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# Optical limiting studies of organic semiconductor molecule with carbon nanotube addition

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**Abstract**

Recent interest in thiophene-based molecules for nonlinear optics (NLO) and optical limiting studies is due to their good solution processability and optical modulation. In order to overcome weakness of thiophene based optical limiter at 532 nm wavelength, versatile carbon nanotubes (CNT) are introduced into the freeform thiophene solution. This paper investigated the role of multi-walled carbon nanotubes (MWCNT) addition in thiophene's third-order NLO characteristics at 532 nm cw laser as equal weight ratios composite. CNT is chosen because of its broadband NLO property, unique structural and electronic properties, and tackling CNTs' dispersion instability can optimize its full potential in photonics and laser applications. Prior to the optical limiting measurement, surface interactions between both materials were analyzed using UV-vis and Raman spectra. Significant improvement of optical limiting at 532 nm was discussed using nonlinear refraction ($n_2$) and absorption ($\beta$) obtained from open and closed aperture z-scan measurements, respectively. It was found that absorption related nonlinearity increased drastically after CNT addition that contributed to a more stable optical limiting behavior at this energy. The reverse saturable absorption characteristics of this organic semiconductor molecule can be exploited as laser protective coating and in other broad areas of materials, optoelectronics and photonics related to 532 nm laser applications.

*Keywords: thiophene; carbon nanotubes; dispersion; 532 nm cw; third-order NLO;*

## 1. Introduction

In the field of nonlinear optics (NLO), behavior and property of material changes under strong light interaction that provides comparable electric field experienced by electrons in molecules [1]. It is the reason why most associated NLO phenomenon are with lasers. Under this circumstance, polarization, $\vec{P}$ in the material is expressed with the presence of higher order term (second-order and so on) as shown in Eq. 1 below.

$$\vec{P} = \varepsilon_0\chi^{(1)}\,\vec{E}(\omega) + \varepsilon_0\chi^{(2)}\,\vec{E}(\omega)\,\vec{E}(\omega) + \varepsilon_0\chi^{(3)}\,\vec{E}(\omega)\,\vec{E}(\omega)\,\vec{E}(\omega) + \ldots\ldots \qquad \text{(Eq. 1)}$$

$$\vec{P}^{(3)}(\omega) = \frac{1}{4}\varepsilon_0\chi^{(3)}\,E^3\cos(3\omega t) + \frac{3}{4}\varepsilon_0\chi^{(3)}\,E^3\cos(\omega t) \qquad \text{(Eq. 2)}$$

The front term of third order NLO response in Eq. 2 describes third harmonic generation and the second term describes intensity dependent refractive index or optical limiting properties [1]. They are key parameters for optoelectronic, photonic devices and laser physics, i.e laser protection, laser pulse generation and optical switching. In recent decades, attractive carbon allotropes had been considered for third order NLO materials such as 3D carbon black suspensions – optical limiter, 0D fullerene – reverse saturable absorber, 1D carbon nanotubes (CNT) – saturable absorber, and 2D graphene – broadband resonance optical limiter [2]. CNT has the potential to become a broadband optical limiter (wavelength range from visible to the near infrared) if its aggregation issue into large bundles in most inorganic and organic solvents can be overcome. In our interest, the need to tackle the obstacle of transferring CNT material into practical device is because of their optical limiting performance can be influenced by solvent, wavelength

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and bundle size [2, 3]. A complex CNT composite formed by covalently or noncovalently functionalizing the surface of nanotubes with metal nanoparticles, organic molecules, and polymers can be considered to solve these stability related problems.

Optical limiters are devices based on the third order NLO property, where they are allowed to exhibit constant transmittance under low light, and reduced transmittance under increasing input intensity [4]. The two origins of optical limiting mechanism observed from a material are; 1) optical Kerr effect, and 2) nonlinear absorptive processes. NLO mechanisms manifested by organic chromophores, dyes and semiconductors are photorefraction, reverse saturable absorption (RSA), multiphoton absorption and induced scattering. Their molecular structure also exhibited strong $\pi$-conjugation and dipole moment difference/charge asymmetry [2]. Known for their excellent optical nonlinearity at certain wavelength bands, they demonstrated ultrafast response and architectural flexibility to tune optical properties through structural modifications [5]. Many novel $\pi$-conjugated NLO compounds designed as push-$\pi$-pull system and D-$\pi$-A configurations were reported as good optical limiters owing to stronger $\pi$-$\pi$ interactions and charge transfer efficiencies [5-7]. In a study by Wang et al, phthalocyanines molecules that were functionalized with CNT produced complementary temporal and spatial nonlinear characteristics as optical limiter [2]. As a result, the hybrid phthalocyanines-CNT can operate at both picosecond and nanosecond regimes [2]. Combination of more than one NLO materials is also desirable when it comes to manipulate and control over multiple nonlinearities origins that can take effect during optical limiting.

