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Indacenodithienothiophene based chromophore with cyclopentadienylidenehydrazine acceptor moieties

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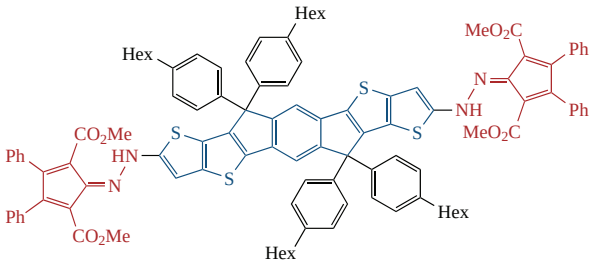
A novel acceptor–donor–acceptor chromophore IDTT-HC2P with an indacenodithienothiophene core linked with two hydrazinylidenecyclopentadiene terminal acceptor groups was designed and synthesized *via* the reaction of dilithiated indacenodithienothiophene with the corresponding diazo compound. The frontier orbital energy levels as well as the bandgap which were estimated from both optical and electrochemical properties are very closely related to those of ITIC which in turn is associated with high power conversion efficiencies.



IDTT-HC2P

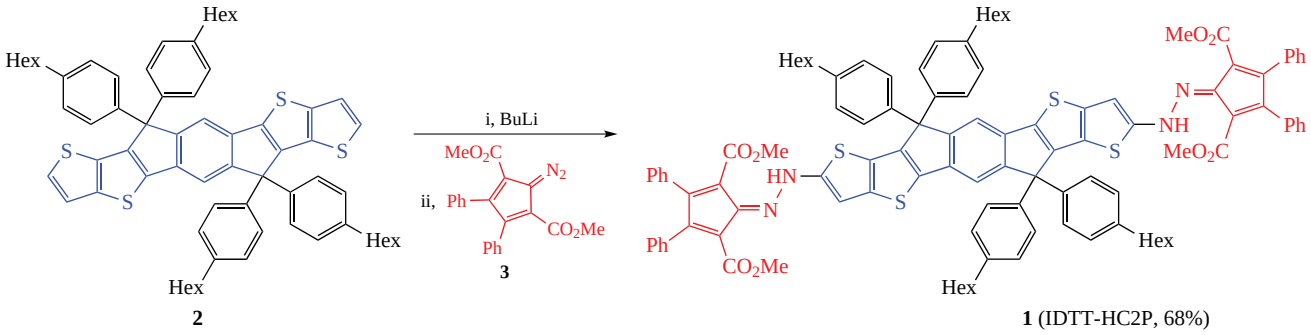
Keywords: non-fullerene acceptor, bulk heterojunction organic solar cells, hydrazinylidene derivatives, hydrazonocyclopentadiene, indacenodithienothiophene.

Organic solar cells (OSCs) are becoming prospective for the transformation of pure and renewable energy into electric power since they possess numerous advantages over classic silicon-based solar cells.[1,2] These advantages include their low cost, flexibility, low weight and the possibility to manufacture transparent devices. Standard OSCs represent a bulk heterojunction cell wherein fullerene derivatives act as an electron acceptor, and either conjugated polymers,[3] or small molecules are used as the donor material.[4] The power conversion efficiencies (PCEs) of the latter in such devices have so far reached 11%.[4] Nevertheless, achieving high efficiencies for OSCs based on fullerene derivatives[5] is challenging due to the disadvantages of fullerene derivatives, such as pour absorption in the visible spectrum, high cost and limited tunability of energy levels.[6,7] Along with the development of classical fullerene OSCs, researchers also studied cells with acceptors of non-fullerene (NF) family.[8,9] These cells had been significantly inferior to fullerene in terms of PCEs due to the difficulties in controlling the morphology of the layer[10,11] until 2015 when Lin suggested an NF acceptor of the acceptor–donor–acceptor (A–D–A) type based on the indacenodithienothiophene core.[12] Therein ITIC, which is 6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-*d*:2′,3′-*d*′]-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (IDTT) equipped with two dicyanomethylidenindanone acceptor groups was used as an NF acceptor in cells whose PCE reached 6.8% and later was optimized to 11.3%.[13] ITIC has become a superior acceptor due to the good π–π stacking with the donor molecule which accounts for the charge separation rate in ITIC systems having three orders of magnitude larger than that of a fullerene acceptor while both demonstrate similar charge recombination rates.[14] Further, the attention was concentrated mainly on the modifications in either non-conjugated fragments or in the indandione acceptor fragment. In addition, IDTT chromophores containing rhodanine,[15] (2-methylchromen-4-ylidene)malononitrile[16] and benzothiadiazolylmethylidenemalononitrile[17] acceptor fragments were also synthesized; however, only the latter were studied as an NF acceptor, and the former were studied only as small molecule donors.

In our earlier works, we performed three syntheses of new dyes containing hydrazonocyclopentadiene acceptor moieties.[18,19] Moreover, we have synthesized two compounds containing various hydrazonocyclopentadiene acceptor and triphenylamine donor fragments connected by a phenylene linker. These compounds were tested in bulk heterojunction OSC as the donor material and the best performance for one of them reached 1.85%.[20] Despite the non-coplanar structure of these molecules, they nevertheless had semiconductor properties and were capable of intramolecular charge separating. Although these efficiencies were not record, however, they were comparable with those for asymmetric low molecular weight analogues containing standard acceptor fragments and donor and linker blocks with complex coplanar structures.[21] Additionally, the analysis of the absorption spectra of dyes with identical donor fragments and different acceptor groups showed that hydrazonocyclopentadiene fragments had a greater acceptor ability compared to the most commonly used terminal acceptor groups.[19] Since indandione acceptor groups are also one of the strongest acceptor fragments (*cf.* IDTT derivatives such as ITIC and IT-2F), it is attractive to obtain IDTT derivative with two hydrazonocyclopentadiene acceptor fragments.

