



and ladder of the band structure of the branch and PL spectra in the visible region, and (4) the PL spectra in the experimental electronic band structure and compared the one-dimensional Si structures. The constructed of the Si-Si bonds exhibit different times. The first calculations suggest atoms with three structures cause the region.

s grateful to the financial support.

v. 89 (1989) 1359.
kura, Y. Morimoto, A. Iler and S. Abe, Phys.

J. Phys. Chem. 95
note, T. Komatsu, K. Solid State Commun.

Asamoto, Phys. Rev.
Rev. B 39 (1989) 11028

Luminescence and relaxation of the excited states in covalent-linked tetratolylporphyrin-phthalocyanine

Kai Dou^{a,*}, Jisheng Zhang^b, Wu Xu^b, Shihua Huang^b, Jiaqi Yu^b, Xurong Xu^b

^aLaboratory Aime Cotton, CNRS 11, Batiment 505, Campus d'Orsay, 91405 Orsay Cedex, France

^bChangchun Institute of Physics, Academia Sinica, 1 Yan'an Road, Changchun 130021, China

Abstract

The feature of the charge transfer in the binary molecules of the covalently bound porphyrin-phthalocyanine has been investigated by using a technique of the nondegenerate four-wave mixing. The energy transfer from porphyrin to phthalocyanine is spectrally found. The relation between the charge transfer and the covalent-bond length is also discussed.

1. Introduction

The covalently bound porphyrin-phthalocyanines and their derivatives are thought to be a more ideal kind of photoelectric transfer materials due to the wider absorption band in the visible light range and the photo-induced charge transfer which was demonstrated by the method of the transient absorption [1,2]. However, our recent investigation reveals that these materials exhibit both the strong optical nonlinearity and the fast nonlinear response by using techniques of the degenerate and the nondegenerate four-wave mixing (DFWM and NDFWM) in addition to the feature of the photo-induced charge transfer [3,4]. Hence, they are expected to be a potential candidate for the optical data processing. In this paper, a spectral investigation on the energy transfer between porphyrin and phthalocyanine is performed. We also study the nonlinear optical properties by DFWM,

measure the charge separate time of these molecules with a variety of bond length by NDFWM, and make efforts to understand the relationship of the covalent-bond length and the charge transfer.

2. Transient grating method

The photo-induced charge relaxation can be analyzed by NDFWM known as a frequency method which is based on the transient grating. It is well known that the ultrafast processes correspond to the wider spectral distribution which is thus more convenient to be measured in frequency domain than in time domain. The transient grating is introduced by the interference of the two coherent light pulses which are incident on the nonlinear medium. On a condition of the resonance excitation, the population of the excited states are modulated by the transient grating and consequently the population grating is produced in the medium. The third light pulse is used to probe the

* Corresponding author.

formed grating and the diffracted signal as a function of time evolution gives the information related to the relaxation of the excited states of the medium.

The modulation produced by the interference of two coherent fields is written as

$$\Delta I(r, t) \propto \exp[-i(\Delta\omega t - qr)], \quad (1)$$

where $\Delta\omega = \omega_1 - \omega_2$ and $q = k_1 - k_2$ (called as grating vector). The population of the excited states will be modulated by $\Delta I(r, t)$.

If $f(t)$ represents a time response function of the medium with respect to the modulation $\Delta I(r, t)$, we detect the signal field $Q(T)$ which should be a convolution of $f(t)$ and $\Delta I(r, t)$, i.e.,

$$Q(T) = \int dt f(t) \Delta I(r, t - T) \\ \propto \exp(i\Delta\omega T) F(\Delta\omega), \quad (2)$$

$$F(\Delta\omega) = \int dt f(t) \exp(-i\Delta\omega t),$$

where $F(\Delta\omega)$ stands for the frequency response function of the medium which may be obtained by calculating accordingly the Fourier transform of the time response function. The probe light is incident on the formed grating and the diffracted signal is proportional to $|F(\Delta\omega)|^2$. Therefore, it is important to obtain the frequency response function $F(\Delta\omega)$ of the measured medium.

