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Synthesis of Nano Crystalline 1-[2-(Trifluoro-Methyl) Benzylidene] Thiosemicarbazide with D-π-A Architecture towards Dyes Sensitized Solar Cells

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Abstract: In this study, 1[-2 (Trifluoromethyl) Benzylidene] Thiosemicarbazide (2-TBT) with a proposed D-π-A molecular arrangement was synthesized as promising sensitizers for solar cell application. The compound was characterized by CHNS micro-elemental analyses, IR, UV-VIS, XRD, ^{1}H and ^{13}C NMR. The compound was also coated on Indium Tin Oxide (ITO) glass substrate through spin coating technique in order to fabricate 2-TBT/ITO thin film. The thin film was tested for electrical conductivity and was found to exhibit a conductivity of 0.1498 S/cm at 125 W/m^2 in a diluted concentration of 1×10^{-5} M.

Key words: Synthesis, thisemicarbazide, electrical conductivity, coating, spin

INTRODUCTION

For the past several decades, increasing of energy demand and drastic climate changes have forced the researchers to take up intensive research on design various types of Dyes Sensitized Solar Cell (DSSC) for harvesting light energy directly from the sun. Many efficient metal-free organic dyes for DSSC have been developed and show good performance. Generally, metal-free organic dyes possess molecular structure of Donor (D) and Acceptor (A) electron group bridged by the π-conjugated unit (D-π-A). This type of molecular arrangement owing intramolecular charge transfer and extend the absorption spectra (Lu *et al*., 2014). Recently, various compounds containing nitrogen and sulphur atoms were studied as a donor unit such as indoline (Wang *et al*., 2014), phenothiazine (Fu *et al*., 2014), triarylamine (Yuan *et al*., 2016). Thiophene and benzene ring are widely used for π-conjugated due to their charge transport behavior and chemical stability (Lu *et al*., 2014). Currently, pyrimidine (Muraoka *et al*., 2016), isoindigo (Gang *et al*., 2014), pyran-4-ylidene malononitrile and cyanoacrylic acid (Khanasa *et al*., 2014) moieties are used as an electron Acceptor (A) unit.

This study is closely related with compounds derived from four N, N, N, S donor atoms, thiosemicarbazide ($NH_2C(S)NHNH_2$). Recently, other derivatives have received attention from many researchers due to their potential in a wide range of applications include anti-viral (Finkielsztein *et al*., 2008), anti-bacterial (Chandra, 2014) and catalysts. However, to the best researcher's knowledge, there is no report on thiosemocarbazide derivatives with D-π-A molecular arrangements for DSSC applications. Therefore, we open up a new opportunities by synthesized a simple D-π-A molecular system (Scheme 1) and study the effect of both trifluoromethyl (CF_3) and thiosemicabazide moieties as an Acceptor (A) and Donor (D) electron units, respectively and connected by π-benzene ring for their electrical conductivity.

MATERIALS AND METHODS

Experimental

Chemical and instruments: 2-(trifluoromethyl) benzaldehyde (Sigma-Aldrich), thiosemicarbazide (Sigma-Aldrich) and ethanol (Hamburg) were purchased and used without further purification.

Melting point was determined using a Stuart Scientific Melting Point SMP3. Carbon, hydrogen, nitrogen and sulphur elemental analyses were carried out using FLASH EA 1112 instrument. The infrared spectra were prepared as Kbr pellets and recorded in the 400-4000/cm region on Perkin Elmer FT-IR spectrometer BX. The UV-Vis spectra were run on a LABMDA BIO 35 UV VIS-NIR (800-200 nm). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. XRD analysis was conducted using the XRD (Bruker D8 Discovery) with a graphite-monochrome Cu-Kα radiation source (λ = 1.54056 Å). Scans were performed in step mode of 0.20 and 0.4 sec/step and the range of the 2-θ

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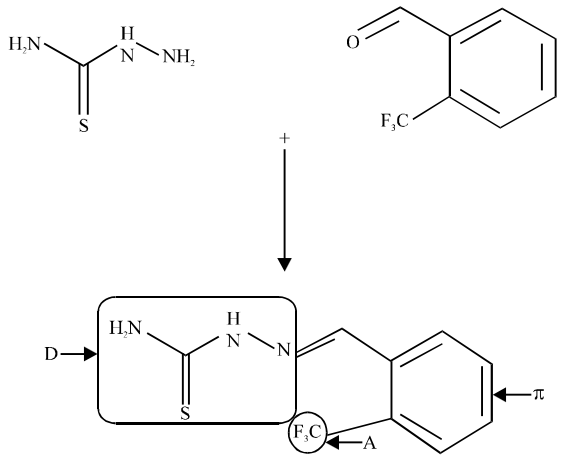

Fig. 1: Preparation and proposed D-π-A molecular arrangement of 2-TBT compound

was from 10-80. The qualitative (phase identification) and quantitative analyses (lattice parameters and crystallite size) of the samples were determined by the Rietveld refinement technique via the X'Pert High Score Plus V.2.2.5 Program.

