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Synthesis, optoelectronic properties and third-order nonlinear optical behaviors of the functionalized acene derivatives

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ABSTRACT

In this work, a novel malononitrile-modified acene 2-(2,7-di-*tert*-butyl-9,17-diphenyl-15H-dibenzo[*hi*,*mn*]indeno[1,2-*b*]tetracen-15-ylidene) malononitrile (**DITAM**) has been synthesized and characterized. Its single crystal X-ray analysis shows that **DITAM** features an antiparallel configuration and has a cis-form in the packing model, which is different from its analogue 2,7-di-*tert*-butyl-9,17-diphenyl-15H-dibenzo[*hi*,*mn*]indeno[1,2-*b*]tetracene (**DITA**). In comparison with UV–vis absorption and fluorescence spectra in different solvents of compounds **DITAM**, **DITAO**, and **DITA**, molecule **DITAM** displays the strongest salvation, inferring that ICT occurs in the excited state. Electrochemical results combined with the theoretical calculation illustrate that the malononitrile unit can effectively lower the LUMO energy level. The third-order nonlinear optical behaviors of the as-prepared compounds were investigated in a comparative manner, where **DITAM** exhibited the best optical nonlinear performance.

1. Introduction

In recent years, considerable efforts have been dedicated to develop novel organic π-conjugated compounds for second- and multi-order nonlinear optics (NLO) because these materials exhibited potential civilian use and military applications including ultrafast optical communication, optical limiting, data storage and processing, optical switching [1–12]. Among them, third-order nonlinear optical material is one that has been received a growing interest, where the resulting two-photon absorption derived from the third-order NLO has been realized as a crucial platform in many aspects such as photodynamic therapy, biomolecular detection and energy up-conversion [13–15]. Benefiting from ease of synthesis, controllable optical properties, especially disclosing the structure-performance relationship in single crystal, organic materials play a vital role over inorganic counterparts. In general, the donor-π-acceptor (D-π-A) molecules have been designed and synthesized for NLO materials because these structural motifs might be in favor of the charge separation and form a large dipole moment upon excitation, which can enhance nonlinear refractive index. For example, Marks et al. described a new concept, tictoid chromophore, in which the resulting twisted configuration through molecular control could decrease π-conjugation to a certain extent. The as-obtained π-systems exhibited excellent third order NLO responses [16–19]. Subsequently, Reynolds and co-workers prepared a series of D (thiophene)-A (pyridine) systems having small energy gaps that displayed resonance-enhanced third-order nonlinear responses [20]. More recently, Nakano predicted that the asymmetric acene analogue modified with the five-membered and seven-membered rings at the terminal to replace the traditional benzene rings in pentacene featured the largest hyperpolarizability by using spin-unrestricted density functional theory [21]. These advances motivate us to prepare novel organic semiconductors and investigate their third-order NLO.

In the search for novel organic materials for NLO, small molecules have become leading candidates because they could be utilized as active candidates in organic devices such as organic light-emitting diodes, organic field-effect transistors, organic photovoltaics, and memory devices. Currently, acenes and their corresponding derivatives have aroused more interest due to the fundamental theoretical prediction and technological application [22–30]. For example, the as-prepared hexacene platelet-shaped crystals were enough stable in the dark under ambient conditions and the hole mobility of the fabricated FET based on the crystals could approach to 4.28 $cm^2 V^{-1} s^{-1}$ with an on/off ratio of 1×10^5 [31]. More interestingly, defined by Pascal, the introduction of end-capping phenanthrene and lateral phenyl groups could form twisted acenes, which enhanced stability to a great extent [32]. Following this direction, Wudl, Zhang, Xiao and co-workers have prepared a family of twistacenes and

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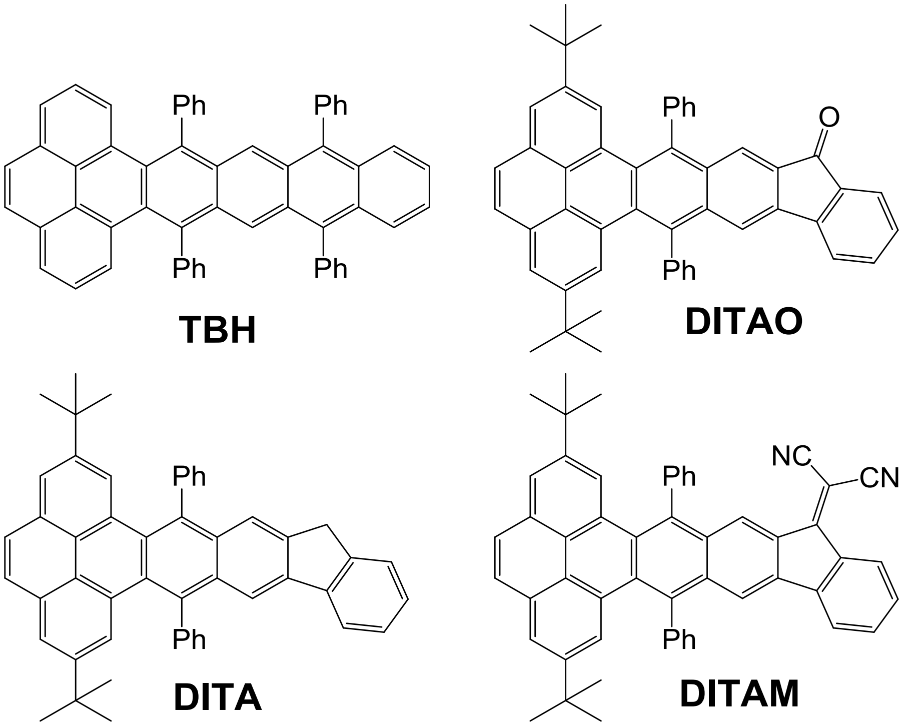

