First Tetrabutylanthradithiophene (TBADT) Derivatives for Solution-Processed Thin-Film Transistors

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Abstract: Three new solution-processable tetrabutylanthradithiophene (TBADT)-based organic semiconductors bearing two phenylethynyl, thiophen-2-ylethynyl, and thieno[3,2-*b*]thiophen-5-ylethynyl substituents have been synthesized and their thermal, optical, and electrochemical properties have been characterized. Preliminary tests of these compounds via drop-casting for thin-film transistors showed p-channel TFT transport with hole mobilities as high as 1.5×10^{-3} cm^2/Vs and with a current on/off ratio of 10^4.

Key words: organic semiconductor, organic thin-film transistor, anthradithiophene, solution process, pentacene

For the last decade, significant efforts have been focused on developing new organic semiconductors as components of organic thin-film transistors (OTFTs) for inexpensive, large-area electronics such as electronic papers, sensors, and smart textiles.[1,2] Pentacene (PEN),[3] anthradithiophene (ADT),[4] and fused thiophene[5] derivatives are among the most widely developed organic semiconductors. These small-molecule semiconductors, however, are not very soluble in common solvents, which limits their applicability in many high-throughput solution processes. Furthermore, photooxidation at the C-6/C-13 positions of the pentacene limits long-term stability.[6] Introducing substituents at the pentacene C-6/C-13 positions has proven to be effective at enhancing the stability of the pentacene framework, as well as improving carrier mobility.[7] Triisopropylsilylethynyl (TIPS)-substituted pentacene (TIPS-PEN; **A**; Figure 1) exhibited enhanced ambient stability compared to unsubstituted pentacene,[7b] while 4-pentylphenylethynyl-substituted pentacene (PPE-PEN; **C**) showed carrier mobility as high as 0.52 cm^2/Vs via extended π-electron delocalization between the pentacene core and the substituents.[7c] Similar approaches have been applied for ADT derivatives, and a solution processable p-channel triethylsilylethynyl ADT derivative (TES-ADT; **B**) with a mobility as high as 1.0 cm^2/Vs has been reported.[8] Recently, four solution-processable PEN and ADT derivatives (**D**–**G**) bearing phenylethynyl and triethylsilylphenylethynyl substituents have been reported.[9] Especially, compounds **F** and **G**, having peculiar 2-D ‘slipped-crossed’ stacking with a bulky triethylsilyl (TES) moiety appended to the phenylethynyl group, showed good TFT performance via drop-casting. All of these studies demonstrated that substituents on the PEN/ADT cores significantly affect the intermolecular stacking of the corresponding molecules and their electrical performance.[10]

In general, ADT-based compounds exhibit superior device performance and photooxidative stability under ambient conditions compared to PEN derivatives.[9] In our previous study, soluble PEN or ADT derivatives (**D**–**G**) accommodated the phenylethynyl substituents in the solid state by adopting a herringbone packing with small dihedral angles (ca. 10–20°) between the main core and the phenyl substituents.[9] To further decrease the dihedral angle and thereby enhance the intermolecular orbital overlap between the core and the substituents of the ADT derivative, thiophenyl (T-) and thieno[3,2-*b*]thiophenyl (TT) substituents have been introduced for the first time in this study. Compared to phenyl substituents, thiophenyl is less crowded and therefore more likely to adopt a decreased dihedral angle between the ADT core and the substituents. Furthermore, more highly conjugated thieno[3,2-*b*]thiophenyl substituents may enhance the molecular orbital overlap between the core and the substituents. Accordingly, phenylethynyl (PE), thiophen-2-ylethynyl (TE), and thieno[3,2-*b*]thiophen-5-ylethynyl (TTE) groups have been employed as core substituents for ADT derivatives (Figure 2). 2,8-Dialkylsubstituted ADT derivatives have been reported as thin-film transistors, but these are typically limited to vacuum deposited films.[4a] In order to further enhance the solubility of ADT derivatives for expanded applicability in solution processes, compounds with tetrabutyl groups at the 2-, 3-, 7-, and 8-positions of the ADT main core have been prepared for the first time in this contribution.[11] In brief, three new soluble tetrabutylanthradithiophenes (TBADTs **1**–**3**; Figure 2) have been synthesized and their thermal, optical, and electrochemical properties have been established. Thin films of all three compounds have been fabricated via drop-casting, and preliminary results indicate that these materials all exhibit p-channel OTFT transport with hole mobilities as high as ca. 1.5×10^{-3} cm^2/Vs.

