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Synthesis of tetraalkyl naphthalene bisanhydride and its model condensations with amines

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Currently, synthesis of new n-type (electron-transporting) organic semiconductors is an essential work in the field of organic electronics, because there are only a limited number of efficient organics that show high electron mobility and good air stability.¹⁻⁶ Among them, poly(benzobisimidazobenzophen-anthroline) (BBL) is of significant research interest.⁷⁻¹¹ BBL, as shown in Figure 1, is a ladder conjugated polymer featuring rigid two-dimensional planar ribbon-pattern framework. BBL not only has excellent mechanical and chemical stability, thermostability and photostability and so on, but also exhibits high electron mobility because its π -electrons can effectively delocalize along the polymeric conjugated main chain. Its glass-transition temperature is above 500 °C. Its n-type conductivity is high up to 0.01–100 S/cm and its electron affinity (EA) value (\sim 4.0 eV) is the highest among the known n-type conducting polymers.⁸ Recently, **BBL** has been combined with poly(phenylene vinylene) (**PPV**) to form a p-n heterojunction which shows good photovoltaic property with power conversion efficiency up to 2%.9 Although the large, rigid, and planar conjugation framework endues BBL unique properties and great potential of application, it also makes BBL insoluble in common solvents, which not only causes structural defects, but also is problematic for characterization and processing.¹⁰ BBL can be dissolved and processed only under very strong acidic conditions which are intolerable or incompatible for most other common materials used in electronics.¹¹ Obviously, the poor solubility is an important issue needing to be addressed before that BBL getting

ABSTRACT

To improve the solubility of naphthalene bisanhydride (**NTCA**), four alkyl groups are incorporated to the naphthalene core via a five-step procedure. The new naphthalene bisanhydride derivative (**TO-NTCA**) shows much higher reactivity than the parent **NTCA** in the model condensations with *ortho*-diaminobenzene and 2-ethylhexylamine and gives corresponding soluble molecules with excellent yields. Hence, **TO-NTCA** is a potential monomer for condensations.

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more widespread applications. However, the attempts to improve **BBL**'s solubility via chemical modifications were seldom reported.

On account of **BBL**'s various good performances, our group directs the efforts toward improving its solubility while without considerable influence of its electronic properties. As shown in Figure 1, two key monomers for **BBL** are 1,2,4,5-tetraaminobenzene (**TAB**) and 1,4,5,8-naphthalenete tracarboxylic bisanhydride (**NTCA**). Therefore, it is easy to come up with an idea of some modifications on the two monomers. Actually, we had already synthesized 2,3,6,7-Tetraamino-9,9-bis(2-ethylhexyl)fluorene (**TABEF**), and investigated the model condensation reaction of **TABEF** with naphthalene dicarboxylic anhydride.¹²

Herein, as a part of our continuous work, we report our new attempt on the modification of the other monomer **NTCA**. 2,3,6,7-Tetraoctyl-1,4,5,8-naphthalene tetracarboxylic bisanhydride (**TO-NTCA**) is designed as a versatile monomer for conjugated ladder polymers/molecules. In our design concept, firstly, a reserved naphthalene core ensures the large π -conjugated backbone into a **BBL**-like framework which will lead excellent stability and fine n-channel conductivity. Secondly, the introduction of alkyl chain to naphthalene core of **NTCA** will bring improvement of solubility.



Figure 1. Synthesis of ladder conjugated polymer BBL.



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Scheme 1. Synthesis of TO-NTCA.

