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2,3,6,7-Tetraamino-9,9-bis(2-ethylhexyl)fluorene: New Multifunctional Monomer for Soluble Ladder-Conjugated Molecules and Polymers

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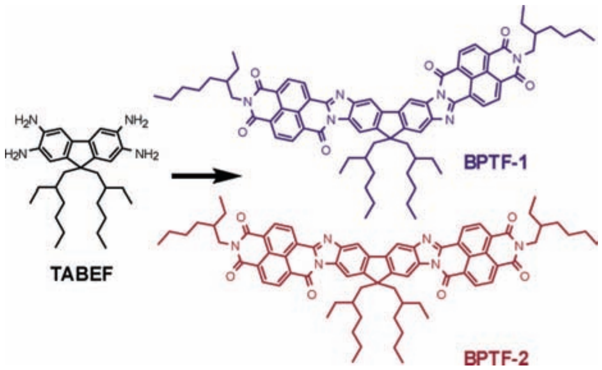
ABSTRACT



2,3,6,7-Tetraamino-9,9-bis(2-ethylhexyl)fluorene (TABEF), as a new multifunctional monomer for ladder-type conjugated molecules and polymers, was efficiently synthesized via a six-step procedure with an overall yield of 30%. Two isomeric ladder compounds based on TABEF building blocks were also synthesized and preliminarily studied.

Conjugated polymers, as typical organic semiconductors, play very important roles in the fields of OLED, solar cells, OFET, and organic solid lasers.[1] Among the vast conjugated polymer classes, most are linear, single-strand polymers, such as polyacetylene, poly(*p*-phenylene), polythiophene, etc., but ladder-type conjugated polymers[2–10] only take a very small portion. The rigid and planar frameworks of ladder-conjugated polymers facilitate electron delocalization and enhance conductivity, compared with linear polymers. Another advantage of ladder polymers is the high resistance to mechanical, thermal, and chemical degradation.[2]

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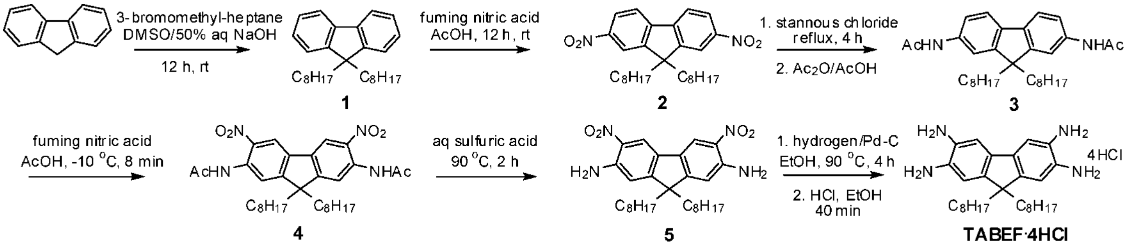
Scheme 1. Synthesis of **TABEF**



As a representative ladder-conjugated polymer, **BBL** (as shown in Scheme 1) has been extensively studied[3–5] and exhibits high n-type conductivity up to 0.01−100 S/cm and the highest electron affinity (EA) value (∼4.0 eV) among the known n-type conducting polymers.[4] In addition, it exhibits good photoconductivity and large nonlinear optical properties.[5] However, **BBL** and its analogues, such as **PQL**,[6] etc., have a problem with poor solubility, particularly in organic solvents. Poor solubility not only inhibits some characterizations and material processing but also causes structure defects which decrease the thermal, physical, and electrochemical properties.[7] As the key and versatile building block of **BBL**-like heteroaromatic ladder polymers, 1,2,4,5-tetraaminobenzene (**TAB**) contributes to such outstanding electronic and optical properties. However, it also causes poor solubility due to the absence of solubility-improving or aggregation-preventing substituents. To our knowledge, an alternative candidate for **TAB**, as a soluble multifunctional building block of n-type ladder polymers, has been little pursued. It has been noticed that the lack of highly conductive, air-stable, and solvent-processable n-type materials has become a bottleneck in the advancement of organic semiconductors. Thus, novel soluble **BBL** analogues will be very promising candidates.

