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Optoelectronic properties of novel alkyl-substituted Triphenylamine derivatives

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ABSTRACT

Hole transport characteristics in three new organic compounds based on triphenylamine (TPA) moiety are presented. The effect on electrical and optical properties of TPA, attached with methyl or *tert*-butyl side groups, has been investigated through measurement of current density versus voltage (*J-V*), capacitance versus voltage (*C-V*), frequency dependent capacitance, *ac* conductivity, Impedance spectroscopy, UV-Vis spectroscopy, Photoluminescence (PL) spectroscopy and X-Ray Diffraction (XRD) studies. These measurements reveal that, the attachment of methyl or *tert*-butyl group in the *para*-position of the TPA moiety leads to improved optoelectronic properties and greater molecular stability. XRD analysis of the samples indicates that the inter-molecular distance is the lowest for TPA with *tert*-butyl side group (3.43 Å) as compared to pure TPA (3.57 Å). This leads to stronger inter-molecular interaction as evidenced by the UV-Vis spectra. PL studies indicate significant Quantum Efficiency (~30%) for alkyl attached TPA. In order to get a better understanding of the charge transport phenomena, the effect of molecular structure dynamics on charge transfer kinetics is analyzed by evaluating the charge carrier hopping rate coefficient and dynamic state factor. The dynamic state factor b has higher value for lower bias voltage, corresponding to dc conductivity, whereas, at higher bias, the value of b is smaller, indicating the dominance of *ac* conductivity. Hopping conductivity is seen to be highest for the device with *tert*-butyl substitution in TPA moiety. Our experiments indicate an order of magnitude enhancement in charge carrier mobility for alkyl-substituted TPA.

1. Introduction

Organic semiconducting materials have a wide range of potential applications in devices such as organic light-emitting diodes (OLEDs) [1–3], organic photovoltaics (OPVs) [4,5] and organic field-effect transistors (OFETs) [6,7]. Molecular engineering, leading to the synthesis of a very wide range of organic materials, together with low temperature technologies for device fabrication, have led to rapid progress in this field. Most of the organic materials employed in the electronic devices are π-conjugated materials which have delocalized electrons. It has been observed that organic materials having high Photo Luminescence (PL) efficiency exhibit rather low charge carrier mobility (~10^{-6} $cm^2V^{-1}s^{-1}$), whereas materials having large carrier mobility show much lower PL - efficiencies [8]. Triphenylamine (TPA) and its derivatives, such as α-NPD and TPD, are an important class of π-conjugated organic compounds used in OLED applications. The reported values of hole mobility for such materials fall in the range 10^{-3}-10^{-7} $cm^2V^{-1}s^{-1}$ [9,10] and the PL quantum efficiencies are seen to be about 30–40% [8]. A proper choice of the side-group for attachment to such TPA molecules is vital for achieving good device performance. In this paper, we use hole-only devices to report on the role of methyl and *tert*-butyl groups, attached to TPA molecules, on the performance of OLED devices.

The mobility in disordered organic compounds is influenced by several factors such as molecular geometry, impurities and traps. Stability of these compounds in the film form in ambient conditions can significantly affect the charge transport [11]. The stability in

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ambient conditions depends on the HOMO-LUMO energy levels. Materials with high-lying HOMO levels are prone to oxidation, rendering them less stable [12]. However, in TPA molecules, the presence of electron deficient nitrogen and C=N double bond, lowers the HOMO energy level, leading to better stability besides enhanced hole-transport [9]. Thus, these molecules can be designed to play multifunctional roles in devices depending on their HOMO-LUMO levels, which can be suitably altered by molecular engineering.

The presence of side groups in the organic molecules leads to modifications in their electronic and optical properties. One such effect is the increase in the number of π-electrons [12]. Secondly, the presence of oxadiazole moiety reduces the steric repulsion and minimizes the torsional disorder between the neighboring units, thereby leading to a more planar structure [13]. Nagakubo et al. [14] observed a reduction in the traps at the organic-substrate interface due to the presence of *tert*-butyl groups, leading to improvement in transistor characteristics [14,15]. In this work, we show that the attachment of *tert*-butyl groups to the TPA moiety results in an order of magnitude improvement in the hole mobility (~10^{-6} $cm^2V^{-1}s^{-1}$) and thin films of this material show significant photoluminescence quantum efficiency (~30%). This is in contrast to materials having high carrier mobility [8] but low PL quantum efficiencies, typically < 1%. Further, the attachment of methyl or *tert*-butyl side group to TPA molecule increases the number of delocalized electrons and also shows higher carrier hopping rate. These investigations suggest that the alkyl-substituted TPA has good potential for OLED applications.

