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Thiophene-fluorene derivatives with high three-photon absorption activities and their application to optical power limiting*

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The three-photon absorption (3PA) properties of two thiophene-fluorene derivatives (abbreviated as MOTFTBr and ATFTBr) have been determined by using a Q-switched Nd:YAG laser pumped with 38ps pulses at 1064nm in DMF. The measured 3PA cross-sections are 152×10^{-78}cm^{6}s^2 and 139×10^{-78}cm^{6}s^2, respectively. The optimized structures were obtained by AM1 calculations and the results indicate that these two molecules show nonplanar structures, and attaching different donors has different effects on the molecular structure. The charge density distributions during the excitation were also systematically studied by using AM1 method. In addition, an obvious optical power limiting effect induced by 3PA has been demonstrated for both derivatives.

Keywords: three-photon absorption, thiophene-fluorene derivative, AM1, optical power limiting
PACC: 4270, 4265

1. Introduction

The synthesis of highly active organic three-photon molecules has received increasing attention due to the numerous potential applications in multi-photon fluorescence imaging,[1−3] up-converted stimulated emission,[4] optical limiting[5−9] and light-activated therapy.[10] Two essential features of three-photon absorption (3PA) are used in these applications, namely the ability to create excited states with photons having one-third of the nominal excitation energy, which can provide improved penetration in absorbing media, and the cubic dependence of the three-photon process on the input light intensity, which allows for excitation of molecules with a high degree of spatial selectivity in three dimensions through the use of a tightly focused laser beam.

To meet market criteria for applications, molecules with large 3PA cross-sections (σ_3') are required. Unfortunately, design strategies to obtain the molecules with large σ_3' have not been well developed. Recent reports[11−17] have revealed two dominating molecular design concepts for efficient 3PA molecules: one is molecular symmetry, in which an electron-donor (D) or electron-acceptor (A) is attached symmetrically to a conjugated linker (π-centre), and the other one is molecular asymmetry such that a D/A pair is separated by the linker (π-centre). The effects of varying the electron-donating or electron-accepting strength of the end groups, introducing additional groups in the middle to vary the charge redistribution, and varying the effective conjugation length have been studied to understand the design criteria for producing structures with enhanced three-photon activity. However, the use of single π-central ring makes it difficult to significantly change the molecular structure in design.

Introducing heterocycle, such as thiophene, furan, pyrrole etc, into the π-centre conjugated system may be a new strategy of enhancing nonlinear opti-

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cal (NLO) activity [18] and diversifying the molecule design. In this paper, we introduce thiophene into fluorenyl ring system, and make thiophene-fluorene system as a whole as π-centre. We investigate the three-photon absorption properties of two thiophene-fluorene-based derivatives, named as 2-(9, 9-bis (2-ethylhexyl)-7 - (5-(4-methoxystyryl) thiophen-2-yl)-9H -fluoren-2-yl) - 5-bromothiophen-e (abbreviated as MOTFTBr) and 4 - (2-(5-(7-(5-bromothiophen-2-yl)-9, 9-b is (2-ethylhexyl)- 9H -fluoren- 2-yl) thiophen-2-yl) vinyl) benzenamine (abbreviated as ATFTBr). We use intensity-dependent transmission measurements to obtain the three-photon absorption cross-sections, and the optical power limiting effects of these two derivatives at 1064nm pumped with ps laser are also demonstrated.

2. Experiment

2.1. Materials

General synthetic routes of two thiophene-fluorene derivatives are outlined in Fig.1. The compound TFT, 2, 2'-(9, 9-bis (2-ethylhexyl) - 9H - fluorene-2, 7-diyl) dithiophene, was synthesized using 2, 7-dibromo-9, 9-bis (2-ethylhexyl)- 9H -fluorene and 2-thiophene boronic acid as the starting materials through the Suzuki coupling reactions,[19] and the synthesis of BrTFTBr followed the method in Ref.[20]. The resulting compounds MOTFTBr and ATFTBr were synthesized via Pd-catalyzed Heck coupling reactions[21] as illustrated in Fig.1. Elemental analysis, MS, IR spectrum, and UV–VIS spectrum have been used to identify the chemical structure of these two compounds. The linear absorption spectra of the two compounds in N,N-dimethyl formamide (DMF) were measured by using Lambada 9 UV/VIS/NIR recording spectrophotometer with a concentration of 2.5×10^{-5}mol/L.