The energy configuration of the binary molecules we studied can be simplified to be the three-level system [3]. The binary molecules are resonantly excited into the excited state (S_1) from the ground state (G) and then the electrons of the excited states deexcite in both ways that they may decay radiatively and/or nonradiatively back to the ground, or the electron transfer takes place from S_1 to the excited state (CT) of the electron transfer. Firstly, the time response function $f(t)$ is attained by calculating the dynamic equations, and secondly, its frequency response function $F(\Delta\omega)$ is given by the Fourier transform of $f(t)$. When the lifetime T_1 of the excited state of binary molecules is much larger than the time constant (T_{CT}) of the charge transfer,

the signal intensity as a function of frequency is thus written in the following form:

$$|F(\Delta\omega)|^2 \propto \frac{1}{1 + (\Delta\omega T_{CT})^2}. \quad (3)$$

Fitting the experimental frequency distribution of the signal of NDFWM of $|F(\Delta\omega)|^2 \sim \Delta\omega$ with expression (3) gives a relaxation time T_{CT} of charge transfer.

3. Experimental

The classical setup of the phase conjugation for DFWM is adopted as the experimental arrangement of NDFWM in present measurement. A 532 nm line from the second harmonic of a Q-switched Nd:YAG laser with the pulse duration 10 ns at a repetition rate of 15 Hz is split into two beams which simultaneously pump two dye lasers. The weak dye laser beam is taken as a probe beam and the stronger one is subsequently split into two equally intense beams which are used as the forward and the backward pumping light at the counterpropagating direction. The probe light is incident at a small angle of $3^\circ - 5^\circ$ with respect to the forward pumping beam. Two pumping lights and the probe beam through Glan polarizers which are employed to match the configuration of the field polarization irradiate exactly the same spot of the 2 mm thick quartz cuvette containing the sample solution. The optical delay lines are used to ensure the temporal overlap of the three light pulses in the sample. The phase conjugate signal retraces the path of the probe beam and a fraction of it is reflected to a spectrometer, and then arrives at a photomultiplier. The signals are finally fed into Boxcar sampling integrator, and processed by a microcomputer.

The studied samples are free-base tetratolyl porphyrin (TTP), metal-free phthalocyanine (Pc), and covalently linked tetratolyl porphyrin-phthalocyanines with different bond length of $-O-$ and $-O-(CH_2)_5-O-$, i.e., TTP-O-Pc and TTP-O-(CH₂)₅-O-Pc. All of them are dissolved in the solvent of N,N-dimethyl formamide with a concentration of 10^{-4} M.

4. Results and discussion

Two groups of spectra of the porphyrin emission from the phthalocyanine spectra of excited porphyrin molecule that of phthalocyanine into the binary absorption spectra Q bands, where the Q band component to 470, 500 nm. In contrast, Pc emission at 650 nm which do not show the self-excitation wave. The excitation wavelength of 500 or 550 nm phthalocyanine, bound porphyrin. We observe the emission in addition to the excitation spectra. It is also apparent that the spectra that the exciting TTP in an analogous behavior longer bond mo examining the spectra. These results in the energy transfer phthalocyanine I.

The third-order $\chi^{(3)}$ for TTP-O- magnitude in comparison with the covalent bond $-O(CH_2)_5O-$, $\chi^{(3)}$ from 6×10^{-10} to investigate the contribution to the nonlinearity. The nonlinear simply mixed signal exists no charge experimental comparison. The binary molecule change is found in nonlinearity. So

4. Results and discussion

Two groups of luminescence bands in emission spectra of the binary molecules have been distinguished by us, one of which comes from the porphyrin emission and the other one originates from the phthalocyanine transition [3,4]. The spectra of excitation, absorption, and emission of porphyrin molecule are obviously different from that of phthalocyanine before they are combined into the binary molecule. The structure of the absorption spectrum of TTP consists of S and Q bands, where the S band centers at 410 nm and the Q band contains four subbands which correspond to 470, 500, 550, and 590 nm, respectively [4]. In contrast, Pc exhibits two absorption at 350 and 650 nm which do not overlap with the TTP absorption. For the selecting excitation, the characteristic excitation wavelength of porphyrin, for instance, 500 or 550 nm, which is not able to excite phthalocyanine, is used to excite the covalent bound porphyrin-phthalocyanine TTP-O-Pc. We observe the luminescence of phthalocyanine in addition to that of porphyrin. Fig. 1 shows the excitation spectra of TTP, Pc and TTP-O-Pc. It is also apparently seen from the excitation spectra that the luminescence of Pc is observed by exciting TTP in binary molecule TTP-O-Pc. The analogous behaviors have been observed in the longer bond molecule TTP-O-(CH₂)₅-O-Pc by examining the spectra of absorption and excitation. These results imply in fact that there occurs the energy transfer from porphyrin TTP to phthalocyanine Pc.