ITO/2-TBT thin film was deposited via spin coating technique by using Spin Coater Model WS-400B-6NPP-LITE. Finally, the electrical conductivity of the thin film was measured by four-point probe which consists of Jandel Universal Probe combined with a Jandel RM3 test.

Synthesis of 1-[2-(Trifluoromethyl) Benzylidene]-Thiosemi carbazide (2-TBT): The synthesized compound, 2-TBT was resynthesized and followed as previous reported (Chen and Jing, 2011) with modification. An anhydrous ethanol solution (50 mL) of thiosemicarbazide (0.91 g, 10 mmol) was added to an equimolar quantity of 2 (trifluoromethyl) benzaldehyde (1.74 g, 10 mmol), also dissolved in hot anhydrous ethanol solution (50 mL). The mixture was refluxed at about 80°C for 3 h. The mixture was then cooled to 0°C in an ice-salt bath for complete crystallization to occur. The light yellow precipitate was filtered off, washed with cold ethanol, recrystallized from absolute ethanol and dried over silica gel. The chemical equation is shown in Fig. 1.

Preparation of Indium Tin Oxide (ITO) substrate: The ITO substrate was cleaned with distilled water followed by acetone and rinsed with distilled water again. Next, it was continued cleaned with ethanol. Finally, the ITO substrate was dried using the hair dryer before kept into a petri dish.

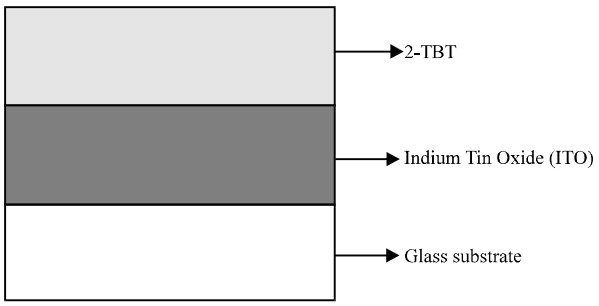

Fig. 2: Illustration of 2-TBT layered on ITO substrate

Preparation of thin film: The synthesized compound, 2-TBT had been deposited on the ITO substrate using spin coating technique. Spin coating is a common procedure used to apply uniform thin film to flat substrates. In the present studies, Spin Coater Model WS-400B-6NPP-LITE was used. The synthesized compound was deposited on the ITO substrate in the following condition.

There were 4 stages of spin; 500 rpm for 10 sec, 1000 rpm for 15 sec, 1500 rpm for 20 sec and 2000 rpm for 30 sec to complete a cycle. Figure 2 shows the illustration of layer arrangement on ITO substrate.

Electrical conductivity measurement of thin film: Four point probe was used to determine the conductivity of thin film. In the present study, the sheet resistivity in produced films was measured with complete four point probing system consists of the Jandel Universal Probe combined with Jandel RM3 test unit. The measurements were recorded in the dark condition and light condition with intensity range of 25-200 W/m^2 with LI-200 pyranometer sensor with LI-1400 data logger. Eppley Precision Spectral Pyranometer (PSP) was used to calibrate the current output.

RESULTS AND DISCUSSION

The present compound, 2-TBT was isolated in 62.71% of yield with melting point of 241.7°C. The compound was stable in solid and solution state at room temperature and can be kept in desiccators for a long period of time without any sign of decomposition. The micro-elemental C, H, N and S analyses of the compound are in good agreement between calculation and experimental (Table 1).