As shown in Scheme 1, TO-NTCA was efficiently synthesized via a five-step procedure with an overall yield of 30%. Firstly, bromination of naphthalene tetracarboxylic bisanhydride (NTCA) with N,N'-dibromoisocyanuric acid (DBI) gave 2,3,6,7-tetrabromonaphthalene tetracarboxylic bisanhydride (Compound **2**) with a yield of 93% according to the literature.¹³ Then, compound 2 was esterified with n-bromobutane to give compound **3** with a yield of 97%. Subsequently, the Stille coupling reaction of compound **3** with 1octvnvltributvlstannane gave compound **4** with a vield of 35%. With Raney nickel as the catalyst, compound 4 was hydrogenized to give compound 5 with a yield of 97.6%. Finally, compound 5 was hydrolyzed to give compound 6 (TO-NTCA) with an excellent yield of 94.6% with para-toluenesulfonic acid as the solvent. Each step of the above route was very effective except the Stille coupling reaction (step III) with a moderate yield of 35%. Due to the strong electron-deficiency of compound **3** containing four carboxylate groups, the major side reaction of dehalogenation under palladium catalysis exhibited a strong tendency.

In our synthesis, there were two key strategies. One was the utilization of naphthalene tetracarboxylic esters as intermediates, considering that the esters have good solubility and suitable polarity to facilitate the reactions and purifications, and more importantly, the esters could be hydrolyzed under mild conditions to generate the corresponding bisanhydride readily.

The other key was the indirect alkylation method involving Stille coupling reaction to introduce alkynyl groups which was followed by hydrogenization of alkynyl to form alkyl groups. As shown in Scheme 2, we tried Negishi and Sonogashira coupling reactions, but both failed to produce target molecules with satisfactory yields. It might be caused by the redox effect between electron-rich alkylzinc reagent and electron-deficient compound **3** in Negishi reaction. Besides, we reasoned that the presence of basic agents required in Sonogashira reaction caused severe debromination and partly ester hydrolysis. Consequently, even if Stille coupling reaction which we adopted finally still needs improvement in terms of the yield, it was the acceptable one among the synthetic strategies discussed above.



Scheme 2. Unsuccessful alkylation methods ever tried.

Next, two model reactions were carried out to test the reactivity of **TO-NTCA**, in order to preliminarily evaluate **TO-NTCA**'s potential as a monomer for the synthesis of **BBL**-analog ladder conjugated polymers. As shown in Scheme 3, **TO-NTCA** underwent condensation with *ortho*-diaminobenzene smoothly in propionic acid, and gave isomers 2,3,6,7-tetraoctyl-1,4,5,8-naphthalene tetracarboxylic bis(benzimidazole) (**TO-NTCBI**: mixture of two isomers) with a yield of 100%. It was impossible to isolate the two isomers via column chromatography or recrystalization. High performance liquid chromatography (HPLC) measurement showed that their retention times were extremely close (Supplementary data). In another model reaction, **TO-NTCA** and 2-ethylhexylamine were condensed to generate the bisimides **TO-NTCI** as the only product with an



Scheme 3. Synthesis of model compounds and their analogs.

excellent yield of 92%. Thus, the high reactivity of TO-NTCA in condensations had been demonstrated. By contrast, under the same reaction conditions, the condensation of NTCA and ortho-diaminobenzene was not so satisfactory. The yield of corresponding product, bis(benzimidazole) NTCBI was just moderate. Thin layer chromatography indicated that in the condensation of NTCA with ortho-diaminobenzene, many by-products were generated. We speculate that NTCA without solubilization group, the monocondensation intermediates are easily precipitated, and as a result, the second condensation will be hampered steeply. The problematic condensations of NTCA decide that there are structural defects of BBL which was prepared formerly. TO-NTCA has no problem related to solubility. Through the above comparison, we can draw the conclusion that TO-NTCA is an ideal multifunctional monomer and it works much better than NTCA for condensations with amines. So, it is reasonable to predict that TO-NTCA can also successfully condense with any other aromatic tetraamino-type multifunctional monomers, such as **TAB** and **TABEF** to give corresponding conjugated ladder polymer analog of **BBL**. It is worth mentioning that **TO-NTCBI** from model reaction have good solubility in common solvents, such as *ortho*-dichlorobenzene (20 mg/mL at room temperature and over 35 mg/mL at 50 °C). Therefore, we predict that **TO-NTCA**-based **BBL** analogs will have better solubility than **BBL**.

