaction process. Laser-induced hole filling and thermally activated hole erasing were demonstrated.

Figure 3 shows the laser-induced hole filling experiment of ZnTPBP/PHBA/PMMA system. A hole was burnt at $\lambda_1 = 632.8$ nm, $P_1 = 400\ \mu W$, $\lambda_2 = 532$ nm, $P_2 = 16.5$ mW and burning time of 15 s. The sample was then irradiated at 532 nm with a laser of power 19 mW for 120 s. The hole was totally erased, which is shown in fig. 3(b). In order to exclude heating effects caused by high laser power, a low power at 532 nm, of 19 mW, was chosen. One can see that laser irradiation of 532 nm could be either a gating light in the hole-burning process, or an erasing light in the hole-filling process. Thus, in order to get a deeper hole during the hole-burning process it was very important to choose a suitable burning power of λ_2 and burning time.

A thermal cycling experiment was carried out for ZnTPBP/PHBA/PMMA. At 20 K, a quite deep hole with depth 14% was burnt. After burning, we raised the temperature of the sample in the cryostat to 30, 40, 50 and 60 K and detected the hole at the respective temperatures. Then we recooled the sample to 20 K and detected the hole at this temperature. It was found that after the thermal cycling, the hole area decreased and the hole width increased. The result indicates that there is thermally activated hole filling and

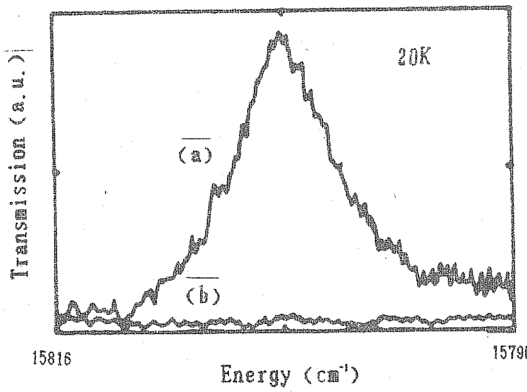

Fig. 3. Laser-induced hole filling with laser irradiation at 532 nm, at 20 K: (a) before hole filling; (b) after hole fitting.

spectral diffusion in our system. Further investigations on the mechanism and process of hole filling are being carried out.

4. Conclusion

New persistent photon-gated spectral hole-burning polymer films MTBP/PHBA/PMMA, were prepared. A range of reduction potentials of the electron acceptor for MTBP as a donor was given, from −3.51 to −1.6 eV. The ratio of Γ_i/Γ_{hole} reaches 2.6×10^3 at 4.2 K. The hole in the system could be efficiently erased by laser irradiation at 532 nm.

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References

[1] W.E. Moerner, ed., Persistent Spectral Holeburning: Science and Applications (Springer-Verlag, Berlin, 1988).
[2] T.P. Carter, C. Brauchle, V.Y. Lee, M. Manavi and W.E. Moerner, J. Phys. Chem. 91 (1987) 3998.
[3] J.W. Verhoeven, Pure Appl. Chem. 58 (1986) 1285.
[4] A. Vogler, B. Rethwisch, H. Kunkley, J. Huttermann and J.O. Besenhard, Angew. Chem. Int. Ed. Engl. 17 (1978) 951.