Scheme 1. Chemical structures of **TBH**, **DITA**, **DITAO** and **DITAM**.

heterotwistacenes incorporated with pyrene unit at the terminal that effectively suppressed intermolecular π-π stacking, and these materials showed appealing electroluminescent performance [33–50]. In addition, the small twistacene-functionalized three dimensional dendrimers self-assembled into multicolor nanoparticles with low cytotoxicity and good photostability that could be witnessed for the feasibility and efficiency in cell fluorescence imaging [51]. More recently, four unsymmetrical twistacenes fused with naphthalene, anthracene, pyrene and phenanthrene units through five-membered ring were synthesized, which showed promising third-order absorption effects [52]. In our lab, we have further synthesized three spindle-type conjugated compounds linked through ethylene, acetylene and double acetylene, in which the systematic investigation suggested that the dimer linked with the double acetylene group could be used for ultrafast broadband optical limiting [53].

In the continuous work, a new malononitrile-grafted acene derivative 2-(2,7-di-*tert*-butyl-9,17-diphenyl-15H-dibenzo[*hi,mn*]indeno[1,2-*b*]tetracen-15-ylidene) malononitrile (**DITAM**) was designed and synthesized (Scheme 1). Its analogues, 2,7-di-*tert*-butyl-9,17-diphenyl-15H-dibenzo[*hi,mn*]indeno[1,2-*b*]tetracene (**DITA**) and 2,7-di-*tert*-butyl-9,17-diphenyl-15H-dibenzo[*hi,mn*]indeno[1,2-*b*]tetracen-15-one (**DITAO**) were re-prepared according to the reported method [46]. Compared to molecule 5,7,14,16-tetraphenyl-8:9,12:13-bisbenzohexatwistacene (**TBH**), the five-membered ring is inserted into the parent backbone of twistacene in **DITA** [37]. The disrupted conjugation in **DITA** makes its absorption and emission spectra blue-shift. Note that the UV–vis absorption and fluorescence spectra red-shift with the increase of the electron-withdrawing ability from **DITA** to **DITAO**, then to **DITAM**. Electrochemical data and the theoretical calculation reveal that the malononitrile unit can effectively lower the LUMO energy level. The third-order nonlinear optical behaviors of the as-prepared compounds were investigated in principle.

2. Experimental

2.1. Synthesis of 2-(2,7-di-tert-butyl-9,17-diphenyl-15H-dibenzo[hi,mn]indeno[1,2-b]tetracen-15-ylidene)malononitrile (DITAM)

$TiCl_4$ (400 μL, 3.6 mmol) and dry pyridine (724 μL, 9.0 mmol) were successively added to a mixture of **TITAO** (120 mg, 0.18 mmol) and malononitrile (595 mg, 9.0 mmol) in anhydrous chloroform (50 mL) under nitrogen. The as-formed solution was refluxed for 36 h. During the procedure, the same amounts of malononitrile, pyridine, and $TiCl_4$ were added. After cooling to room temperature, brine was added. The mixture was extracted with dichloromethane (40 mL × 3). The collected organic phase was dried with Na_2SO_4 and removed in reduced pressure. The crude residue was further purified with PE/CH_2Cl_2 (v/v, 5:1) to afford **DITAM** as a red solid (80 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 9.03 (s, 1H), 8.46 (d, J = 7.8 Hz, 1H), 8.19 (s, 1H), 8.16 (s, 1H), 7.91 (t, 5H), 7.61–7.49 (m, 12H), 7.35 (t, ^1J = 7.8 Hz, ^2J = 7.2 Hz, 1H), 1.13 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ = 160.8, 147.7, 147.4, 142.9, 141.9, 141.3, 139.6, 137.0, 136.20, 136.15, 134.6, 134.2, 134.1, 132.4, 132.1, 131.9, 131.8, 131.7, 130.43, 130.41, 130.0, 129.5, 129.2, 129.1, 128.93, 128.89, 128.2, 128.0, 127.9, 127.5, 127.1, 127.0, 126.7, 124.3, 123.9, 123.4, 122.9, 121.3, 118.3, 114.2, 113.6, 73.3, 34.85, 34.82, 31.4. MALDI-TOF: (*m/z*) calcd for $C_{54}H_{40}N_2$ 716.3; found 716.2. HR-MS: Calc. for $C_{50}H_{40}N_2$ [*m/z*], 716.3191; Found, 716.3184.

2.2. Z-scan experiments

A femtoseconds laser system (Phros SP, Light Conversion) is used to pump an optical parametric amplifier (Orpheus, Light Conversion), which is employed as the laser source of Z-scan. The incident pulse has 190 fs pulse width and the output wavelength could be tuned from UV to near-infrared. Sample is placed on a translation stage that moves along the Z direction. Energy probes are used to monitor the energy change of the transmitting pulses. Both the stage and energy meter are connected to a computer and controlled by software.

3. Results and discussion

3.1. Synthesis

The synthesis of **DITAM** is outlined in Scheme 2. The target molecule was conveniently obtained in 62% yield through a simple condensation reaction between **DITAO** and malononitrile in the presence of $TiCl_4$/