Although there are plenty of core substituted naphthalene diimides (NDIs) ever reported,^{13–18,21} they usually derive from a few kinds of precursors of naphthalene tetracarboxylic bisanhydride, namely, 2-chloro-naphthalene bisanhydride, 2,6-dichloronaphthalene bisanhydride, mono-, di-, tri-, tetra-, bromo substituted naphthalene tetracarboxylic bisanhydride and their derivatives 2,3,6,7-tetrathienylnaphthalene bisanhydride as well as, 2perfluorooctvlnaphthalene bisanhvdride. 2.6-diperfluorooctvlnaphthalene bisanhydride previously developed by our research group.¹⁶ In fact, these core-substituted naphthalene tetracarboxylic bisanhydride often show not so satisfactory reactivity, especially for those core halogen substituted naphthalene tetracarboxylic bisanhydrides which usually need a two-step procedure to prepare corresponding NDIs and give moderate yields. For example, Gao et al. reported their work about preparation of 2.3.6.7-tetrabromonaphthalene diimide using tetrabromonaphthalene tetracarboxylic bisanhydride with an unsatisfactory yield of 30%;¹⁷ Krüger et al. also reported their work about preparation of 2,3,6,7-tetrathienylnaphthalene diimide using tetrathienylnaphthalene tetracarboxylic bisanhydride with a moderate yield of 35%.¹⁸ By contrast, 2,3,6,7-tetraoctylnaphthalene tetracarboxylic bisanhydride in this work showed high reactivity in condensations with both 2-ethylhexylamine and ortho-diaminobenzene, and the yields were 92% and 100%, respectively. Besides, derivatives of benzimidazole are rarely reported due to their poor solubility in organic solvents.^{19,20} And for the same reason, this class of molecules is usually hard to be clearly characterized and is hampered for further research. It is worth noting that our model molecules of **TO-NTCBI** show good solubility in dichlorobenzene even at room temperature.

In order to find out how the four octyls affect the electronic properties, the fundamental spectral and electrochemical properties of the model compounds were investigated. The spectra are recorded in Figure 2, and the corresponding data are listed in Table 1. The absorption and emission maxima of **TO-NTCI** showed small redshifts of 8 and 24 nm, respectively, relative to **NTCI**, indicating that they have similar energy gaps (E_{0-0}). The difference of E_{0-0} is



Figure 2. UV-vis absorption (left) and fluorescence emission (right) spectra of NTCI, TO-NTCI, and TO-NTCBI in CHCl₃.

Table 1			
UV-vis absorption and fluorescence emission	properties of NTCI,	TO-NTCI, and	TO-NTCBI in CHCl3

	λ_1^a (nm)	$\epsilon_1^{a} (M^{-1} cm^{-1})$	$\lambda_2^{\mathbf{b}}$ max (nm)	${\epsilon_2}^{\rm b} ({\rm M}^{-1} {\rm cm}^{-1})$	λ_3^{c} (nm)	$\epsilon_{3}^{c} (M^{-1} cm^{-1})$	$\lambda_{\rm em}$ (nm)	s ^d (nm)	${\Phi_{\mathrm{fl}}}^{e}$
TO-NTCBI	419	25 564	453	28 189	478	26 273	549	96	0.47
TO-NTCI	371	18 937	389	21 192	407	18 046	409 432	43	0.03
NTCI	361	20 586	381	25 771	/	/	388 408	27	0.02

^a The first absorption peaks and corresponding molar extinction coefficients.

^b The second absorption peaks and corresponding molar extinction coefficients.

^c The third absorption peaks and corresponding molar extinction coefficients.

^d Stoke shift.

^e Determined with quinine sulfate as reference.