Infrared spectroscopy analysiss: As concerns the 2-TBT compound was formed through a Schiff base reaction (Fig. 1), a peak for carbonyl ν(C = O) group at around

Table 1: CHNS microelemental analyses of 2-TBT compound

Compound	Calc. (Found) (%) C	H	N	S
2-TBT	44.82 (43.76)	3.34 (3.15)	17.42 (18.13)	13.29 (11.93)

Table 2: IR spectroscopic data for the 2-TBT compound

Functional groups	Frequency (cm^{-1})
ν(N-H)	3442
ν(C-N)	1279
ν(C = N)	1602
ν(N-N)	1111
ν(C = S)	1176
ν(C-F)	1312

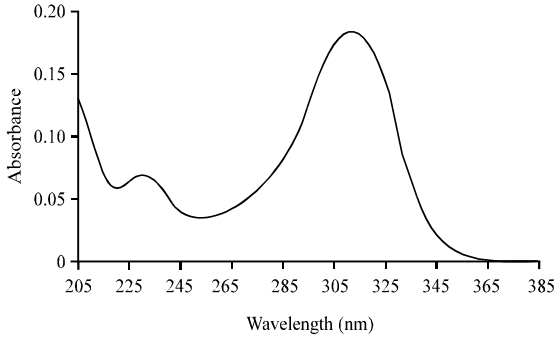

Fig. 3: UV-visible spectra of 2-TBT

1700/cm were disappeared and a new peak at 1602/cm indicate a presence of ν(C = N) functional group would give an indication that the reaction was completely occurred (Kamel, 2015). Formation of 2-TBT can be further confirmed by presence of both ν(N-H) and ν(N-N) functional groups by peaks at 3442 and 1111/cm, respectively. Same patterns were also observed for 1-(1-(3-Methoxyphenyl) Ethylidene) Thiosemicarbazide compound (Saravanan *et al*., 2015).

Both functional groups for ν(C-N) and ν(C = S) in 2-TBT can be identified by a peaks at 1279 and 1176/cm, respectively and not much different with previous reported which appeared at 1296 and 1166/cm for (E)-1-[1-(4-Chlorophenyl) Ethylidene] Thiosemicarbazide (Saravanan *et al*., 2014) and 2-formylquinoline thiosemicarbazide (Kamel, 2015). Finally, peak at 1312/cm for ν(C-F) moiety in 2-TBT was in a normal range of CF_3 stretch at 1350-1120/cm (Govindasamy and Gunasekaran, 2015). Data of IR spectroscopic of the 2-TBT compound is tabulated in Table 2.

UV-visible spectroscopy analysis: UV-V is absorption spectra of the 2-TBT in ethanol (1×10^{-6} M) is given in Fig. 3. The first weak absorption bands at 233 nm are assigned to $\pi\rightarrow\pi^*$ transitions of the phenyl ring (Govindasamy and Gunasekaran, 2015). The other one of the strong intense band 319 nm are due to $n\rightarrow\pi^*$ transition of thione (C = S) moiety (Akgemci *et al*., 2015). Both absorptions are commonly observed for other thiosemicarbazone derivatives (Singh and Singh, 2015; Lukmantara *et al*., 2014).

Table 3: ^1H and ^{13}C NMR data for 2-TBT

^1H NMR	Chemical shift, δ_H(ppm)
NH	11.70 (s, 1H)
N = CH	8.18 (s, 1H)
NH_2	8.44 (s, 1H), 8.38 (s, 1H)
$CH_{Ar.}$	8.53,8.51 (d, 2H, $^3J_{HH}$ = 8Hz)
$CH_{Ar.}$	7.78, 7.76 (d, 2H, $^3J_{HH}$ = 8Hz)
$CH_{Ar.}$	7.72, 7.70, 7.68 (t, 2H, $^3J_{HH}$ = 8Hz)
$CH_{Ar.}$	7.61, 7.59, 7.57 (t, 2H, $^3J_{HH}$ = 8Hz)
^{13}C NMR	Chemical shift, δ_C(ppm)
C = S	177.03
N = CH	135.99
CF_3	128.37
$C_{Ar.}$	124.31-131.15

