유기 색소 분자의 비선형 흡수

Nonlinear Absorption in Dithienothiophene-based Chromophores

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There has recently been a considerable amount of interest in two-photon(TP) processes because of their applications to 3-D optical data storage and imaging, up-conversion lasing, and optical power limiting. Recently, the role of Dithienothiophene(DTT) as π-center of two-photon absorption(TPA) molecules was reported to give a large enhancement of TPA, compared with the benzeniods counterparts.[1] In this report, we carried out two experiments to investigate nonlinear optical absorption of the molecules in which central DTT is attached through conjugation to either a D/D or a D/A pair at the ends, forming a D-π-D(1 and 3) or D-π-A(2 and 4) sequence(Fig.1). All the samples were prepared in solutions with the same molar concentration.

First, we observed the TP-excited luminescence to find the TP resonance for each material. We used a beta-barium borate(BBO) crystal-based optical parametric oscillator(OPO) pumped by the third harmonic(λ =355 nm) of a Q-switched Nd:YAG laser, and loosely focused the OPO beam to a quartz cuvette containing a sample solution. The luminescence from the sample was passed through a monochromator and measured by a photomultiplier tube, while tuning the OPO wavelength in the near-infrared transparency region of each material.

Fig. 2 shows the TP-excitation spectra for the materials. The samples 1 and 3 have TP resonances around 740 and 770 nm, while 2 and 4 have around 950 and 970 nm. These TP absorption peak locations and intensities are determined by the molecular orbitals depending on their specific molecular structures and constituent atoms. From the above results, we could locate the TP state for each sample, and found that they do not always coincide with the single-photon resonance. (That is, the TP-resonance wavelength is not exactly twice the single-photon resonance wavelengt). This disagrees with a simple theory on non-centrosymmetric molecules.[2] However, this may be due to the degrees of parity-breaking in the Franck-Condon sub-states that comprises of the broad envelops in the observed single-photon and TP-spectra.

Next, we fixed the pumping wavelength at the TP-resonance for each sample, and measured the transmitted pulse energy versus input pulse energy. The pumping beam was focused to the sample cell, making a full-width half-maximum diameter of 0.1 mm. The pulse energies of input and

transmitted beams were measured simultaneously. As shown in Fig. 3, all our samples have nonlinearity, however, the molecule 3 shows a distinct nonliearity among them, demonstrating that it is a potential material for optical limiting. It is obvious that this material shows not only the two-photon absorption, but also significant excited absorption followed by the TPA.

As a future work, we plan to carry out a series of further experiments for understanding the nonlinear absorption mechanism, that is, the excited state dynamics of this molecule, which will give directions for designing highly nonlinear molecules for optical limiting applications.

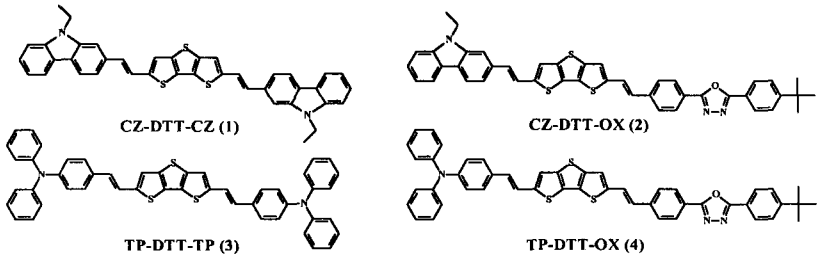

Fig. 1 Chromophore structures based on DTT as π-center.

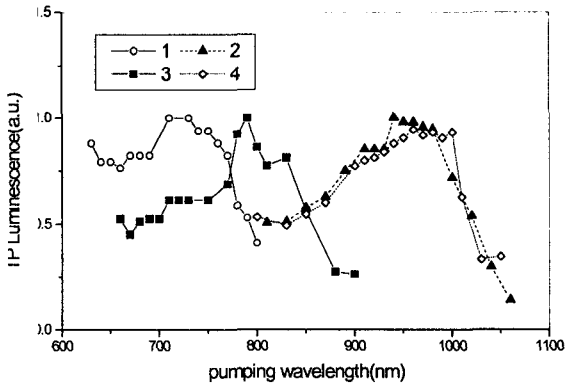

Fig. 2 TP-Excitation spectra for 4-materials

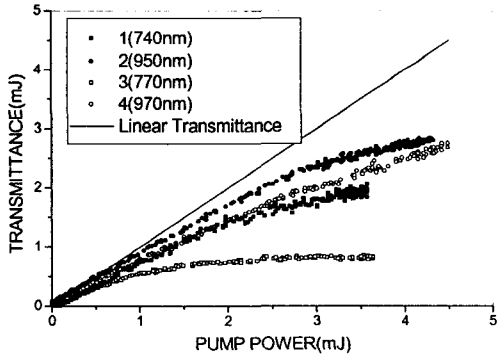

Fig. 3 Optical limiting behaviors

References

[1] O.Kim, K.Lee, H.Woo, K.Kim, G.S.He, J.Swistkiewicz, and P.N.Prasad, Chem. Mater. 12, 284, 2000

[2] D.Beljonne, J.L.Bredas, M.Cha, W.E.Torruellas, G.I.Stegeman, J.W.Hofstraat, W.H.G.Hosthuis, and G.R.Mohlmann, J.Chem.Phys., 103(18) 7834, 1995