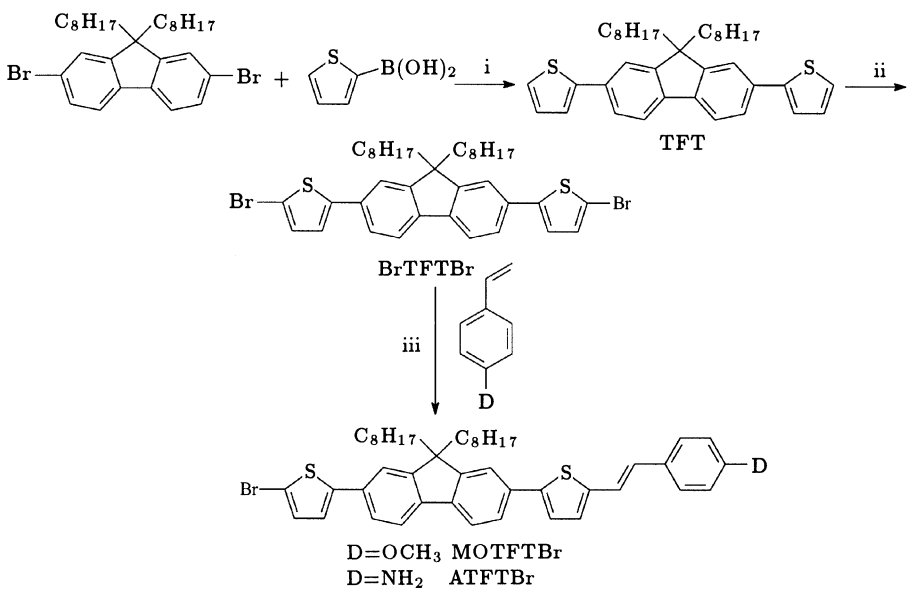


Fig.1. Synthetic routes of two thiophene-fluorene derivatives. Reagents and conditions: (i) $[(PPh_3)_4]Pd(0)$ (1.0 mol %), Toluene/2 M K_2CO_3(3:2), Reflux; (ii) 2NBS, $CHCl_3/CH_3COOH$(1:1); (iii) $Pd(OAc)_2$, Et_3N, P(o-tolyl)$_3$, DMF, 75°C.

2.2. Measurement of nonlinear transmission

In the measurement of nonlinear transmission, the incident 1064nm lasing was provided by a Q-switched Nd:YAG laser (Continuum, PY61C-10) with a pulse duration of 38ps, repetition rate of 10 Hz. The pump energy was controlled by rotating a half-wave plate between two polarizers. The energies of the incident and transmitted beams were measured using two large-area silicon photodiodes connected to a two-channel energy meter (Molectron EPM 2000). The input energy was adjusted from low to high and corresponding output energy can be obtained simultaneously.

2.3. Quantum chemistry calculations

Theoretical calculations can be used to demonstrate that attaching different donors to the conjugated skeleton affects such property as the charge density distribution. The optimized geometries of the two molecules and the charge density distributions in both ground- and excited-states were calculated using

AM1 semi-empirical method in the MOPAC quantum chemical package.[22]

3. Results and discussions

3.1. Linear absorption spectra

Figure 2 shows the linear absorption spectra of the two thiophene-fluorene derivatives in DMF. The influence of the cuvette and the solvent has been excluded. Both the two compounds show strong UV absorption in the spectral range of 280–500nm with absorption peaks at 370nm and 390nm, respectively, both of which correspond to transitions $S_1 \leftarrow S_0$.[23] There is no one-photon absorption in these two molecules in the entire near IR region and most (>500nm) of the visible spectral range. The three-photon energy of 1064 nm radiation just falls into the range of strong UV absorption, and therefore the three-photon absorption in this solution may be expected.