On the other hand, an ideal combination of a rigid π-conjugation in the main chain with an optimal processability from common organic solution has been realized by ladder poly(*p*-phenylene) (**LPPP**)[8] and its analogs.[9] In these successful examples, the formation of 9,9-bissubstituted-fluorene structure is the dominant factor. The incorporation of a fluorene moiety is not restricted to the design of **LPPP** type materials, it has become a frequently adopted design component for high-efficient and solution-processable semiconductors.[10]

Herein, we designed 2,3,6,7-tetraamino-9,9-bis(2-ethylhexyl)fluorene (**TABEF**, as shown in Figure 1) as the multifuntional monomer for ladder-conjugated polymers/molecules. In our strategy, first, a maximum π-conjugated backbone into a rigid planar **BBL**-like skeleton endows the novel ladder materials with good n-channel conductivity and excellent stability. Second, bulky substituents at C-9 position ensure good solubility and, thus, processability of the corresponding ladder-type macromolecules;[11] the tetrahedral arrangement of the C-9 atom prevents the conjugated backbones from compact packing in the solid state by forcing the bulky and branched alkyl groups to assume an orthogonal disposition with respect to the fluorene plane and counteracts the aggregation trend induced by large planar structures. It is also worthwhile to note that the subtle equilibrium between the rigid large conjugated planar structure and the branched bulky side chain can help improve the material morphology and meliorate the efficiency of photoelectronic devices.[12]

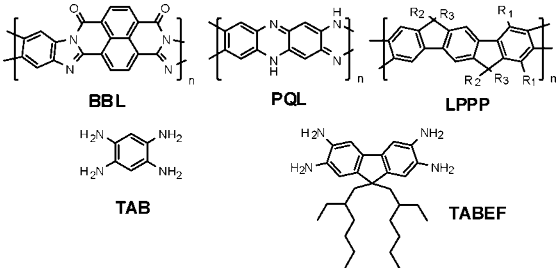


Figure 1. Molecular structures of **BBL**, **PQL**, **LPPP**, **TAB**, and **TABEF**.

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Although tetraaminofluorene without any substituents on the 9-position was synthesized in the 1960s,[13] this parent compound itself caused so little attention that the information available for the synthesis of its derivatives was scarce. It has also been found that not only some of the early synthetic conditions were not optimized but also some were inaccessible for 9,9-bisalkylfluorene derivatives, such as the nitration of 2,7-diacetamido-9,9-bisalkylfluorene. Therefore it is valuable and necessary to report a systematic synthetic route for 2,3,6,7-tetraamino-9,9-bisalkylfluorene.

As shown in Scheme 1, **TABEF** was successfully synthesized via a 6-step (actually 8 synthetic reactions, because both step 3 and 6 contained two continuous reaction operations) procedure. All the steps had satisfactory yields shown in Supporting Information. In our synthesis, the nitration of compound **3** with fuming nitric acid in glacial acetic acid gives binitro compound **4** with a yield of 91.4%. However, only a small amount of compound **4** could be obtained according to the reported nitration condition (fuming nitric acid in acetic anhydride)[14] of 2,7-diacetamidofluorene. In the final step, compound **5** was hydrogenized with Pd/C as the catalyst to yield **TABEF**, and in order to avoid oxidation, **TABEF** was immediately converted to the air-stable tetrahydrochloride (**TABEF•4HCl**) with good yield and high purity, by bubbling HCl gas into the ethanol solution of **TABEF**, which was an improvement different from conventional method.[15] In short, this six-step synthetic method from fluorene to **TABEF•4HCl** was efficient with a total yield of 30%.

