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Kwang-Sup Lee^a, Jong Hyoup Lee^a, Haeyoung Choi^b,
Myoungsik Cha^b, Myoung-Ae Chung^c, Young Jun Kim^c &
Sang-Don Jung^c

^a Department of Polymer Science and Engineering, Hannam University, Taejeon, 306-791, Korea

^b Department of Physics, Pusan National University, Pusan, 609-735, Korea

^c Basic Research Lab., Electronics & Telecommunications Research Institute, Taejeon, 305-350, Korea

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Fluorene-Based Organic Molecule with High Two-Photon Absorption Activities

KWANG-SUP LEE^{1*}, JONG HYOUNG LEE¹,
HAEYOUNG CHOI², MYOUNGSIK CHA²,
MYOUNG-AE CHUNG³,
YOUNG JUN KIM³ and SANG-DON JUNG³

¹Department of Polymer Science and Engineering, Hannam University,
Taejeon 306-791, Korea, ²Department of Physics, Pusan National University,
Pusan 609-735, Korea and ³Basic Research Lab., Electronics &
Telecommunications Research Institute, Taejeon 305-350, Korea

Abstract High two-photon absorption (TPA) molecule having a fluorene π -center (TP-Flu-TP) was prepared by the Heck reaction of 2,7-dibromo-9,9-diethylhexyl-9H-fluorene and 4-(diphenylamino)benzstyrene. The linear absorption maximum of the TP-Flu-TP was observed at 410 nm. The dispersion of the TPA intensity for the chromophore was measured by nonlinear transmission using 7 ns laser pulse. Since the maximum wavelength of this molecule occurred at 740 nm, we fixed the pumping wavelength at 740 nm for TP-Flu-TP and measured the transmitted pulse energy versus the input pulse energy. From this experiment we observed a distinct nonlinearity from TP-Flu-TP demonstrating that it is a potential material for optical limiting. The calculated two-photon absorption cross section (δ) by the Hartree-Fock Hamiltonian with single configuration interaction formalism was 1.37×10^{-47} cm⁴ sec/photon.

INTRODUCTION

Two-photon absorption (TPA) behavior of organic molecules is defined as a third-order nonlinear resonant process where two photons are absorbed simultaneously to put the subject molecule into a real excited

state. Since the end of 1990s, the more recent design and synthesis of new organic molecules with greatly increased effective two-photon cross-sections have opened up more practical applications of existing technologies [1,2]. Thus, TPA materials with a large cross section, σ , have a variety of applications such as for two-photon-excited fluorescence microscopy, optical power limiting, three-dimensional optical data storage, two-photon pumped upconverted lasing, and photodynamic therapy [3].

Most of early materials for TPA studies were limited to commercially available common organic dyes like Rhodamine B and 6G, spiropyran, etc. Such materials showed low values of effective TPA cross-section and weak upconverted fluorescence emission. Recently, a wide variety of TPA molecules have been synthesized. Among them, fluorene derivatives have been considered as one of best potential materials in the field of TPA science because of their unique properties involving the ease of increasing the effective conjugation length and polarizability of the molecule [4]. In this paper we report the synthesis and the calculated TPA cross-section value as well as optical power limiting property of fluorene compound having electron donating (ED) pair of *N,N*-diphenylamine at both ends.

EXPERIMENTAL

Synthesis of TP-Flu-TP: 1.00 g (1.82 mmol) of 2,7-dibromo-9,9-diethyl-hexyl-9H-fluorene, 1.04 g (4.00 mmol) of 4-(diphenylamino)-benzstyrene, 0.02 g (0.11 mmol) of palladium acetate, 0.07 g (0.22 mmol) of tri-*o*-tolylphosphine and 0.74 g (4.00 mmol) of tributylamine in 15 mL of *N,N*-dimethylformamide (DMF) were refluxed for 24 h. The solvent was removed, and the mixture was poured into water and extracted in CH_2Cl_2 . The product was purified on a silica gel column, resulting in a bright yellow solid (44% yield). FT-IR (KBr pellet, cm^{-1}): 3400-3300 (Ar-H), 3000 (=C-H), 1600 (C=C), 700 (C=C). $^1\text{H-NMR}$

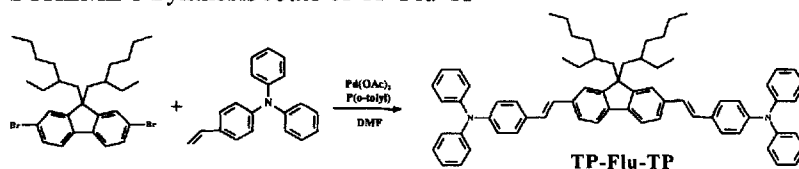
(CDCl₃, ppm): δ =7.8-7.1 (38H, Ar-CH), 2.1 (4H, -C(CH₂)₂-), 1-0.5 (30H, -CH₂-, -CH₃).