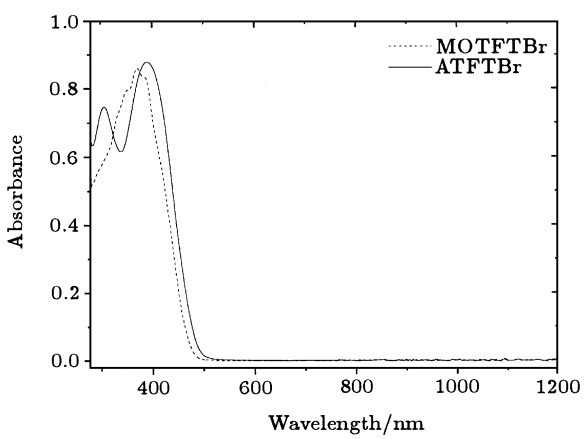


Fig.2. Linear absorption spectra of MOTFTBr and ATFTBr in DMF at concentration of 2.5×10^{-5}mol/L.

3.2. Three-photon absorption cross-sections and intramolecular charge transfer

3.2.1. Three-photon absorption cross-sections

Using intensity-dependent transmission measurement we have measured the three-photon absorption coefficients for both compounds in DMF solution with concentration of 0.02mol/L at 1064nm wavelength. According to the basic theoretical consideration of three-photon absorption, neglecting linear absorption at the pump wavelength, the intensity change of an excitation beam along the optical propagation path z is simply written as

$$\mathrm{d}I(z)/\mathrm{d}z = -\gamma I^3(z), \tag{1}$$

where γ is the three-photon absorption coefficient of the given sample medium. The solution of Eq.(1) can be simply obtained as[5]

$$I(z) = I_0/\sqrt{(1+2\gamma z I_0^2)}, \tag{2}$$

where I_0 is the incident intensity of the excitation beam. From the relationship between $I(z)$ and I_0, the three-photon absorption coefficient γ can be easily deduced.

Figure 3 shows the transmitted intensity as a function of the incident intensity. In Fig.3, the open circles represent the measured data obtained from the 1-cm-long solution sample with a concentration of d_0=0.02mol/L and the filled circles represent the data from a 1-cm-long pure DMF solvent sample. The solid lines in Fig.3 represent the theoretically fitted curves using Eq.(2) with the best-fit values of γ=5.25×10^{-20}cm^3/W^2 and 4.79×10^{-20}cm^3/W^2 for MOTFTBr and ATFTBr, respectively.

