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A New N-Type Organic Semiconductor Synthesized by Knoevenagel Condensation of Truxenone and Ethyl Cyanoacetate

Xin-Ran Zhang,[†] Wei Chao,[†] Yu-Tao Chuai,[‡] Yan Ma,[†] Rui Hao,[†] De-Chun Zou,[‡] Yong-Ge Wei,[§] and Yuan Wang*[,†]

Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, and Department of Polymer Science and Technology, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, P. R. China, and Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

wangy@pku.edu.cn

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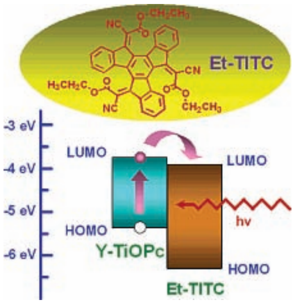
ABSTRACT



A novel n-type organic semiconductor, Et-TITC, was synthesized by Knoevenagel condensation of truxenone and ethyl cyanoacetate. Ultrasonication improved the yield of Et-TITC by more than 10 times. The molecular structure of Et-TITC was determined by X-ray analysis. Et-TITC possesses a large electron affinity and excellent solubility in many organic solvents. A positively charged xerographic photoreceptor with an excellent photosensitivity ($E_{1/2}$) of 0.32 μJ cm^{-2} was prepared using Et-TITC as the charge-transport material.

n-Type organic semiconductors (NOS, electron transport materials) have attracted much attention since electron transporting is an important issue in organic electronics,[1−3] and excellent NOS are particularly needed in the pursuit of high-performance organic electronic devices such as organic thin film transistors (OTFT),[1a] organic light-emitting diodes (OLED),[1b] and xerographic photoreceptors,[1c] etc. The design and synthesis of new NOS having a suitable electron affinity larger than oxygen, excellent electron-transporting properties,

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[†] State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University.

[‡] Department of Polymer Science and Technology, College of Chemistry & Molecular Engineering, Peking University.

[§] Department of Chemistry, Tsinghua University.

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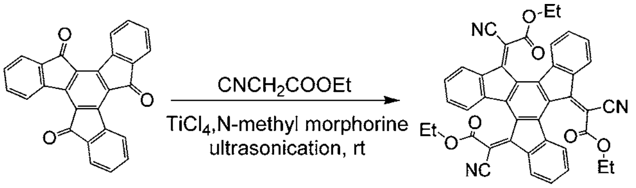
and good solubility in organic solvents present a challenge for chemists, and the long exploration on this subject has shown the difficulty in fulfilling all of these desired properties simultaneously. The strategy of modifying a highly conjugated core with electron-withdrawing substituents is effective in designing promising NOS.[1a,2,3] The most frequently used side groups so far were fluoro/fluoroalkyl[2] and cyano/dicyanomethylene[3] substituents. However, these compounds usually have to be processed by the evaporation method in their purification and the fabrication of devices due to their poor solubility in common organic solvents. NOS simultaneously showing excellent electron-transporting properties and solubility are very attractive,[4] since thin films of these compounds, embedded in a polymer matrix when necessary, can be fabricated using low-cost solution-processed techniques such as spin coating or casting.

In this paper, we report a novel n-type organic semiconductor, tris(ethyl)-2,2′,2″-(5*H*-tribenzo[*a*,*f*,*k*]trindene-5,10,-15-triylene)tris(2-cyanoacetate) (Et-TITC), which was synthesized from the Knoevenagel condensation of truxenone and ethyl cyanoacetate (Scheme 1). As the choice of appropriate conjugated system is crucial to achieve the desired electronic structure,[5] truxenone was selected in this work to form a star-shaped conjugated core of fused rings, and ethyl cyanoacetate was used to endow the target compound with both high electron affinity and ideal solubility. As expected, Et-TITC exhibits excellent solubility in many organic solvents such as dichloromethane, 1,2-dichloroethane, acetone, tetrahydrofuran, toluene or acetonitrile. The solubility of Et-TITC in dichloromethane or 1,2-dichloroethane is higher than 100 g/l. These properties make Et-TITC quite suitable for the construction of positively charged dual-layer photoreceptors, which was thought to be the next generation of xerographic photoreceptors.[6]

Scheme 1. Synthetic Route to Et-TITC



Historically, negatively charged dual-layer xerographic photoreceptors have gained general acceptance in commercial xerographic copiers and laser printers.[1c,6] In the negatively charged working mode, the corona emits a large amount of undesirable ozone which is harmful to the operators' health and the stability of the photoreceptors.[1c,6] Positively charged photoreceptors are much more "healthy", because the amount of ozone emitted in this mode is less than 10% of that in the negatively charged mode. However, the photoconductive properties of previously reported positively charged dual-layered photoreceptors were much poorer than their negatively charged counterparts due to the lack of suitable NOS,[1c,6] especially that possessing electronic levels suited with those of charge generation materials. Et-TITC was found to be very promising in solving this problem. Excellent xerographic properties, with a photoconductive sensitivity ($E_{1/2}$) of 0.32 μJ cm^{-2}, were achieved in a prepared positively charged dual-layer photoreceptor, in which Et-TITC was used as the electron transport material (ETM).