The synthesis of three soluble TBADTs was achieved by a modification of established synthetic approaches toward PEN and ADT derivatives (Scheme 1).[9] Starting from two equivalents of 4,5-dibutylthiophene-2,3-dicarbaldehyde

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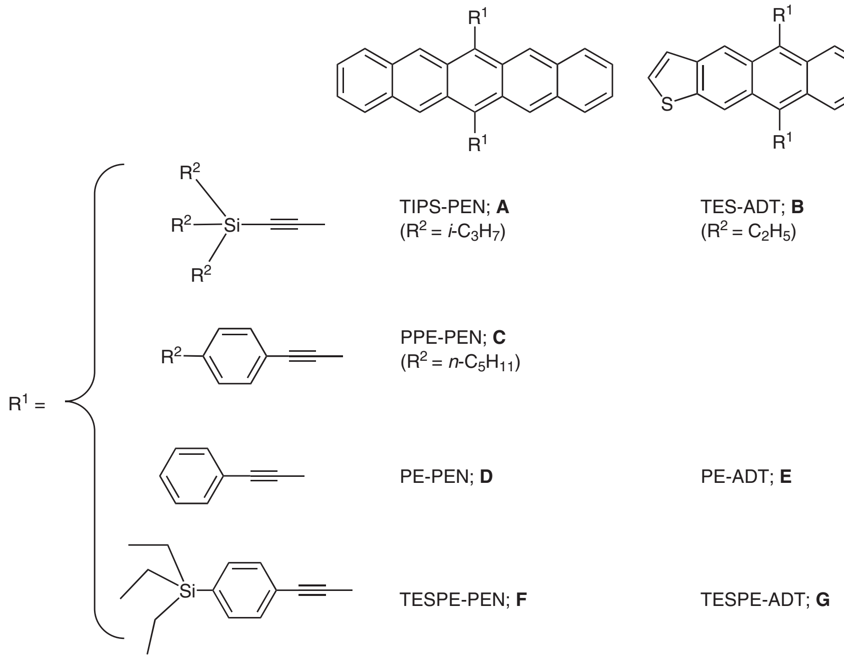


Figure 1 Examples of soluble PEN and ADT semiconductors used in OTFT

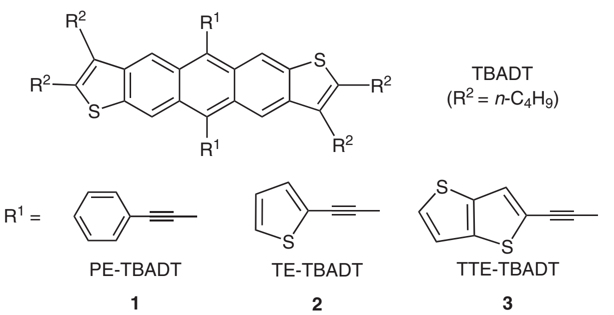
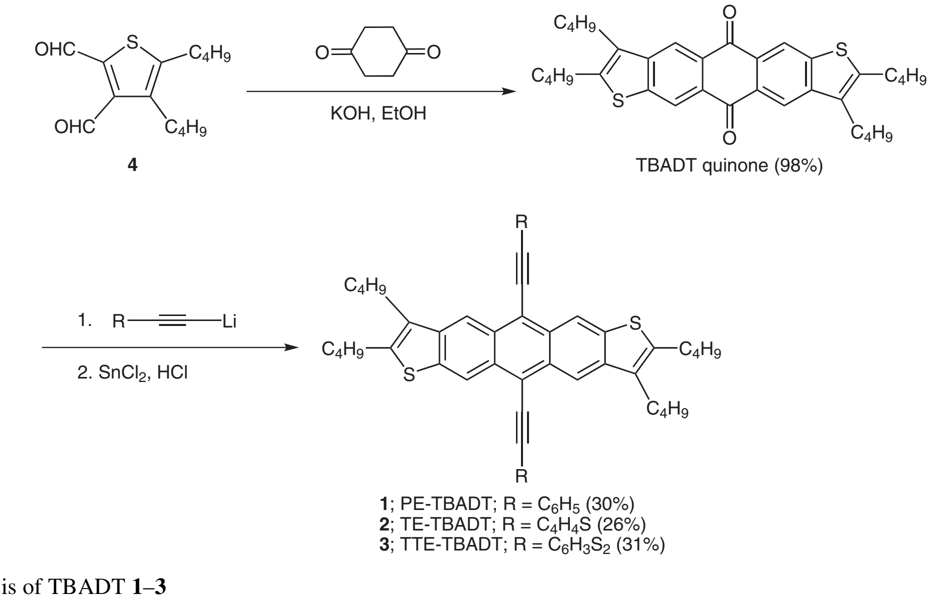


Figure 2 Chemical structures of new soluble tetrabutylanthradithiophene (TBADT) derivatives employed in this study.