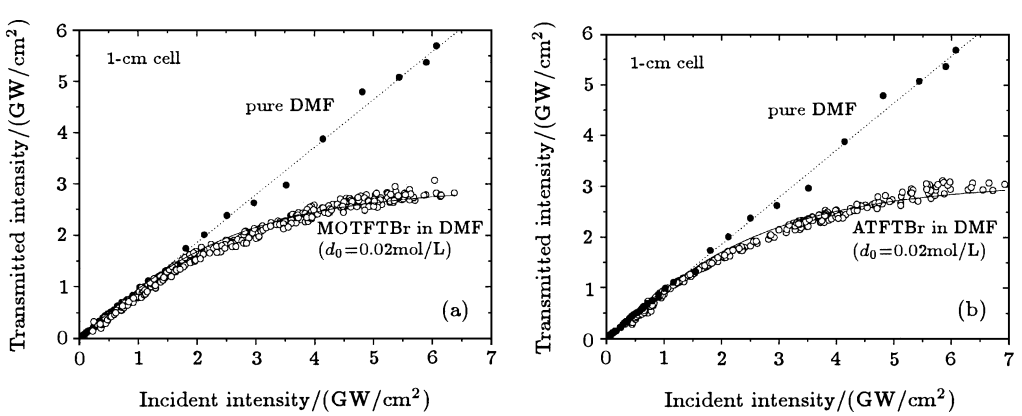


Fig.3. Transmitted intensity versus input intensity of MOTFTBr (a) and ATFTBr (b) in DMF at 0.02mol/L. The solid lines are the theoretical best-fit curve with the parameter of $\gamma_{\mathrm{MOTFTBr}}$=$5.25\times10^{-20}$cm^3/W^2 and γ_{ATFTBr}=4.79×10^{-20}cm^3/W^2.

Based on the known γ value of the measured solution sample, the molecular absorption cross section σ_3' (in units of cm^6s^2) for the given sample in solution is obtained[14]

$$\sigma_3' = \frac{\gamma}{N_A \cdot d_0 \times 10^{-3}} \left(\frac{hc}{\lambda}\right)^2 . \quad (3)$$

Here, N_A is Avogadro's constant, d_0 is the concentration of the sample in solution (in units of mol/L), and $h(c/\lambda)$ is the energy of an incident photon at 1064nm. So the intrinsic molecular σ_3' values can be easily estimated to be $152\times10^{-78}cm^6s^2$ and $139\times10^{-78}cm^6s^2$ for MOTFTBr and ATFTBr, respectively. Due to the influence of the quartz and the uncertainty of the incident intensity, the final results of γ and σ_3' of these two molecules have an experimental uncertainty of 10%. Obviously, the measured values of σ_3' are as high as $10^{-76}cm^6s^2$ for ps pulses. These values are of the same order of magnitude as those for reported stilbazolium and stilbazolium-like derivatives,[12,13] and significantly larger than that we previously reported for symmetric homologous ones.[15] This result indicates that the 3PA cross-sections can also be enhanced by introducing heterocycles into the fluorine-conjugated system.

3.2.2. Intramolecular charge transfer

The delocalization of π-electrons occurring in the conjugated system can lead to significant enhancement of the high-order optical nonlinearity. Attaching different donors to the conjugated skeleton will result in fundamental variations in the molecular structure, which will cause the difference of charge transfer. Optimized ground-state geometries of the two fluorine-thiophene derivatives have been obtained by AM1 method. The serial number and the selected geometrical parameters we calculated are shown in Fig.4 and Table 1.

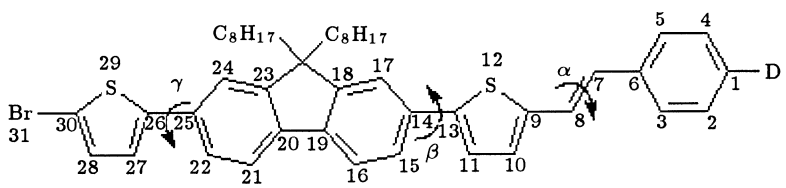


Fig.4. Atom labelling scheme for molecules studied in this paper.

Table 1. The optimized geometrical parameters (bond length (Å) and dihedral angel (deg.)) for MOTFTBr and ATFTBr.

Geometrical parameters	MOTFTBr	ATFTBr
$C_{(6)}$-$C_{(7)}$	1.4500	1.4483
$C_{(7)}$-$C_{(8)}$	1.3458	1.3462
$C_{(8)}$-$C_{(9)}$	1.4351	1.4351
$C_{(13)}$-$C_{(14)}$	1.4432	1.4431
$C_{(25)}$-$C_{(26)}$	1.4438	1.4438
$C_{(30)}$-$Br_{(31)}$	1.8312	1.8312
α	17.0	3.2
β	26.0	25.9
γ	26.5	26.5

From Table 1, one can see that these two molecules show nonplanar structures, and it should be noticed that donors have much more effect on the bond length and dihedral angle that are near the donors, than on those far away from the donors. They are almost equal to each other for these two molecules (see Table 1). It is noted that the optimized dihedral angle, α, between benzene-ring and thiophene-ring in ATFTBr (α=3.2°) is obviously less twisted than that in MOTFTBr (α=17.0°), indicating that the conjugated degree of ATFTBr is slightly better than that of MOTFTBr. In order to see these structures clearly, we plot the ball & stick diagrams of these two molecules in Fig.5.