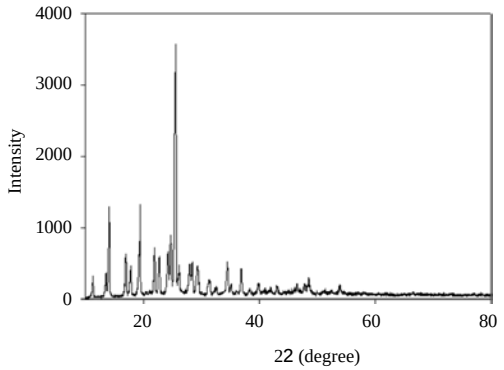

Fig. 4: XRD diffraction patterns of 2-TBT compound

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) analysis: ^1H NMR data of the 2-TBT is recorded in d_6-DMSO is listed in Table 3. The 2-TBT shows a singlet peak at the most downfield region at δ_H11.70 ppm are indicate presence of NH proton (Lobana *et al*., 1998). This is due to deshielding effect of sulphur atom and intermolecular hydrogen bonding which decreases the electron density of the moiety (Wan *et al*., 2013). Whereas, a sharp singlet peak at δ_H 8.18 ppm has been attributed to azomethine proton (N = CH) of 2-TBT (Xie *et al*., 2016). The peak of primary amine proton (NH_2) appeared at two different singlet peaks at both 8.38 and 8.44 ppm. These unexpected signals are due to the intermolecular hydrogen bond between hydrogen atom of primary amine (-NH_2) for 2-TBT compound and sulphur atom of d_6-DMSO solvent (Lobana *et al*., 2006). A multiple peaks at the range of δ_H 8.53-7.57 ppm are commonly due to phenyl proton.

The ^{13}C NMR spectrum of 2-TBT shows two signals at the most deshielded region which are at δ_c = 177.03 and δ_c = 135.99 ppm corresponding of carbon of thione (C = S)

Table 4: The electrical conductivity values of present and absence of 2-TBT in ITO substrate at 1×10^{-3} M

	Electrical conductivity (σ (S/cm))	
Light intensity (W/m^2)	Without 2-TBT	With 2-TBT
0	0.1417	0.1440
25	0.1418	0.1443
50	0.1420	0.1446
75	0.1422	0.1448
100	0.1425	0.1449
125	0.1424	0.1448
150	0.1422	0.1447
175	0.1418	0.1445
200	0.1417	0.1441

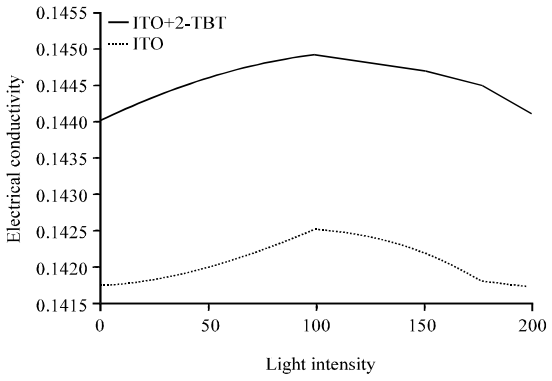

Fig. 5: The comparable graph of electrical conductivity in both conditions with and without 2-TBT compound

and azomethine (C = N), respectively (Lobana *et al*., 2006; Fabian *et al*., 2007). Signal for carbon of trifluoromethyl can be found at δ_c = 128.37 ppm (Hasan and Shalaby, 2016). Whereas, the aromatic carbons usually appear as a multiple peak at a range between δ_C 124.31-131.15 ppm.

X-Ray Diffraction (XRD) analysis: Figure 4 shows the XRD pattern of 2-TBT. It can be seen that the highest intensity (100%) of XRD peak which is appeared at ~25.5° and other peaks can be assigned to orthorhombic phase (Chen and Jing, 2011).

The lattice parameters (a = 8.6118, b = 6.9613 and c = 18.1797) of synthesized 2-TBT in this study were slightly smaller than previous single crystal data (Chen and Jing, 2011). This suggests that the structural rearrangement had occurred in the 2-TBT. Moreover, small crystallite size of the 2-TBT maybe contributed to smaller lattice parameters obtained. The crystallite size of 2-TBT was found to be 39.02 nm which is <100 nm. Thus, the synthesized 2-TBT compound can be classified as nanocrytalline materials.

