THERMAL AND OPTICAL PROPERTIES OF 6, 13-BIS (TRI-ISOPROPYLSILYLETHYNYL) TIPS-PENTACENE

G.MURTAZA^{a,,c,*}, I. AHMAD^a, A. HAKEEM^b, J.WU^c

^aDepartment of Physics, Bahauddin Zakariya University, Multan 60800 Pakistan ^bDepartment of Physics, Govt. Post Graduate College Jampur, Pakistan ^cDepartment of Polymer Science and Engineering, Zhejiang University, Hangzhou 310037 PR China

We report on the thermal and optical properties of small molecule of 6, 13-bis (triisopropylsilylethynyl) pentacene (TIPS-pentacene). TIPS-pentacene is preferable to other organic materials due to their remarkable electronic properties, stability and solubility. Thermal behavior has been studied by Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC). Thermal properties show that the material decomposes at 412 °C and melts at 263 °C. Fourier transform infrared spectroscopy (FTIR) is used to confirm the presence of different elements making bonds with the structure of TIPS-pentacene and Photoluminescence indicate the presence of infra emission bands and it also shows the material is sensitive to light.

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1. Introduction

The interest in organic semiconductors based on conjugated materials has been emerged in the early 1980. Conjugated polymers and small molecules are now a day's subject to intense research owing to their potential applications in photonic and optoelectronics [1-2]. TIPSpentacene is a solution processable small molecule that forms Van der Waals bonded molecular system. TIPS pentacene small molecule is formed when tri-isopropylsilylethynyl acetylene is added to a pentacene. TIPS-pentacene molecules assume two-dimensional π - π stacking within unit cell. The presences of the isopropyl group makethis material soluble in common organic solvent. The low cost, ease of fabrication and tunable properties make the organic semiconductor more preferable than inorganic semiconductor. Among the solution processing organic semiconductors, 6, 13-bis (tri-isopropylsilyethynyl) pentacene is a known well due to its high Hole mobility and environment stability. However, its tendency to form randomly oriented needle shaped crystals, when its solution is crystallized, leads to significant performance variations in organic thin film transistors performance. TIPS pentacene stacked in two dimensional columnar arrays, gave rise to an electronic structure that is different from pentacene. [3-7]. TIPS pentacene can be crystallized in the thin film form, leading to a strong bathochromic shift, which indicates strong π - π interactions. Since crystalline thin films absorb further into the red then un-substituted pentacene, this leads to higher photocurrent and power conversion efficiency [8]. TIPS-pentacene, rubrene exhibits the highest mobility as a result these are commonly used in the organic field effect transistors and in the optoelectronic devices [9-12]. These materials are classified into two major groups, the small molecule based and polymer based organic semiconductor both having different microstructures. Small molecule based films can possess longer range order, regular arrangement of these small molecules within each domain enhances exciton and charge diffusion, improving device performance while Polymer based films are dissolved with small extent. TIPS pentacene

^{*} Corresponding author: mrkhichi@gmail.com

marked the turning point in the field of organic thin film transistors as the molecule is easily synthesized in good yield, stable in normal conditions and exhibits carrier mobility comparable to and better than amorphous silicon. Recent research however expands the expertoire of semiconducting materials to include certain organic molecules. Such organic semiconductors are superior to their inorganic counterparts because they are easily processable to deposit on a substrate, light in weight and significantly more flexible. In this paper, we have described the thermal and optical properties of TIPS-pentacene.

2. Experimental

A solution of TIPS-pentacene (sigma Aldrich) is made by mixing the solvent m-xylene (sigma Aldrich) and carbon tetrachloride (CCl₄) of Sigma Aldrich with volume ratio 1:1. The prepared solution of TIPS-pentacene having concentration 0.2 mgml^{-1} , 0.4mgml^{-1} , 0.6 mgml^{-1} , 0.8 mgml^{-1} and 1.0 mgml^{-1} , respectively is used to measure the photoluminescence while its thermal properties are studied by using the powder form of TIPS-pentacene.

3. Results and Discussions

In order to study thermal stability, thermal gravimeter of TIPS-pentacene indicates high thermal stability in the range of 50 to 350°C. The thermal stability depends on the substituent group and it changes with the change of substituent's positions. Not only the addition of 6, 13-bis (tri-isopropylsilylethynyl) increases the solubility but also the thermal stability. A typical Thermo gravimetric analysis trace is represented in Fig. 1.



Fig. 1. Weight Loss and Derivative Weight Loss % of TIPS-Pentacene

The inflection at 412 °C is related to the decomposition process of TIPS-pentacene. In significant decomposition related residue is observed at 498 °C which is close to the reported value by Jae-Hong Kwon et al [13]. The 60% weight loss is due to breakage of bonds and the curve shows again stability after 600 °C and this stability confirms the presence of inorganic element in the chain of TIPS-Pentacene. The material melts at about 263 °C after which its degradation or oxidation takes place as shown in Fig.2. The DSC scan of TIPS-pentacene shows that the material is in crystalline form at low temperature 35°C to 63.5°C as depicted by the second time heating and cooling curve respectively, a glass transition takes place at 165.51 °C, that is depicted by the heating curve as shown in Fig.3 [14].



Fig. 2.Differential Scanning calorimeter sketch of TIPS-pentacene.