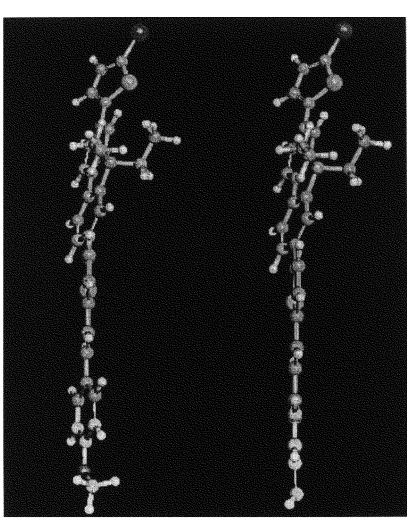


Fig.5. The ball & stick diagrams for MOTFTBr (a) and ATFTBr (b).

Using AM1 semi-empirical method, we have calculated the intrinsic parameter of the molecules, namely the charge density redistribution. Table 2 gives the charge density distributions of MOTFTBr and ATFTBr in both ground-state (S_0) and excited-state (S_e). Charge density redistribution can reflect the extent of intramolecular charge transfer. We divide the molecular structure of the skeleton into three parts: ρ_D, ρ_B, and ρ_{Br}. Here, ρ_D describes the average charge density on the donor (D), and ρ_B describes the average charge density of atoms on the conjugated bridge (C1 to C30), while ρ_{Br} describes the corresponding average value on the atom Br. The charge density difference between the excited state (S_e) and ground state (S_0), $\Delta\rho_D/\Delta\rho_B/\Delta\rho_{Br}$, is thus an intramolecular charge transfer character. The unit of charge on every atom is e. It can be found that the charge density on the atom Br of MOTFTBr is extremely close to that of ATFTBr for both ground and excited states. The charge densities ρ_D and ρ_B exhibit different values due to the different donor strengths. The charge redistributions occur obviously during the excitation. The charge density difference ($\Delta\rho_D/\Delta\rho_B$) for ATFTBr is +0.16e/−0.167e, clearly larger than that for MOTFTBr, $\Delta\rho_D/\Delta\rho_B$=+0.064e/−0.07e, indicating that the intramolecular charge transfer that occurs in ATFTBr is larger than that in MOTFTBr.

Table 2. Three-photon absorption cross-sections (σ_3') and the charge distributions of ground-and excited- states.

Molecules	3PA cross-sections $\sigma_3'/10^{-78}\mathrm{cm}^6\mathrm{s}^2$	$\rho_D/\rho_B/\rho_{Br}$/e	$\Delta\rho_D/\Delta\rho_B/\Delta\rho_{Br}$/e
MOTFTBr	152	−0.026/−0.119/+0.065 (S_0) +0.038/−0.189/+0.073 (S_e)	+0.064/−0.07/+0.008
ATFTBr	139	+0.212/−0.354/+0.065 (S_0) +0.372/−0.521/+0.071 (S_e)	+0.16/−0.167/+0.006

Based on all the calculated results mentioned above, we can expect that the 3PA cross-section of ATFTBr should be larger than that of MOTFTBr. However, surprisingly, the facts prove the contrary. According to Ref [24], a strong one-photon absorption (OPA) state can be a strong 3PA state as well. The excitation energies to the dominant OPA state (S_1) are around 3.36eV and 3.18eV for MOTFTBr and ATFTBr respectively, while the three-photon excitation energy with respect to 1064nm of the laser is 3.5eV that is much closer to the $S_1 \leftarrow S_0$ transition energy of MOTFTBr than that of ATFTBr. In this case, it helps the electrons of MOTFTBr to be excited to the 3PA state. Therefore, MOTFTBr exhibits a slight larger $'\sigma_3$ value than ATFTBr.