Measurements: The TPA activity for TP-Flu-TP molecule was detected in 0.005 mol/L of THF solution. 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 was employed. The OPO output beam had a pulse width of 8 ns, repetition rate of 10 Hz, and a spectral width of about 2 nm. 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 the material.

RESULTS AND DISCUSSION

As shown in Scheme 1, TPA molecule, TP-Flu-TP, was synthesized by the Heck reaction of 2,7-dibromo-9,9-diethylhexyl-9H-fluorene and 4-(diphenylamino)benzstyrene using palladium acetate as a catalyst. Here, pendant alkyl chains were introduced to the aromatic bridge on the fluorene π -center for improving the solubility and intramolecular charge transfer. In this TPA molecule, the central alkyl fluorene moiety is attached through conjugation to a D/D pair at the ends, forming a D- π -D sequence.

SCHEME 1 Synthesis route of TP-Flu-TP



The absorption maximum of the resulting molecule was detected at 410 nm. The nonlinear transmission measurements have been per-

formed for TP-Flu-TP in the range of 550–900 nm wavelength. Figure 1 shows the dispersion of the TPA absorptivity for our molecule in THF solvents. Since the maximum wavelength of TPA band was observed at 740 nm the pumping wavelength was fixed at the TPA resonance region for TP-Flu-TP and measured the transmitted pulse energy versus the

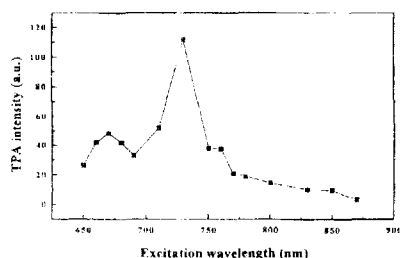


FIGURE 1. Wavelength dependence of TPA intensity for TP-Flu-TP in THF

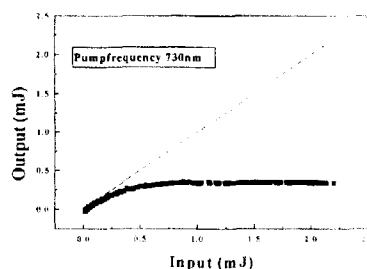


FIGURE 2. Optical power limiting property of TP-Flu-TP in THF

input pulse energy. The pumping beam was focused on the sample cell making a full-width half-maximum diameter of 0.1 mm. The pulse energy of input and transmitted beams were measured simultaneously. From Fig. 2, we can find that TP-Flu-TP is a good candidate for optical power limiting device.

TPA cross section value δ value is calculated with the energy and transition dipole moments for the ground state and multiple excited states. At first we have performed full geometry optimizations with the self-consistent force-field theory. The energy and transition dipole moment values were calculated by combining the Hartree-Fock Hamiltonian coupled with single configuration interaction (HF-SCI) formalism. The TPA at an optical field frequency is related to the imaginary part of the third-order polarizability $\text{Im}\gamma(-\omega; \omega, \omega, -\omega)$ is given as,

$$\delta(\omega) = \left(\frac{8\pi\eta\omega^2}{n^2c^2} \right) L^4 \text{Im}\gamma(-\omega; \omega, \omega, -\omega)$$

where c is the speed of the light, L is a local field factor (equal to 1 for vacuum), n denotes the refractive index of the medium (vacuum assumed for the calculations), and η is the Planck's constant divided by 2π . For the calculation of the imaginary part of the third-order polarizability, the sum-over-state (SOS) expression was used. The damping factor Γ has been set to 0.1 eV for all cases in this study as suggesting by Brédas *et. al.* [5]. Under this assumption, calculated TPA cross section δ was 1.37×10^{-47} cm⁴ sec/photon.

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