The third-order nonlinear optical susceptibility $\chi^{(3)}$ for TTP-O-Pc increases about 2.5 orders of magnitude in comparison to TTP and Pc. When the covalent bond length grows from -O-O-(CH₂)₅-O-, $\chi^{(3)}$ increases more than 10 times from 6×10^{-10} to 8.5×10^{-9} esu. In order to investigate the contribution of the charge transfer to the nonlinearity, we examine carefully the simply mixed samples of TTP and Pc where there exists no charge transfer but keeping other experimental conditions in consistence with that in the binary molecules. As a result, no obvious change is found in the measurement of the optical nonlinearity. So we attribute the nonlinear en-

of frequency is

(3)

y distribution of
 $2 \sim \Delta\omega$ with ex-
 ie T_{CT} of charge

conjugation for
 mental arrange-
 t measurement.
 armonic of a Q-
 pulse duration
 is split into two
 p two dye lasers.
 as a probe beam
 tly split into two
 used as the for-
 ng light, at the
 e probe light is
 ith respect to the
 mping lights and
 arizers which are
 ition of the field
 same spot of the
 ning the sample
 re used to ensure
 ight pulses in the
 nal retraces the
 fraction of it is
 then arrives at
 e finally fed into
 d processed by

se tetratolyl por-
 yanine (Pc), and
 l porphyrin-
 d length of -O-
 TP-O-Pc and
 am are dissolved
 formamide with

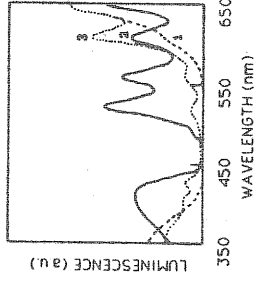


Fig. 1. Excitation spectra for Pc (1), TTP (2) and TTP-O-Pc (3), and monitoring wavelength (1) 680 nm, (2) 655 nm, and (3) 680 nm.

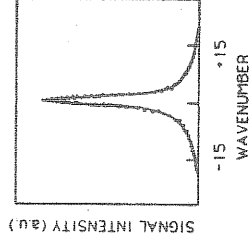


Fig. 2. Theoretical (solid line) and experimental (dots) results of the signal intensity of NDFWM as a function of frequency shift for TTP-O-Pc. T_{CT} is fitted to be 18.5 ps.

hancement in the binary molecules to the charge transfer.

Owing to the strong optical nonlinearity of the binary molecules, the excited state relaxation permits to be studied by the NDFWM. The experimental and theoretical fitting results of the frequency distribution of the signal intensity of NDFWM are presented in Fig. 2 for TTP-O-Pc, and the charge transfer time T_{CT} is obtained to be 18.5 ps. Similarly, T_{CT} is obtained to be 82 ps for TTP-O-(CH₂)₅-O-Pc. Based on the above results, we conclude that as the covalent bond length increases, the charge transfer time becomes longer. In other words the charge transfer rate is inversely proportional to the covalent bond length. In the theoretical fitting to the experiment, the effects arising from both the nonresonant nonlinear processes and the absorption section variation due to laser frequency scanning on the frequency response profiles have been taken into account. Compared to the measurements of the charge

transfer in binary porphyrin-porphyrin system [5], our results are quite reasonable.

5. Conclusion

Based on the spectral investigation, we found the energy transfer from the porphyrin to the phthalocyanine in the covalently bound binary molecules, and the photo-induced charge transfer predominates the energy transfer process. The transient grating method is used to measure the charge transfer of the binary molecules. Our results reveal that the charge transfer rate is inversely proportional to the covalent bond length, but the optical

nonlinearity becomes much stronger as the bond length increases.

References

- [1] N. Mataga, H. Yao, T. Okada and Y. Kanga, *Chem. Phys.* 131 (1989) 473.
- [2] J.X. Liu, Q.F. Zhou, Q. Yu and H.J. Xu, *J. Chem. Soc. Commun.* 3 (1990) 260.
- [3] K. Dou, J.S. Zhang, S.H. Huang and X.R. Xu, *Acta Optica Sinica* 13 (1993) 1.
- [4] K. Dou, J.S. Zhang, S.G. Hou, W. Xu, X.Y. Zhang and X.R. Xu, *Chinese J. Lumin.* 14 (1993) 7.
- [5] U. Rempel, B. Maltzan and C. Borczykowski, *J. Lumin.* 48&49 (1991) 415.

Abstract

Concentrations of aluminum silicates observed for dependent

1. Introduction

The study via sol-gel process of great deal of variety of economic a great deal of fabrications of configurations described works in entrapped medium.

The optical properties of a family series of vortices to spectroscopy (NLO) effects in these cases

* Corresponding author

0022-2313/94
SSDI 0022-2313(94)00022-0