In characterizing the above new fluorene derivatives, some results in the NMR spectra attracted our interest. For ^1H NMR spectra of compound **3**, **4**, and **TABEF•4HCl**, a triplet (1:2:1) signal is observed in aromatic region. Here we provide the proton assignment of compound **4** as a representative example, illustrated in Figure 2. Briefly, the HMBCGP spectrum (Supporting Information) indicates that such triplet resonance should be assigned to 1,8-protons because of its coupling signal with the 9-position carbon atom (center carbon on fluorene moiety), which is easily distinguished from other aliphatic carbon atoms. Although gCOSY spectra (Supporting Information) suggest a remote coupling effect between 1,8-protons and 4,6-protons, the ascription of such triplet resonance to remote coupling effect can be ruled out, since the *J* value is too large (16 Hz). We conclude that such a split results from three stable conformations constructed by a special steric effect: 1,8-protons are sandwiched in a very crowded region due to the steric hindrance from the rigid acetylamide and the giant isooctyl substituents on the 9-position. In particular, such steric interaction can be proved by the NOE spectrum (Supporting Information) in which a steric coupling effect between 1,8-protons and the methene protons is clearly observed. Another exceptional finding in the proton assignment for compound **4** is that triplet signal of 1,8-protons (with amide groups on ortho-positions) resonates at lower field than the singlet signal of 4,5-protons (with nitro groups on ortho-positions). Such resonance result contradicts theoretical conclusion. Futher explanation of this phenomenon can be a good subject for therotical chemists or NMR specialists and is beyond the scope of this letter. However, the above proton assignment provides important clues for the charcterazition of more complicated compounds derivated from **TABEF**.

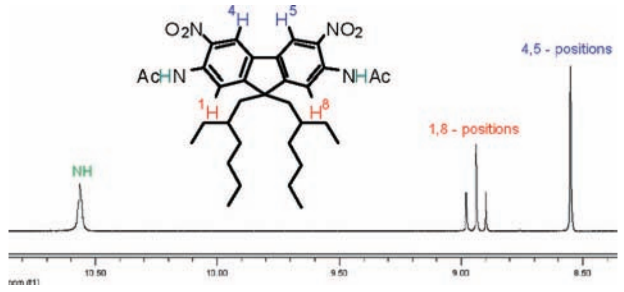
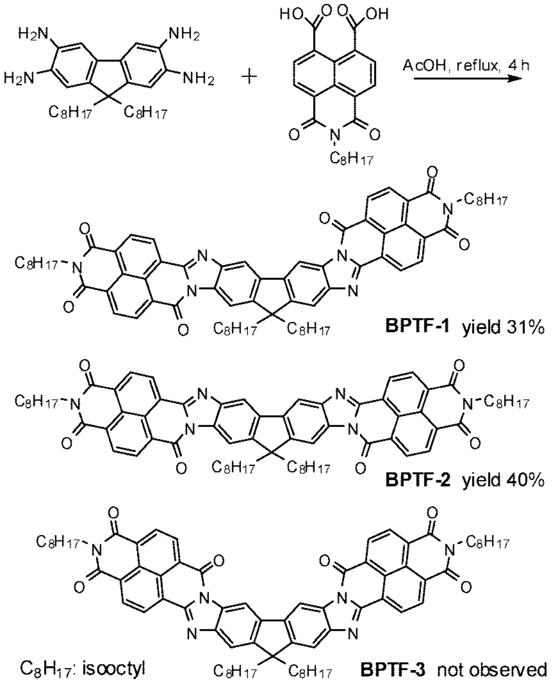


Figure 2. Aromatic region expanded ^1H NMR spectra of compound **4** in $CDCl_3$.