Electrical conductivity of thin film of 2-TBT: The electrical conductivity of 2-TBT/ITO thin film in the dark and under various light intensities (W/m^2) was measured

Table 5: The electrical conductivity values of present and absence of 2-TBT on ito substrate at 1×10^{-3}, 1×10^{-4} and 1×10^{-5} M

	Electrical conductivity σ (S/cm)		
Light intensity (W/m^2)	(1×10^{-3} M)	(1×10^{-4} M)	(1×10^{-5} M)
0	0.1440	0.1475	0.1487
25	0.1443	0.1477	0.1488
50	0.1446	0.1478	0.1489
75	0.1448	0.1480	0.1492
100	0.1449	0.1481	0.1495
125	0.1448	0.1479	0.1498
150	0.1447	0.1478	0.1496
175	0.1445	0.1476	0.1495
200	0.1441	0.1473	0.1493

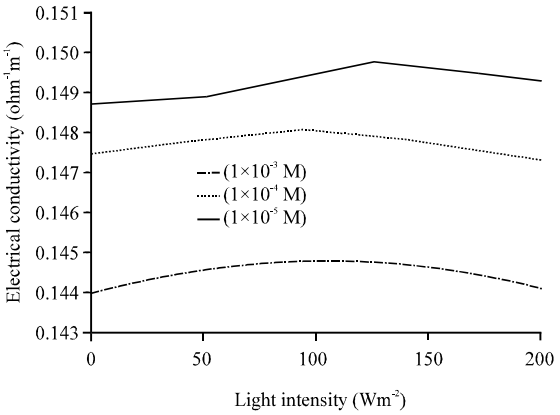

Fig. 6: The comparable graph of electrical conductivity of 2-TBT compound at 1×10^{-3}, 1×10^{-4} and 1×10^{-5} M

by four-point probe. The results obtained were listed in Table 4 and Fig. 5. Figure 5 shows that the presence of 2-TBT compound in thin film would increase the electrical conductivity. Electrical conductivity gradually increases by the increasing of light intensity until 100/Wm^2 with the maximum conductivity values of 0.1449/Scm. In addition, 2-TBT compound gave conductivity values of 0.1440 S/cm even in dark condition (light intensity = 0 W/m^2). Hence, the present compound, 2-TBT has potential to be a conducting material in organic solar cell even in no light environment.

Electrical conductivity of thin film in different concentration of 2-TBT: Electrical conductivity in three different concentrations which are 110^{-3}, 1×10^{-4} and 1×10^{-5} M were carried out. Here, the effect of concentration of 2-TBT compound to the thin film was studied. Table 5 shows the values of electrical conductivity of 2-TBT with selected concentrations. Figure 6 was obtained from the values.

The graph showed that 2-TBT compound gives the electrical conductivity in all concentrations and increased with the increasing of intensity of light. This indicates that the 2-TBT compound in ITO thin film are suitable to

make as solar cells due to their ability to change the light energy to electrical energy even in diluted solution.

The most potential electrical conductivity by 2-TBT compound was in 1×10^{-5} M. In addition, it has the highest electrical conductivity (0.1487 S/cm) even in a lowest intensity of light compared with other concentrations. The conductivity was simultaneously increased with the increasing of the intensity of light which had been reached a maximum conductivity (0.1498 S/cm) at 125 W/m^2 and start declining until 200 W/m^2. Interestingly, the present finding was higher than previous disubstituted thiourea with electrical conductivity of 0.1472 S/cm at 100 W/m^2.

However, lower maximum electrical conductivity of 2-TBT compound in both concentrations of 1×10^{-3} and 1×10^{-4} M were shown at 0.1449 and 0.1481 S/cm, respectively. Both graphs give a similar pattern where conductivity increased with increasing of intensity of light. Then, gradually decline when exposed to the intensity of light with >100 W/m^2.

This result indicated that the promising performance of the 2-TBT at the most diluted concentration (1×10^{-5} M). It is due to light penetration and scattering on ITO surface are easily occurred (Hwang *et al*., 2013). In addition, well dispersion and disaggregation of 2-TBT compound on ITO surface would effects the electron transfer occurred more efficient (Tang *et al*., 2013). Thus, the performance of the thin film was improved.

CONCLUSION

A thiosemicarbazide derivative, 2-TBT has been successfully prepared and spectroscopically characterized via CHNS micro-elemental analyses, IR, UV-VIS, XRD, ^{1}H and ^{13}C NMR. The deposition of different concentration of 2-TBT onto ITO glass substrate is also successfully done by spin coating technique.The maximum electrical conductivity of the thin film ITO/2-TBT formed was 0.1498/Scm at 125 W/m^2 in a diluted concentration of 1×10^{-5} M. Based on the analytical obtained, the present compound with proposed D-π-A molecular arrangement shows a promising material as a metal-free organic dyes. It is suggested that the present performance could be enhance with the combination of nature dyes, chlorophyll due to ability to absorb more photon of light.

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