In this paper, thiophene oligomer named 3,3'''-didodecyl - 2,2':5',2":5",2'''-quaterthiophene with intrinsic conductivity of $10^{-9}$ Sm$^{-1}$ is reported as optical limiter at 532 nm wavelength for the first time [8]. There has been significant number of thiophene based derivatives with a thiophene unit either as a central core or peripheral group explored as active materials in organic electronics [9-10], including for NLO studies [11-14]. NLO application of thiophene is restricted by narrow absorption band in the visible range. Hence, CNT introduction into thiophene organization will improve its efficiency at these wavelengths. The improvement on the optical limiting system can be used as protection from frequency-agile laser weapons that works by absorbing, refracting, deflecting, or scattering laser radiation. The research objectives are to i) investigate optical characteristics of thiophene-CNT composite, ii) measure third order NLO properties from thiophene-CNT composite, and iii) understand origin of optical limiting in thiophene-CNT composite, dedicated at 532 nm continuous wave laser.

## 2. Materials and methods

Pure 3,3'''-didodecyl - 2,2':5',2":5",2'''-quaterthiophene ($C_{40}H_{58}S_4$, $M_w$ = 667.15 g/mol, Sigma Aldrich) and hydroxyl multiwalled carbon nanotube (MWCNT, Industrial grade, Nanostructures & Amorphous Materials Inc, 10-30 nm tube diameter) were dissolved in chloroform and stirred for 3 hours. Equal weights of thiophene and MWCNT were used in this preliminary investigation. Final product of pristine thiophene and thiophene-MWCNT composite solution were used as homogenous dispersion. Optical characterizations of samples were taken using UV-vis spectrophotometer (Genesys$^{TM}$, Thermo Scientific) and confocal micro-Raman imaging spectroscopy (Model DXR2xi, Thermo Scientific). In Raman spectroscopy, 632 nm excitation line, 3 mW irradiation with beam size of 1 $\mu m^2$ was used to obtain optimum scattering intensity. In z-scan experiment, the sample in cuvette is moved from one side of focus to the other along the propagation path (Z-axis) of a tightly focused Gaussian beam. Closed aperture transmittance of the sample is measured as a function of the sample's position to deduce the magnitude of the nonlinear refractive index and open aperture transmittance data inferred the magnitude of the nonlinear absorption. Parameters of the z-scan measurement on solution samples are tabulated in Table 1.

Table. 1. Parameters of z-scan setup

| Parameters | Value |
|---|---|
| Focal length, $f$ | 20 cm |
| Rayleigh length, $r_a$ | 0.19 cm |
| Gaussian beam spot radius, $w_0$ | 0.0023 cm |
| Laser wavelength, $\lambda$ | 532 nm |
| Linear transmittance aperture, $S$ | 0.42 |

## 3. Results and discussions

### *3.1 UV-vis and Raman studies*

Firstly, UV-vis absorption of thiophene, thiophene-MWCNT and MWCNT were obtained and characterized. Fig. 1(a) shows presence of $\pi$-$\pi$ absorption band of thiophene ranging from 300 nm- 470 nm while MWCNT spectrum in Fig. 1(b) has broad absorption spectrum across visible wavelength. The $\pi$-$\pi$ absorption band that indicated energy gap between highest occupied molecular orbital, HOMO – lowest unoccupied molecular orbital, LUMO of an organic semiconductor molecule can be red-shifted with increasing number of thiophene rings in the $\pi$-spacer [15]. Alkyl side chains interactions also contributes to electronic structure of thiophene's absorption band. At 532 nm, absorption is seen to increase after MWCNT addition as thiophene's absorption broadened toward longer wavelength. This change implied that new interaction between MWCNT and thiophene either at $\pi$-conjugation length or alkyl side chains of the thiophene molecules. The long tail absorption edge becomes more prominent as MWCNT's weight ratio in the composite increases [16]. This modified energy gap will lead to stronger nonlinear optical response and now, the z-scan excitation energy of 532 nm can be resonant to linear absorption of the composite [15]. Another advantage of using thiophene-MWCNT composite is the improved dispersion stability of MWCNT which is important when it comes to solution processing and film fabrication. Here, the stability of MWCNT dispersion was determined by naked eye observation. Figure 2 shows the states of MWCNT suspensions with and without thiophene solution three days after preparation. In the former, it can be seen that some of black suspensions collapsed to the bottom of the vial and overall dispersion appeared as inhomogeneous. The thiophene-MWCNT sample, on the other hand appeared to be more homogenous and stable dispersion.

