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A facile synthesis of 2,3,6,7-tetrabromonaphthalene diimides toward new π -extended naphthalene diimides

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Core-substituted naphthalene diimides (cNDIs) are rapidly emerging as a class of π -functional molecules, which have been widely used in supramolecular chemistry, chemical/biological sensors, artificial photosystems, anion transport, and organic semiconducting devices.¹ cNDIs can be mainly divided into disubstituted compounds and tetrasubstituted ones. 2,3,6,7-tetrabromonaphthalene diimides (TBNDIs) are the key precursors of the synthesis of tetrasubstituted cNDIs.² As shown in Scheme 1, a synthetic method for TBNDIs by a dehydrohalogenation-based imidization reaction should be highlighted,^{2a} which significantly enhanced the development of π -extended NDIs.³ However, this synthetic procedure is relatively complex, because two different solvents (acetic acid and toluene) were respectively used at high temperature (>100 °C) and the crude intermediate product should be separated from the reaction mixture in the first step.^{2a} Herein, we present an improved synthetic method for TBNDIs, where only one solvent (such as CH₂Cl₂ or THF) is used at low temperature (<50 °C) without isolating the intermediate product. Using this modified synthetic method (Scheme 2), N,N'-bis(n-octyl)-TBNDI (2)^{2a} was achieved in 72% yield from the starting material 2,3,6,7-tetrab-

romonaphthalene dianhydride (TBNDA),² and this yield is much higher than that obtained by the old synthetic method (about 31.4%).^{2a} The nucleophilic aromatic substitution (S_NAr) reaction of **2** with potassium cyanocarbonimidodithioate⁴ in THF afforded

ABSTRACT

A 2,3,6,7-tetrabromonaphthalene diimide (**2**) was readily synthesized in high yield from 2,3,6,7-tetrabromonaphthalene dianhydride by an improved dehydrohalogenation-based imidization reaction. The further nucleophilic aromatic substitution (S_NAr) reaction of **2** with potassium cyanocarbonimidodithioate afforded a new π -extended naphthalene diimide (**1**), which exhibits n-type behavior in organic transistors and interesting response to F⁻ among halide anions in solutions.

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a new NDI derivative fused with two (1,3-dithiol-2-ylidene)cyanamide groups (Scheme 2, **1**), namely, NDI-DTYC2, in 64% yield. Herein, we introduce =N-CN moiety as the terminal group, which was widely used as organic acceptors for organic conductors and optoelectronic application.⁵ The introduction of =N-CN group allows for the following points: (1) this introduction was easily performed through simple S_NAr reaction and thus caters to the low cost organic electronics; (2) in comparison with its NDI-DTYM2 analogue,^{3b,c} the slightly smaller π -conjugated core endows NDI-DTYC2 derivative better solubility; (3) the strong electron-withdrawing ability of the =N-CN group could reduce the LUMO level of the molecule for realizing efficient electron injection and air-stable electron transport; (4) the =N-CN moiety is more prone to achieve coplanar π -systems relative to the =C(CN)₂ group.^{5a}



Scheme 1. Synthesis of TBNDIs.^{2a}





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Scheme 2. Synthesis of a π -extended naphthalene diimide (1).

NDI-DTYC2 (1) was characterized by ¹H NMR, MS, elemental analysis, and IR spectrum. In the IR spectrum, the peak at 2193 is assigned to the stretching vibrations of the terminal cyano moieties of **1**. To estimate the position and energies of frontier orbitals of **1**, Density Functional Theory (DFT) calculations were performed using the Gaussian 03 program at the B3LYP/6-31G(d) level. The model molecule of NDI-DTYC2, where *N*-*n*-octyl chains were replaced by *N*-methyl groups, has a rigid and entirely coplanar π conjugated backbone (Fig. S1). As shown in Figure 1, the coefficients of the HOMO orbital are delocalized throughout the central naphthalene skeleton and two lateral DTYC moieties while the coefficients of the LUMO orbital are mainly focused on the parent NDI core. The HOMO and LUMO energies of NDI-DTYC2 estimated by the DFT method are -7.0 and -4.3 eV, respectively, with the HOMO-LUMO gap of 2.7 eV. In comparison with the frontier orbitals of unsubstituted NDI (HOMO: -7.0 eV, LUMO: -3.4 eV and HOMO-LUMO gap: 3.6 eV),^{2a} NDI-DTYC2 has an almost unchanged HOMO level, a much lower LUMO level and a narrower HOMO-LUMO gap.