To preliminarily evaluate the potential of **TABEF** for the synthesis of **BBL**-analogue ladder polymers, 2-(2-ethylhexyl) isobutyl-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinoline-6,7-dicarboxylic acid as bifunctional substrate was chosen to undergo condensation reaction with **TABEF**, as shown in Scheme 2. Even under relatively mild conditions (reflux

Scheme 2. Synthesis of Model Compounds: **BPTF**



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in acetic acid), this model reaction processed readily. The products were obtained as a mixture of two isomeric ladder molecules (theoretically, there should be three regioisomers), which were successfully isolated via column chromatography. On the basis of the ratio of aromatic protons resonance integration to proton number and the sum of resonance of aromatic carbons in ^{13}C NMR, it is clearly demonstrated that one isomer has an unsymmetrical structure that is identified to be **BPTF-1**. Meanwhile the other isomer is symmetrical and shows a triplet signal at 8.92 ppm and a singlet peak signal at 7.98 ppm in its ^{1}H NMR spectra. The triplet peak resonates at lower field than the singlet peak, this is in accordance with the resonance result observed in compound **4** and indicates that imide groups are at the 2,7-positions rather than the 3,6-positions. Therefore, the structure of this isomer is identified as **BPTF-2**.

Since the above model reaction is highly efficient, we conjecture that **TABEF** can also favorably condense with aromatic tetraacid-type multifunctional monomers, such as 1,4,5,8-naphthalene tetraacid, perylene-3,4,9,10-tetracarboxylic dianhydride, etc., to give ladder conjugated polymers. It is also noticeable that the model compounds **BPTF-1** and **BPTF-2** have good solubility (over 20 mg/mL) in common solvents such as $CHCl_3$, toluene, and 1,2-dichlorobenzene, despite their large, rigid, and planar π-conjugation frameworks. Thus, we predict that **TABEF**-based ladder polymers will also have better solubility than **BBL**.

Preliminary study has indicated that the model compounds themselves have intriguing properties. As shown in Figure 3, **BPTF-1** and **BPTF-2** exhibit very strong absorption across a broad wavelength range. The ladder molecules show distinct red-shift of absorption maxima and significant increase in absorption intensity, compared with the counterpart compound **BIPT** with half of the conjugation length of these isomers. Voltammograms (Supporting Information) of **BPTF-1** and **BPTF-2** both exhibit two reversible reduction waves and one reversible oxidation wave. The first reduction waves for **BPTF-1** and **BPTF-2** are observed at -1.12 V vs Fc/Fc+ and -1.13 V vs Fc/Fc+, respectively. The LUMO values of the model compounds are low and nearly equal to the commonly used n-type naphthalene-1,4,5,8-tetracarboxylic dianhydride (**NDI-C8**) (-1.10 V vs Fc/Fc^{+}).[16] These features, in combination with good solubility, make **BPTF-1** and **BPTF-2** promising N-type materials for polymer solar cells.

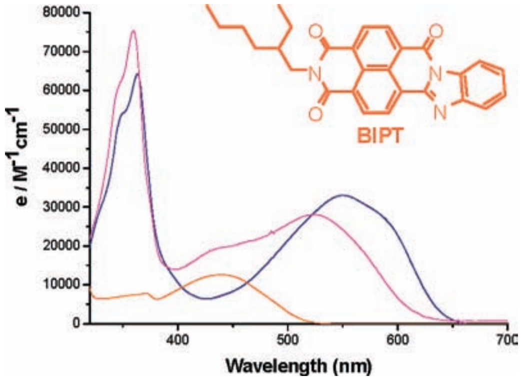

Figure 3. UV−vis absorption spectra of **BPTF-1** (magenta line), **BPTF-2** (blue line), and **BIPT** (orange line) in chloroform. Inset: the molecular structure of **BIPT**.

In conclusion, 2,3,6,7-tetraamino-9,9-bis(2-ethylhexyl)fluorene (**TABEF**) as a key multifunctional monomer for novel soluble ladder-conjugated polymers/molecules was efficiently synthesized. **TABEF** readily underwent a condensation reaction with dicarboxylic acid substrate to give corresponding ladder-type model compounds with good solubility. The development of other novel ladder-type conjugated molecules and polymers is currently being pursued.

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Supporting Information Available: Experimental procedures for all compounds, ^{1}H and ^{13}C NMR spectra for key compounds, and HMBCGP, gCOSY, and NOE spectra of compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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