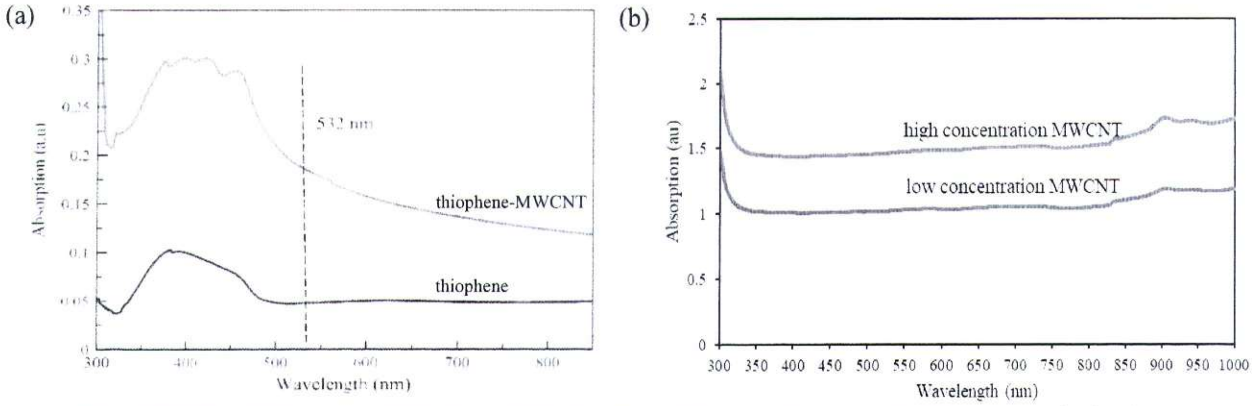

Fig. 1. Absorption spectra of (a) thiophene and thiophene-MWCNT samples, (b) high and low MWCNT concentration in solvent.

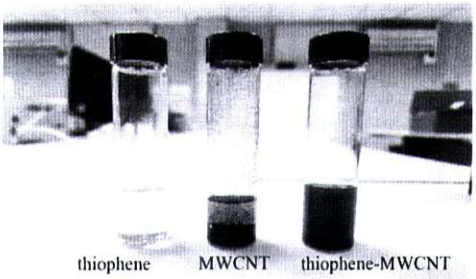

Fig. 2. Dispersion states of thiophene, MWCNT and thiophene-MWCNT samples. The thiophene-MWCNT suspensions appeared more stable compared to thiophene.

Vibrational spectroscopies were used to confirm microscopic interactions between the organic semiconductor molecule and carbon nanotube in the composite. Infrared absorption of pristine thiophene and thiophene-MWCNT show no significant change in C-H vibrational modes, meaning there is no evidence of alkyl side chains interactions with the MWCNT. In contrast, C=C vibrational modes traced from Raman analysis shown in Fig. 3 (a) indicated there is relatable $\pi$-conjugation modification in thiophene-MWCNT. Three prominent peaks observed in Raman spectra are 1450 $cm^{-1}$ of thiophene vibrational mode, CNT vibrational modes' 1330 $cm^{-1}$ (defect, D-band) and 1570 $cm^{-1}$ (graphene, G-band). Similar bands are also present in the composite's spectrum. It can be seen that the ratio of $I_D/I_G$ presented in Table 1 has increased from 1.09 to 1.20 after MWCNT is added. This evaluation of the $I_D/I_G$ ratio indicated higher density of $sp^3$ hybridized carbon sites as consequent of higher interaction between carbon nanotube wall and thiophene molecules [17]. Previous studies with poly(3-hexylthiophene)-CNT composite inferred that adsorption of thiophene backbones on nanotube surface by strong $\pi$-$\pi$ interactions affinity is the origin of higher density of $sp^3$ hybridized carbon sites [16, 18]. To produce this adsorption, thiophene ring is stacked on top on CNT's benzene ring as simulated in Fig. 3 (b).