Attachment of *tert*-butyl group to certain organic molecules such as quarter thiophene, TTF and its derivatives, etc., improves their stability and also electronic properties due to the delocalization of π-electrons [15]. In contrast, the attachment of s-alkyl and n-alkyl side groups to these molecules does not bring in these beneficial changes. In addition, the *para*-position of the substituents is responsible for additional electron donation due to a special type of resonance contribution known as hyperconjugation [16]. It is therefore important to choose appropriate molecules as side groups for achieving the desired optoelectronic characteristics.

We present the experimental investigation of hole transport in three new compounds containing electron donating TPA moiety. The compounds denoted for further discussion as X_1, X_2 and X_3 are listed below:

a) 2-(4-(5-(4-(diphenylamino)phenyl)-1,3,4-oxadiazol-2-yl)benzylidene)malononitrile
b) 2-(4-(5-(4-(di-*p*-tolylamino)phenyl)-1,3,4-oxadiazol-2-yl)benzylidene)malononitrile
c) 2-(4-(5-(4-(bis(4-(*tert*-butyl)phenyl)amino)phenyl)-1,3,4-oxadiazol-2-yl)benzylidene) malononitrile.

In these compounds, X_2 and X_3 are obtained from compound X_1 by attaching methyl and *tert*-butyl substituents, respectively, to the TPA moiety. A brief account of their synthesis along with their NMR spectra, mass spectra, photophysical characterization and XRD has been given in the supplementary information to this paper (Scheme 1, Figs. S1–S17, Tables S1–S2). Detailed synthesis along with electrochemical and thermal properties will be reported elsewhere.

We have determined hole mobility by employing Impedance Spectroscopy which is widely used to study organic materials having dispersive transport [17]. Besides this, we have also carried out current density-voltage (*J-V*), capacitance-voltage (*C-V*) as well as frequency dependent capacitance (*C-f*) and conductivity (σ-*f*) measurements on the devices fabricated in order to get an insight into the charge transport process.

Previous theoretical studies [12,18–20] indicate that the molecular structural dynamics is responsible for interaction between the neighboring localized hopping sites. For hopping transport, electronic coupling and structural relaxation are key parameters which can be altered by appropriate side-group substitutions. Hence, we have investigated the role of side-groups on the transport and the frequency dependence of hopping rate in detail. We have also analyzed the effect of molecular structural oscillations on charge transfer kinetics in these devices.

2. Fabrication and characterization of hole-only devices

The hole-only device structure used in this study is shown in Fig. 1 (a), which includes 10 nm thick layers of *N,N*′-Di(1-naphthyl)-*N,N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (α-NPD) on either side of compounds X_1, X_2 or X_3 to facilitate hole transport from 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) layer as well as to block electron injection from the Al cathode. The hole mobility measured in our devices is in the range 10^{-6} -10^{-7} $cm^2V^{-1}s^{-1}$ and is seen to improve with alkyl substitution. These

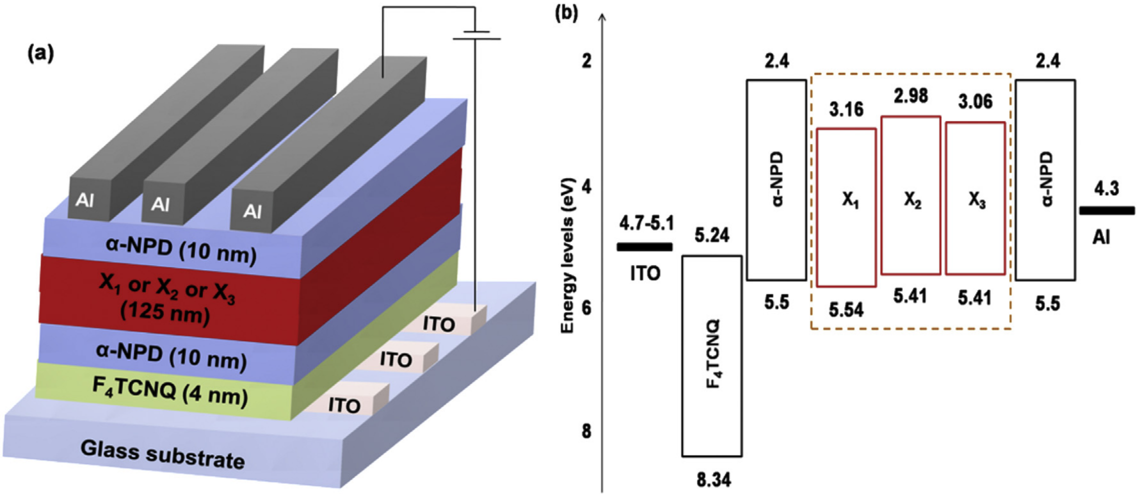

Fig. 1. (**a**) Schematic representation of the device structure and (**b**) energy level diagram of various layers, where layers X_1, X_2 and X_3 correspond to devices $\mathbf{P_1}$, $\mathbf{P_2}$ and $\mathbf{P_3}$, respectively.