Fig. 3. Differential Scanning Calorimeter Sketch showing the heating and cooling curve

The FTIR spectroscopy of TIPS-pentacene powder is shown in Fig. 4, which reveals the presence of Si-O, Si-C and stretching vibrations of Si-OH at 678 cm⁻¹, 736 cm⁻¹ and 888cm⁻¹ respectively. The C-Cl stretching peak arises in the range of 590-700 cm⁻¹ and C= C stretch is generally present in the range of 1475-1600 cm⁻¹. The bands observed near 1130cm⁻¹ are due to C-C stretching. The bands at 1374 cm⁻¹, 1450 cm⁻¹ represent the isolated pentacene anion vibration mode and Si-C stretching vibrations. The bands which are present at the position of 1978 cm⁻¹, 2656 cm⁻¹ represents the asymmetric stretching vibrations of methyl(-CH₃) group. The band at the position of 2740 cm⁻¹ represents C-H stretching vibration mode and the band at the position 3456 represents the O-H stretching vibration due to moisture content [15-18].



Fig. 4. Fourier transforms infra red spectroscopy of TIPS-pentacene

The photoluminescence spectra of TIPS pentacene solution having different concentrations is shown in Fig. 5. It is clear from the photoluminescence spectrum that the intensity in the blue and red wavelength region is high as compared to other regions of visible spectrum. Maximum photoluminescence is 1.2×10^7 at a wavelength of 468nm. A blue and a red shift is exhibited by the materials at a wavelength of 664nm, 706nm having intensity of 9.1×10^6 and 6.6×10^6 , respectively. A low photoluminescence indicate the presence of infra emission bands as reported by Xiaoxia et al [19]. It is clear from the photoluminescence that the material is sensitive to light because the absorption phenomenon is high in the visible region and two regions red and blue are prominent in absorption [20, 21]. Bathochromic shift and Hypochromic shift are observed by photoluminescence spectrum.



Fig.5. Photoluminescence spectra of TIPS-pentacene powder

4. Conclusions

Photoluminescence indicate that the material is photosensitive and it is applicable in optoelectronics. The thermo gravimetric analysis shows that the material decomposes at 412°C and the differential scanning calorimeter indicates that the material is crystalline at a low temperature. Glass transition takes place at about 165.5 °C and the melting temperature is 263 °C. These values indicate that the material is semiconducting and applicable to organic field effect transistors, optoelectronics and in electrochemical displays.

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References

[1] T.Kobayashi (Ed.), Springer, (1989).

[2] S.Etemad, Z.G.Zoos, R.J.H.Clark, R.E. Hester (Eds.). Wiley, New York(1991).

[3] J.E.Anthony, J.S.Brooks, D.L. Eaton, S.R.Parkin, J.Am.Chem.Soc.123,9482 (2001).

[4]C.C.Matthews, G.A.de Wijs, R. A.D.Groots, T.T.M. Palstra, J.Am.Chem.Soc **125**, 6323(2003).

[5] R.C. Haddon, X.Chi, M.E. Itkis, J. E.Anthony, D.L.Eaton, T. Siegrist, C.C. Mattheus,

- T.T.M.Palstra, The J.Phys.Chem.B 106,8288 (2002),.
- [6] M.T. Lloyd, A.C. Mayer, A.S.Tayi, A.M.Bowen, T.G. Kasen, D.J.Herman,
- D.A. Mcurey, J.E. Anthony, G.G. Malliaras, Org. Elect. 7,243 (2006).
- [7] D. -S. Kim, J. H. Kwon, S. Y. Cho, C. Lee, K. –S. Lee, T. –D. Kim, Synth. Met. **161**,2422 (2011).
- [8] M.T. Lloyd, J.E. Anthony, G.G. Malliaras, Materials Today 10, 11 (2007).
- [9] J.E. Anthony, Chem. Rev. **106**, 5028 (2006).
- [10] G. Murtaza, I. Ahmad, H. Chen, J. Wu, Synth. Met. 194, 146 (2014).
- [11] S.I.Shin, J.H. Kwon, H.Kang, B.K.Ju, Semicond. Sci.Technol. 23,(2008).
- [12] S.K. Park, T.N. Jackson, J.E.Anthony, D.A. Mourey, App. Phy. Lett. 91,063514 (2007).
- [13] K.Haubner, E. Jaehne, H.-J.P.Adler, D. Koehler, C. Loppacher, L.M.Eng, J. Grenzer,
- A.Herasimovich, S.Scheinert, phys.stat.sol (a) 205, 430 (2008).
- [14]J.S. Brooks, R. Vasic, T.Tokumoto, D. Graf, O.H. Chung, J. E. Anthony,
- S.A.Odom, Current Appl.Phys., **4**,479 (2004).
- [15] Y. Hosoi, K.Okamura, Y. Kimura, H.Ishii, M. Niwano, Appl.Surf.Sci.244, 607 (2005).
- [16] T. M. Halasinski, D. M. Hudgins, F. Salama, L. J. Allamandola, T. Bally, J. Phys. Chem A, **104**(2000), 7484-7491.
- [17] A. Imani, G. Farzi, A. Ltaief, Inter. Nano Letters, 3, 52 (2013).
- [18] N. P. S. Chauhan, R. Ameta, R. Ameta, S. C. Ameta, Indian J. Chem. Tech., 18, 119 (2011),
- [19]X. Jang, F. Chen, W. Qiu, Q. Yan, Y. Nan, H. Xu, L. Yang, H. Chen, Solar Energy Materials & Solar Cells, **94**,2223 (2010).
- [20] M. Yoshida, H. Kawai, T. Kawai, S. Uemura, S. Hoshino, T. Kodzasa, T. Kamata, Proc. Of SPIE,**5940**,594003-1 (2005).
- [21]B. A. Paez, S. I. Thurzo, G. Salvan, R. Scholz, D. R. T. Zahn, H. Von Seggern, Proc. Of SPIE,**5940**,59400F-1 (2005).