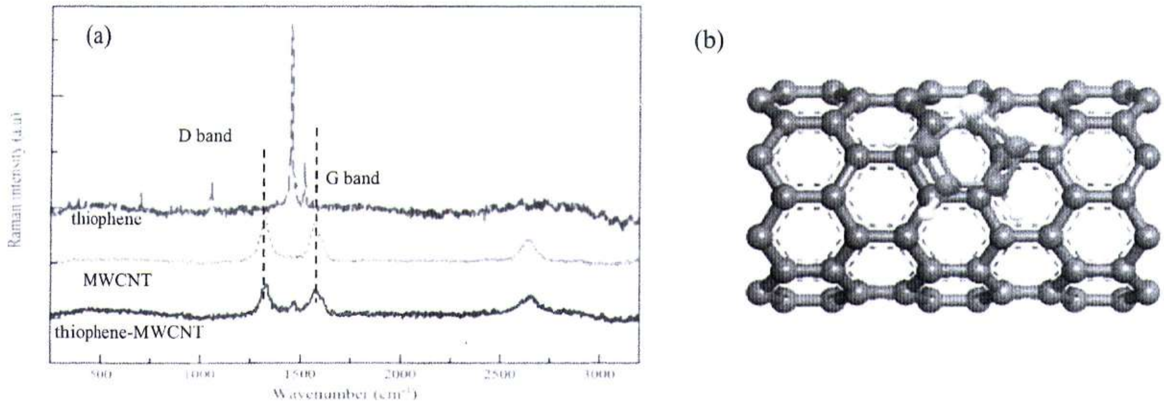

Fig. 3. (a) Raman spectra of the thiophene and MWCNT samples. (b) Simulated single thiophene molecule adsorption on CNT surface with carbon atoms (black), hydrogen atoms (white) and sulfur atom (yellow).

Table 1. $I_D/I_G$ analysis of MWCNT and thiophene-MWCNT samples.

| **Sample** | $I_D/I_G$ |
|---|---|
| MWCNT | 1.09 |
| thiophene-MWCNT | 1.20 |

### *3.2 Z-scan measurement*

Figure 4 and 5 show the result of closed aperture and open aperture z-scan measurement of both thiophene and thiophene-MWCNT composite measured at various laser intensities. There is negligible contribution from chloroform, the solvent used in this sample. The closed aperture configuration will produce the magnitude of nonlinear refractive index, $n_2$. At the first glance, both samples can be identified as self-defocusing lens as depicted by the peak-valley shape of the closed aperture z-scan measurements in Fig. 4. Similar characteristic that was also reported for thiophene based polymers and other thiophene derivatives [19]. Apart from higher magnitude of $n_2$ measured at 0.8 $kW/cm^2$ from thiophene-MWCNT sample, the refractive index of thiophene and composite is observed at small disparity throughout the measurement. Their magnitude of $\times 10^{-8}$ values are within the range typically observed in NLO organic materials. It is concluded that addition of MWCNT into thiophene has no big impact to nonlinear refraction of thiophene.

On the other hand, nonlinear absorption, $\beta$ calculated from the open aperture measurements show that their magnitude increases with laser intensities for both samples at different intensity scale (Fig. 5). Both thiophene and thiophene-MWCNT demonstrate valley-shaped z-scan characteristic of RSA. The positive nonlinearity of pristine thiophene sample can only be measured above 5.0 kW/cm$^2$ while RSA of thiophene-MWCNT samples is observed at low fluence. The increasing trend of $\beta$ with fluence indicated it is accumulative nonlinearity are produced by resonant in energy. In our case, effective $\beta$ from the thiophene-MWCNT composite is almost double of thiophene's since its linear absorption coincide with the 2.33 eV (532 nm) photon energy used in the z-scan.