3.3. Optical power limiting at 1064nm

As mentioned above, these two thiophene-fluorene

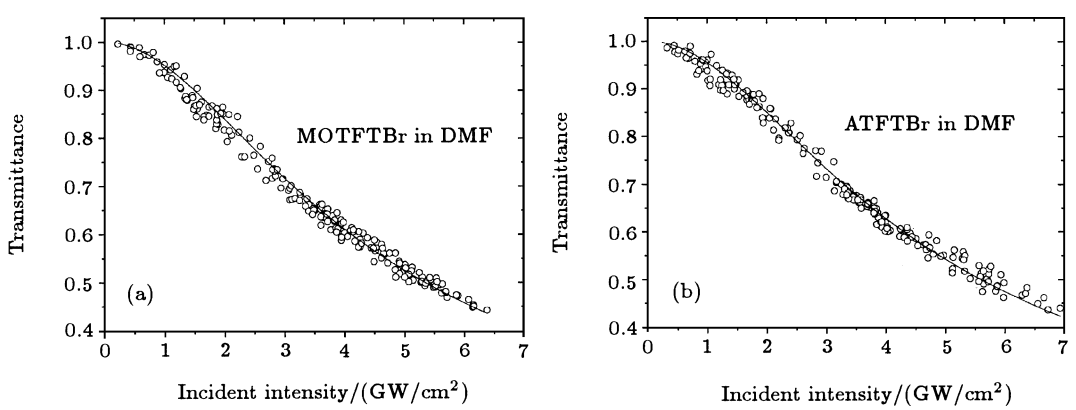


Fig.6. The intensity-dependent transmittance responses for MOTFTBr (a) and ATFTBr (b) in DMF with a concentration of 0.02mol/L.

derivatives exhibit large three-photon absorption cross-sections. Hence the optical power limiting performance could be expected based on the strong 3PA effect. The intensity-dependent transmittance responses for MOTFTBr and ATFTBr in DMF with a concentration of 0.02mol/L are shown in Fig.6, where the transmittance decreases nonlinearly as the input intensity increases. The solid lines in Fig.6 are the fitting curves drawn by using the obtained parameters of γ=5.25×10^{-20} and 4.79×10^{-20}cm^3/W^2 for MOTFTBr and ATFTBr, respectively. When the input intensities reach about 5.3 and 5.6GW/cm^2, respectively, the transmittance drop down dramatically to one half of the initial transmittance (T/T_0=0.5) for MOTFTBr and ATFTBr, from which the optical limiting threshold is obtained.

4. Conclusion

In summary, we introduce thiophene into the fluorenyl ring system and synthesize two novel thiophene-fluorene derivatives, MOTFTBr and ATFTBr. The three-photon absorption cross-sections and optical limiting effects of the two compounds have been determined using a ps pulse at 1064nm. The measured 3PA cross-sections are in the order of 10^{-76}cm^{6}s^2. The geometries of these two molecules were calculated by AM1 method. The theoretical results revealed that these two molecules show nonplanar structures, and attaching different donors has different effect on the molecular structure. Calculated results of charge density redistribution (defined as $\Delta\rho_D/\Delta\rho_B/\Delta\rho_{Br}$) indicate that the intramolecular charge transfer that occurs in ATFTBr is larger than in MOTFTBr. But MOTFTBr exhibits a slight larger σ_3' than ATFTBr. We consider that the three-photon energy of 1064nm laser is much closer to the $S_1 \leftarrow S_0$ transition energy of MOTFTBr than that of ATFTBr, and it can helpful for the electrons of MOTFTBr to be easily excited to the 3PA state. In addition, obvious optical power limiting effects induced by 3PA have also been demonstrated for both compounds. When the input intensities reach about 5.3 and 5.6GW/cm^2, the optical limiting thresholds are obtained for MOTFTBr and ATFTBr respectively.

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