For the synthesis of Et-TITC, the major problem to be overcome is the low yield under usual reaction conditions. Previously, Jacob et al. reported the synthesis of 2,2′,2″-(5*H*-tribenzo[*a*,*f*,*k*]trindene-5,10,15-triylene)tris(propanedinitrile) from the condensation of truxenone and malononitrile;[7] the solubility of this compound is not enough for the fabrication of a photoreceptor via a solution process. When we applied the same synthetic conditions to the mixture of truxenone and ethyl cyanoacetate, however, conversions of truxenone could hardly reach 3%, and more than half of the products were molecules with one or two carbonyl groups intact. This was most probably due to the larger steric hindrance of ethyl cyanoacetate than that of malononitrile. The yield of Et-TITC was remarkably improved to 40% by ultrasound irradiation during the reaction course. The promotion effect of ultrasound irradiation on the Knoevenagel condensation reaction of soluble reactants have been known for a few years.[8] Our success in the effective synthesis of Et-TITC from truxenone suggests that this promotion effect is also significant for the reaction system containing an insoluble or slightly soluble reactant such as truxenone.

X-ray analyses were carried out on the single-crystal grains of Et-TITC. It was found that two kinds of crystal grains could be obtained from simple crystallization of Et-TITC in mixed ethanol and dichloromethane. One is thick grains composed of only one isomer of Et-TITC (Et-TITC-1), characterized by the same configuration of the three cyanoacetate moieties, as shown in Figure 1. The truxene moiety, a fullerene fragment,[9] in Et-TITC-1 shows a bowl-like shape, and the three cyanoacetate moieties protrude out of the backside of the bowl. The other is thin crystal platelets composed of 80% of Et-TITC-1 and 20% of another isomer of Et-TITC (Et-TITC-2), in which one of the three cyanoacetate moieties has a different configuration (see the Supporting Information, Figure S2), Therefore, the molar ratio of Et-TITC-1 to Et-TITC-2 is higher than 4:1 in the products. When the crystallization speed was controlled to be very slow, the thick crystal grains of Et-TITC-1 could be obtained exclusively.

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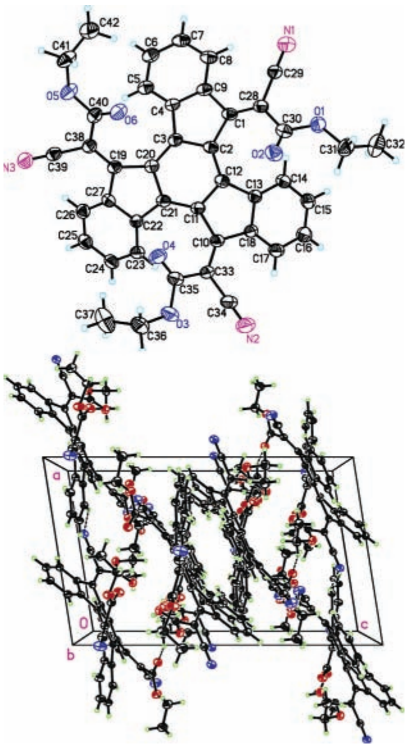

Figure 1. Molecular structure of Et-TITC-1 obtained from a thick crystal grain ($0.40 \times 0.30 \times 0.30$ mm^3 in size) and its cell packing along the *b* axis.

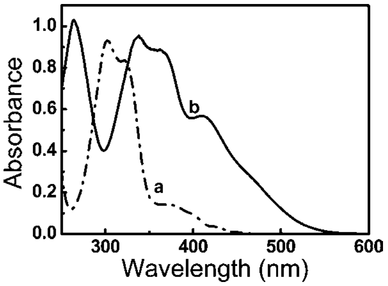

Figure 2. UV−vis spectra of truxenone (a) and Et-TITC (b) in 1,2-dichloroethane. The concentrations in both cases are 4×10^{-2} mM.

UV−vis spectra of Et-TITC and truxenone are shown in Figure 2. The absorption peaks of Et-TITC in the UV−vis spectrum were found to significantly red-shift compared to those of truxenone. This is caused by the more extended conjugated system in Et-TITC and the strong lowering effect of the electron-withdrawing groups (cyanoacetate moieties in our case) on the lowest unoccupied molecular orbital (LUMO).[1a] Moreover, the intensity of the long-wavelength absorption of Et-TITC is remarkably elevated compared with that of truxenone. The energy gap of Et-TITC calculated from the onset of its spectrum is 2.12 eV, which is much smaller than the value of truxenone (2.67 eV). The cyclic voltammogram (CV) of Et-TITC (Figure 3) exhibits four chemically reversible reductive peaks and one irreversible oxidative peak. The half-wave potential of the first reductive peak is −0.46 V vs Ag/AgCl. The reference potentials (25 °C) of Ag/AgCl and calomel electrodes in saturated KCl aqueous solutions are 0.198 and 0.245 V vs standard hydrogen electrode, respectively. Thus, the reductive potential of Et-TITC was calculated to be −0.51 V vs SCE. This value is more positive than that of oxygen (ca. −0.8 V vs SCE), suggesting that oxygen will have no significant influence on the electron-transporting properties of Et-TITC. According to the literature,[10] the electron affinity of Et-TITC is estimated to be -0.51 (V vs SCE) $+ 4.4 = 3.9$ eV, which is a high value for NOS. The half-wave potential of the oxidative peak is 1.92 V vs Ag/AgCl. And the energy gap calculated from the CV is $1.92 - (-0.46) = 2.38$ eV, a little larger than that calculated from the onset of its spectrum. These data were obtained from the thin crystal platelet samples in which the molar ratio of Et-TITC-1 to Et-TITC-2 is 4:1. The CV of pure Et-TITC-1 was also recorded, and it is very similar to that of the mixture. Thus, it is reasonable to believe that the two isomers of Et-TITC would have quite similar electronic structure.