Two of our three previous synthetic methods to obtain hydrazonocyclopentadiene chromophores[22] are not suitable for the current target molecule since both amino- and hydrazinothiophenes required for our purpose should not be stable.[22] However, the third approach based on the reaction of diazo compounds with lithiated (hetero)arenes[19] seemed promising (Scheme 1).

Synthesis of IDTT **2** which was performed in seven stages from *p*-xylene following the reported procedure.[26] This



Scheme 1

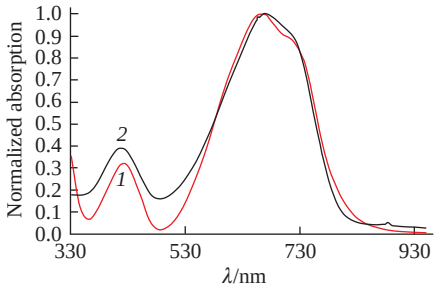


Figure 1 Normalized absorption spectra of **1** in (*1*) a thin film and (*2*) a dilute solution in chloroform.

compound was lithiated, and the subsequent reaction with excess 5-diazo-3,4-diphenylcyclopentadiene-1,4-dicarboxylate **3**[18] gave the desired product **1** in a yield of 68% (see Scheme 1) with a trace amount of monosubstituted IDTT. Compound **1** is the symmetrical A–D–A chromophore with an IDTT core and terminal hydrazinylidene groups. The new chromophore was named IDTT-HC2P indicating that it has hydrazinylidene cyclopentadiene acceptors with two phenyl groups.

Compound **1** demonstrates intense absorption within 500–800 nm in chloroform with a maximum extinction coefficient of 8.67×10^4 dm^3 mol^{-1} cm^{-1} at 669 nm (Figure 1). The absorption spectrum in a film has a similar absorption maximum which apparently indicates the absence of a significant molecular organization therein and its amorphous nature. The optical band gap for **1** in a film was estimated from the absorption edge (800 nm) as 1.55 eV.

The electrochemical behavior of compound **1** was investigated by cyclic voltammetry (Figure 2). It demonstrated irreversible reduction and three quasi-reversible oxidation waves. The frontier orbital levels were estimated as –5.42 eV (HOMO) and –3.80 eV (LUMO) which are nearly identical to those of ITIC (–5.48 eV for HOMO and –3.83 eV for LUMO). Thus, we conclude that our product is appropriate for the use as an acceptor material in OSCs.

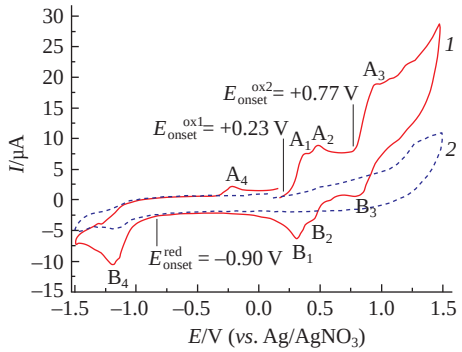
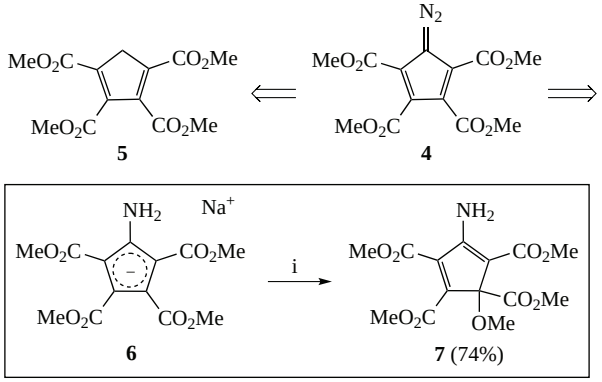


Figure 2 Cyclic voltammetry curves for (*1*) 2 mM solution of IDTT-HC2P **1** and (*2*) 0.1 M Bu_4NPF_6 in CH_2Cl_2 as supporting electrolyte.



Scheme 2 *Reagents and conditions*: i, isoamyl nitrite, TFA, MeOH.

Diazo reactant **3** was obtained from 1,3-dimethoxycarbonyl-4,5-diphenylcyclopentadienone according to our previously developed procedure.[18] On the other hand, diazotetrakis(methoxycarbonyl)cyclopentadiene **4** (Scheme 2) looks more attractive since its four ester groups can provide better photovoltaic properties.[20] The former approach is not appropriate for the synthesis of **4** as the corresponding cyclopentadienone is hardly available. Two other approaches *via* either diazo transfer onto the corresponding cyclopentadiene **5** or diazotization of the corresponding amine **6** are worth to consider. However, attempted preparation of compound **5** *via* the reported decarboxylation of pentakis(methoxycarbonyl)-cyclopentadienyl potassium[23] proceeded with very low conversions.[24] The reaction of aminocyclopentadienyl sodium **6**[25] with isoamyl nitrite in methanol in an acidic medium gave 5-methoxy-3-aminocyclopentadiene derivative **7** which arised from oxidation of amine and addition of methanol to the substrate. Other conditions for the nitrosation turned out to be non-selective.

In conclusion, we have synthesized a novel derivative of indacenodithienothiophene with cyclic hydrazinylidene acceptor moieties by the reaction of dilithiated indacenodithienothiophene with the corresponding diazocyclopentadiene. The new dye, whose optical and electrochemical properties were estimated herein, demonstrated potential in photovoltaic applications.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.032.

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