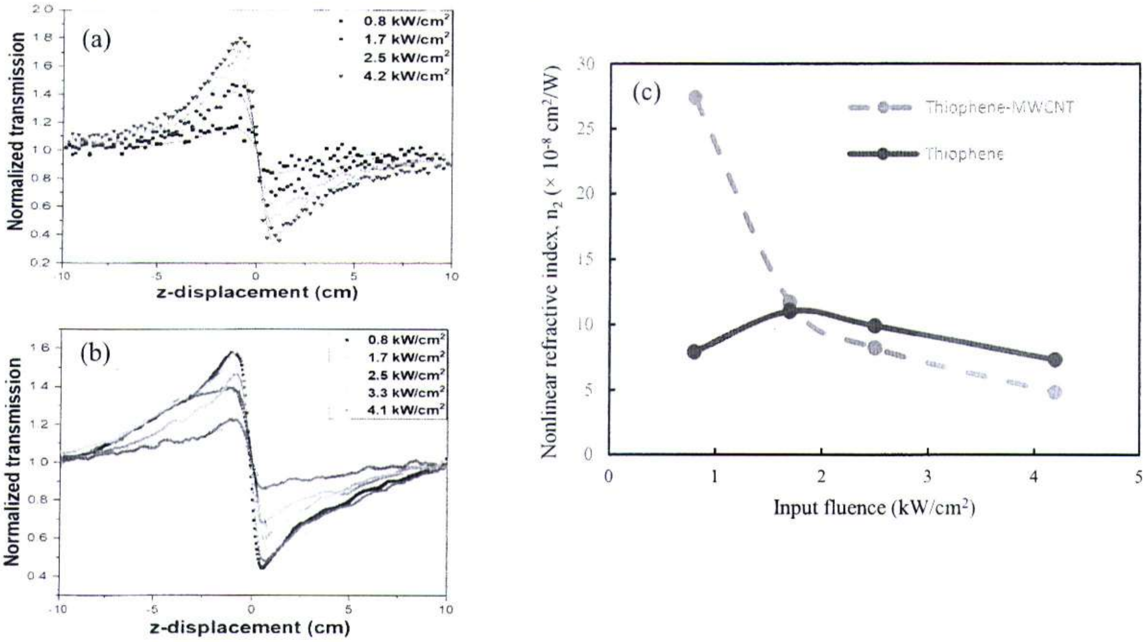

Fig. 4 (a-b) Closed z-scan curve for thiophene (top) and thiophene-MWCNT (bottom) (c) Variation of nonlinear refractive index, $n_2$ with different laser fluences.

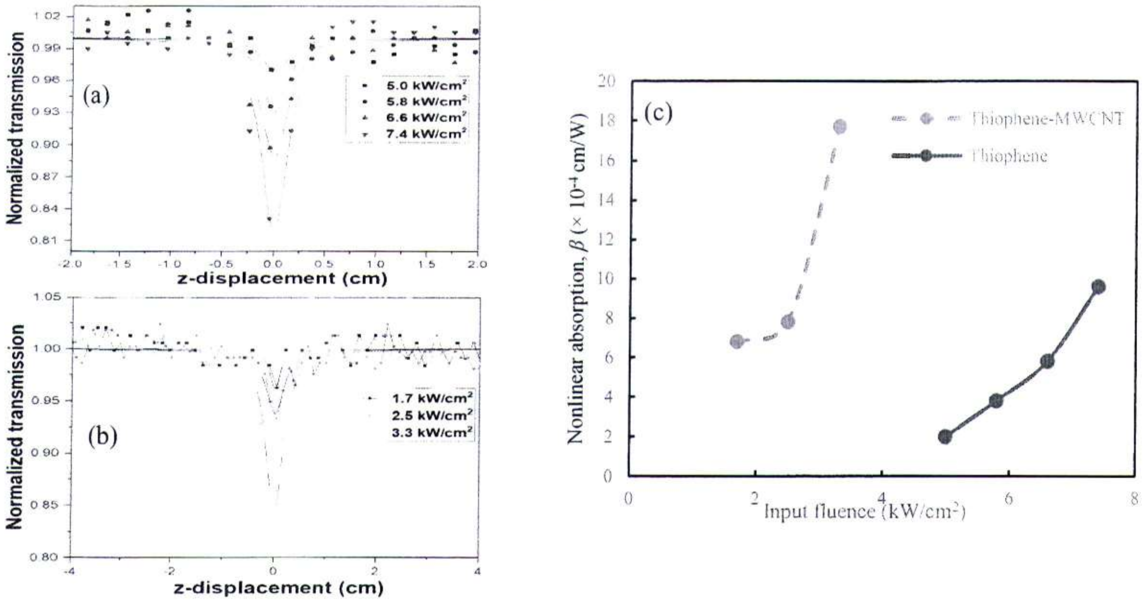

Fig. 5 (a-b) Open z-scan curve for thiophene (top) and thiophene-MWCNT (bottom) (c) Variation of nonlinear absorption, $\beta$ with different laser fluences.