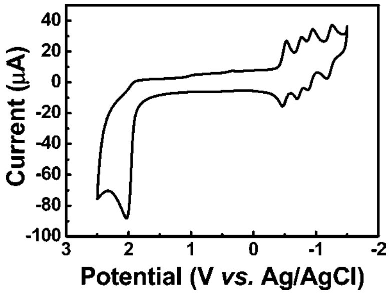

Figure 3. Cyclic voltammogram of Et-TITC (1 mM) in oxygen- and moisture-free acetonitrile containing tetraethylammonium perchlorate (0.1 M).

To show the potential of Et-TITC as a promising electron-transport material, a dual-layer photoreceptor composed of a charge generation layer (CGL) covered with an electron-transport layer (ETL) on an Al substrate was fabricated (for device fabrication, see the Supporting Information). The CGL is made of 67% (weight ratio) of Y-type oxotitanium phthalocyanine (Y-TiOPc)[11] embedded in a poly(vinylbutyral-*co*-vinyl alcohol-*co*-vinyl acetate) (PVB) film. The ETL is a polycarbonate (PC) film containing 50% of Et-TITC as the ETM. When this photoreceptor was positively charged and taken exposure to a 780 nm light, excellent photoconductivity was obtained. Typically, the photoreceptor could be charged to 572 V, and the photoconductive sensitivity

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$E_{1/2}$ (the exposure energy required for discharging the surface potential to the half of its initial value) was 0.32 μJ cm^{-2}, with the dark decay rate of 34 V s^{-1}. To our knowledge, the photoconductive sensitivity of the present photoreceptor is one of the best for positively charged dual-layer photoreceptors, and it is even comparable with those of negatively charged photoreceptors reported in the literature.[6,12] X-ray diffraction (XRD) patterns of the ETL showed that Et-TITC was uniformly dispersed within the polycarbonate (PC) resin, forming an amorphous film. This is quite beneficial for elongating the lifetimes of xerographic photoreceptors, as the possibility of harmful crystallization of the ETM within the polymer film is avoided.[1c]

The photoinduced discharging process in the present photoreceptor is considered as follows. The photogenerated electron−hole pairs are effectively separated by electron injection from Y-TiOPc to Et-TITC at their interface, and then the electrons travel across the ETL to neutralize the surface positive charges. This model could be substantiated by comparing the energy levels of Y-TiOPc with those of Et-TITC. Electrochemical data of unsubstituted TiOPc was absent in the literature, due to its poor solubility in common solvents. Thus, the cyclic voltammetric measurements on Y-TiOPc were conducted by embedding it in a PVB film (containing 67% of Y-TiOPc, the same composition with that of the CGL in the photoreceptor), which is coated on the glassy carbon working electrode. In these measurements, only one reductive peak and one oxidative peak, with the values of half-wave potential of −0.63 and 0.97 V vs Ag/AgCl, respectively, were observed. These values were quite close to those of a soluble compound of alkylated TiOPc reported in the literature.[13] Compared with the reductive potential of −0.46 V vs Ag/AgCl of Et-TITC, it could be deduced that the LUMO of Et-TITC is 0.17 eV lower than that of Y-TiOPc. Such an offset value should facilitate the photoinduced electron injection from Y-TiOPc to Et-TITC.

In summary, we have succeeded in synthesizing a new excellent n-type semiconductor with large electron affinity and excellent solubility by the ultrasound-assisted Knoevenagel condensation of truxenone and ethyl cyanoacetate. The molecular structure and energy levels of Et-TITC were well characterized. A positively charged dual-layer xerographic photoreceptor, which is more environmentally friendly than the commercial negatively charged dual-layer photoreceptors, was prepared using Et-TITC as the ETM. This photoreceptor exhibits excellent xerographic properties with a value of photoconductive sensitivity ($E_{1/2}$) being 0.32 μJ cm^{-2}, which is one of the best value so far for positively charged photoreceptors, and is even comparable to that for currently adapted negatively charged photoreceptors. The excellent photoconductivity of the prepared photoreceptor is partly derived from the well-suited electronic levels of Et-TITC and TiOPc.

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Supporting Information Available: ^{1}H NMR spectrum, molecular structure obtained from a thin crystal platelet, experimental procedures, and crystallographic information in CIF format for both kinds of crystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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