Figure 3. CVs of NTCI (black), TO-NTCI (blue), and TO-NTCBI (red) measured in $CHCl_3$ of 0.1 M $TBAPF_6$ with a scan rate of 50 mV/s (Hg/Hg_2Cl_2) .

only 0.06 eV. As shown in Figure 3, the first reduction waves for **TO-NTCI** and **NTCI** were observed at -1.53 V versus Fc/Fc⁺ and -1.27 V versus Fc/Fc⁺, respectively, indicating that the introduction of four octyls results in a 0.26 eV elevation of LUMO energy le-

vel. There will be a clearer image of the fluctuation range of NDIs's LUMO energy level when considering some other common substitutes, such as chloro, bromo, cyano, alkoxyl, alkyl sulphanyl, alkyl amino, etc. In general, substitutes with electron-withdrawing ability will lead to decrease of LUMO energy level of molecules while those with electron-donating ability will result in increase of LUMO energy level.¹⁴ Thalacker et al. reported decline of LUMO energy level of **NDIs** by 0.15 eV for two chloro substituent groups and raise by 0.28 eV and 0.30 eV for two 4-tert-butylphenylamino substituent groups and two *n*-octylamino substituent groups respectively.²¹ Gao et al. also found a decrease of LUMO energy level by 0.31 eV after four bromo substituent groups were incorporated to the **NDIs** core.¹⁷ Furthermore, work of Röger et al. demonstrated that four ethyloxyl, ethyl sulphanyl, n-hexylamino substituent groups caused increases of LUMO energy level of four bromo substituted NDIs by 0.52 eV, 0.35 eV, 0.94 eV, respectively.¹³ In spite of a positive influence from halogens, NDIs with halogen substituent groups are more often used as precursors and intermediates for various coupling reactions as mentioned before. It is worth noting that alkyls exhibit excellent stability in common chemical environments since they bear no heteroatoms or functional groups. Besides, one of our design concepts is to enhance the solubility of **BBL** by developing monomers with good solubility while halogens and cyano on aromatic cores would not be competent to reduce strong π - π stack among them. Based on the discussion above, the overall performance seems to be acceptable after modifying the naphthalene bisimides core with four alkyl groups. Besides, the first reduction wave for **TO-NTCBI** was observed at -1.4 V versus Fc/Fc⁺, indicating its strong electron-accepting capability.

It is worth noting that previously reported spectral characteristics of **BBL** and **NTCBI** were measured in strong acidic solvent or



Figure 4. UV-vis absorption (left) and fluorescence emission (right) spectra of TO-NTCBI in CHCl₃ (red) and mixture of CHCl₃ and trifluoroacetic acid (TFA) (blue), respectively.

Lewis acid, where **BBL** and **NTCBI** were protonized, and thus, could not be taken as their intrinsic characteristics. Herein, as shown in Figure 4, we report the first measurement of **TO-NTCBI**'s spectral characteristics in organic solvent. **TO-NTCBI** showed broad emission band centered at 549 nm and it exhibited a high fluorescence quantum yield of 0.47. Besides, **TO-NTCBI** had a large stokes red shift of 96 nm. So, **TO-NTCBI** can be classified as an efficient fluorescent dye. As for **TO-NTCBI** in CHCl₃ with 10% equivalent trifluoroacetic acid (**TFA**) by volume, both UV–vis absorption intensity and fluorescence emission intensity dropped sharply with a fluorescence quantum yield of 0.11 compared with **TO-NTCBI** in pure CHCl₃.

In conclusion, we efficiently synthesized a tetraalkyl naphthalene tetracarboxylic bisanhydride via a five-step procedure and investigated its reactivity. In the model condensations, **TO-NTCA** readily underwent condensations with *ortho*-diaminobenzene and 2-ethylhexylamine to give corresponding soluble molecules with excellent yields. Therefore, we think it is a potential monomer for synthesis of soluble ladder conjugated polymers. This work on the synthesis of **TO-NTCA** lays a solid foundation for the future development of novel **BBL** analogs with ladder conjugated frameworks but enhanced solubility.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.04. 030.

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