### *3.3 Optical limiting studies and discussion*

Optical limiting behaviour 532 nm cw laser of thiophene (a) and thiophene-MWCNT (b) are shown in Fig. 6 below. The operation of thiophene based optical limiters at 532 nm cw laser are of reverse saturable absorption in which the transmission began to decrease with increasing input power. In the graphs, the optical limiting threshold, $OL_{Th}$ of the composite is smaller than that of pristine thiophene sample. It achieved 50% transmission approximately 18 kW/cm$^2$ while the 50% transmission of pristine thiophene optical limiter was achieved at ~ 35 kW/cm$^2$. This is consistent with open aperture z-scan result of thiophene which can only be obtained at higher laser intensity due to weaker nonlinear absorptive origins of the thiophene (Fig. 5). The $\mathrm{OL}_{\mathrm{Th}}$ will increase with decrease of either $n_2$ or $\beta$. Mechanisms that leads to optical limiting is discussed according to limited information obtained from this investigation. First, the self-defocusing originated from thiophene solution that acts as a thermal lens. It is widely known that NLO in organic material is dominated by imaginary component of nonlinear absorptive origins such as charge transfer, RSA and multiphoton absorption [7]. Charge transfer and multiphoton absorption can be ruled out since they can only be observed in pulsed laser application [7]. It can be that optical limiting of thiophene-MWCNT composite was enhanced by induced scattering by MWCNT aggregates. This is due to the size MWCNT aggregates (diameter and length) that similar to the wavelength, and acts as scattering centres causing transmission to quickly decrease [20]. Hence, we believed that more detailed experiment to study the effect of MWCNT concentration in thiophene optical limiting can highlight more crucial information to understand potential of this thiophene composite. Optical limiting studies using thiophene film and in operation of pulsed laser operation can be highly interesting for this feasible organic material. Based on our finding, the reverse saturable absorption RSA demonstrated by thiophene-based materials can be exploited in optical limiting applications such as eye and sensor protection systems, which require high transmission of low intensity radiation but high absorption at high input.

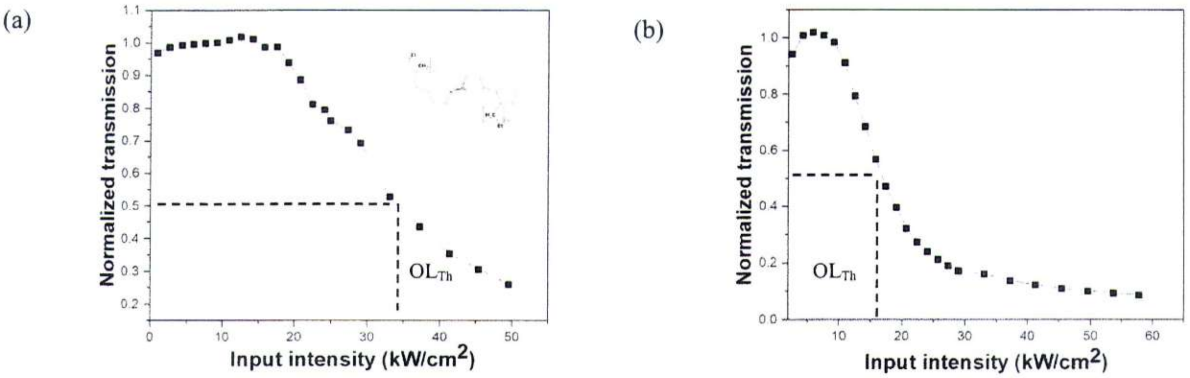

Fig. 6 Optical limiting behaviour for (a) thiophene and (b) thiophene-MWCNT. The non-centrosymmetric structure of thiophene is shown in the subset.

## 4. Conclusion

Thiophene semiconductor has been investigated for its third order nonlinear optical (NLO) studies at 532 nm cw laser. Multi-walled carbon nanotubes (MWCNT) were added into the thiophene to improve its NLO and optical limiting performance. At this excitation energy, the third order nonlinearity is dominantly caused by nonlinear absorption, $\beta$ that increased after CNT addition as better optical limiting behaviour was observed for the composite. The nonlinear absorption can be traced to both strong $\pi$-$\pi$ non-covalent interactions between MWCNT and thiophene molecules and also induced absorption by MWCNT scattering centres. Thiophene-MWCNT construction is also found to have higher dispersion stability compared to pristine MWCNT dispersion which enable easy transition of solution material into film devices.

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