TGA analysis shows that the thermolysis onset temperature for 1 is 382 °C (Fig. S2), indicating that 1 has enough thermal stability for its application in thin film devices. The absorption spectra of 1 in CH₂Cl₂ solution and in thin film are shown in Figure S3. The maximum end absorption of 1 in CH_2Cl_2 is at about 512 nm, with the optical energy gap of 2.4 eV, which is comparable to the DFT calculated value (2.7 eV). In thin film, this maximum end absorption of **1** becomes a broad and red-shift absorption, with the optical energy gap of 2.2 eV, implying the formation of π - π stacking and/ or J-type aggregation in the solid state.⁶ As shown in Figure S4, 1 exhibits two reversible reduction processes in CH₂Cl₂, 1/1;⁻ and **1**^{·-}/**1**²⁻, the first and second half-wave potentials $(E_{red1}^{1/2})$ and $(E_{red2}^{1/2})$, vs SCE) are at about -0.13 and -0.64 V, respectively. **1** has a deep LUMO level of -4.31 eV estimated by the electrochemical results using ferrocene (-4.8 eV to vacuum) as an internal standard,⁷ which is well consistent with the DFT calculated value (-4.3 eV) and meets a key condition of ambient-stable electron injection and transport in organic transistors.⁸

The electron-transporting property of **1** was studied by fabricating and testing their vacuum-deposited organic thin film transistors (OTFT) (see Supplementary data for details). All devices displayed n-type behaviors in air. As shown in Figure 2, an OTFT based on **1** gives an electron mobility of $0.012 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a threshold voltage of 5 V and a current on/off ratio of 10^5 , demonstrating its good electron-transporting property. One sharp reflection was observed in the XRD plot of thin film of **1** (Fig. S5), indicating the formation of thin-film crystalline on the substrate. AFM image of thin film of **1** exhibits a generally rough morphology with a small grain size and a large density of grain boundaries (Fig. S6), which might explain the relatively low electron mobility of **1**-based devices (about $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The device performance of **1** should be much enhanced when the thin film morphology was improved.



Figure 1. HOMO orbital (left) and LUMO orbital (right) of a model molecule for NDI-DTYC2, obtained by DFT calculations.



Figure 2. Output (a) and transfer (b) plots of an OTFT device based on 1.



Figure 3. Colourimetric changes of **1** (30 μM in CH₂Cl₂) toward halide anions as their TBA salts: (a) no anion, 5 equiv of F⁻, 30 equiv of Cl⁻, Br⁻, and l⁻, respectively; (c) 0, 1, 2, 5, 10, 15, and 30 equiv of F⁻, respectively. (b) Spectroscopic responses of **1** to F⁻, Cl⁻, Br⁻, and l⁻. (d) UV-vis titration of **1** with F⁻ (0–30 equiv).

In addition, due to its strong π -acidity (LUMO: -4.3 eV), we envision that 1 might be a promising anion receptor, and the interactions between halogen anions and 1 were explored. As shown in Figure 3a and S7a, using 1 in CH₂Cl₂ and o-dichlorobenzene, F⁻ anions could be detected by naked eyes from other halide anions. UV-vis spectroscopy was conducted to guantify the F⁻-induced colorimetric change of 1. As depicted in Figure 3d and S8b, upon the addition of Bu₄NF from 0 to 30 equiv, the intensity of the band at about 512 nm was steadily decreased with the appearance of four enhanced new peaks at around 568, 616, 708, and 790 nm, respectively. The electrochemical reduction of **1** in CH₂Cl₂ was applied at V = -149 mV versus Ag/AgCl (the first reductive potential of **1**). The electrochemical generated **1**^{.-} radical anions displayed a new weak absorption band at 790 nm (Fig. S9), with the similar peak shape to those generated by F⁻ (Figure 3, S7 and S8), suggesting the addition of F⁻ contributed to the formation of 1^{-} radical anions. The evident EPR signal generated by 1 in the presence of F^- (Fig. S10, g = 2.003) further confirmed the formation of paramagnetic **1**^{.-} radical anions. Since the electron transfer from F^- to NDI is so difficult and unintelligible,⁹ the mechanism of this $1 \rightarrow 1^{-}$ transformation is still unclear and needs further studying.

In conclusion, we present a facile synthesis of TBNDIs, and this synthetic method would promote the development of π -extended NDIs. Accordingly, a new π -extended NDI, NDI-DTYC2 (**1**), is readily synthesized in high yield. The **1**-based OTFT gave an electron mobility of about 0.012 cm² V⁻¹ s⁻¹ in air, demonstrating its good electron-transporting property. The responses of **1** to halide anions were also studied. F⁻ could be detected by naked eyes from other halide anions with **1** in some organic solvents, rendering the color change from yellow to lilac due to the formation of **1**⁻⁻ radical anions.

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Supplementary data

Supplementary data (including details of experimental procedures, synthesis and characterizations of **1** and **2**, solution investigations, and additional data or spectra) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.tetlet.2013.02.075.

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