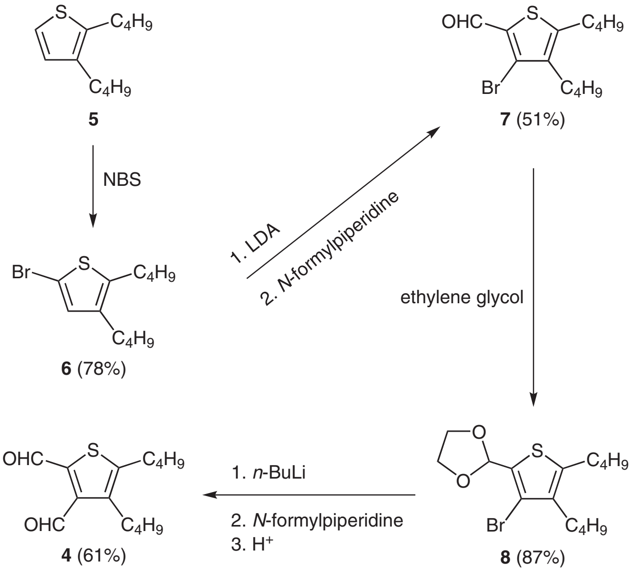
(**4**; Scheme 2), treatment with one equivalent of 1,4-cyclohexanedione in the presence of KOH, led to isolation of TBADT quinone in 98% yield. PE-substituted **1**, TE-substituted **2**, and TTE-substituted **3** were obtained via the corresponding ethynyl anion alkylation and $SnCl_2$/HCl reduction of TBADT quinone, in overall yields of ca. 30%.[4d] Of particular note, when isopropyl magnesium chloride was employed instead of *n*-butyllithium for the deprotonation of phenylacetylene, PE-TBADT (**1**) was obtained in only 9% yield.[7c] Compared to PE-ADT or PE-PEN, without substituents at 2-, 3-, 7, and 8-position of the core, TBADT **1**–**3** exhibited significantly enhanced solubility in common organic solvents, such as benzene, toluene, and CH_2Cl_2. For example, these three soluble



Scheme 1 Synthesis of TBADT **1**–**3**

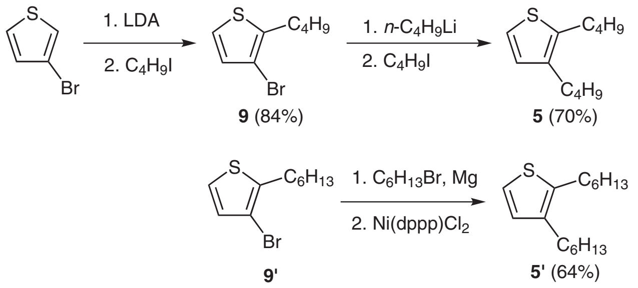
TBADT could be purified by chromatography using 10% benzene–hexanes as eluent.

The new tetrasubstituted thiophene, 4,5-dibutylthiophene-2,3-dicarbaldehyde (**4**), was prepared as shown in Scheme 2. Bromination of 2,3-dibutylthiophene (**5**) with NBS afforded **6**, which was treated with LDA for the '2-Br' rearrangement,[12] followed by direct formylation with *N*-formylpiperidine to give **7**. Protection of the aldehyde with ethylene glycol offered **8**, which was then debrominated with *n*-butyllithium, formylated with *N*-formylpiperidine, and protonated to generate **4** in a yield of ca. 22% for the seven-step sequence.



Scheme 2 Synthesis of 4,5-dibutylthiophene-2,3-dicarbaldehyde (**4**)

Dibutyl-substituted thiophene **5** was prepared as shown in Scheme 3. 3-Bromothiophene was deprotonated with LDA and alkylated with butyl iodide to give **9**. Lithium–halogen exchange and alkylation with butyl iodide gave **5** in good yield (70%). For comparison, dihexyl-substituted thiophene (**5′**) has been reported recently via the reaction of corresponding brominated thiophene (**9′**) with Grinard reagent ($C_6H_{13}MgBr$) catalyzed by Ni(dppp)Cl_2 in a yield of 64%.[13] Our synthetic route provides a simpler alternative to the dialkyl-substituted thiophene with better yield.



Scheme 3 Synthesis of 2,3-dibutylthiophene (**5**)

2-Ethynylthieno[3,2-*b*]thiophene (TTE) was prepared as shown in Scheme 4, by employing a similar synthetic procedure used for the synthesis of 2-ethynylthiophene (TE).[14,15] Via a Witting reaction with carbon tetrabromide and PPh_3, 2-thieno[3,2-*b*]thiophenecarboxaldehyde was converted into 2-(2,2-dibromovinyl)thieno[3,2-*b*]thiophene, which was then treated with *n*-butyllithium to give TTE in an overall yield of 45%.

Weight loss of the three new soluble TBADTs was observed only at a temperature >372 °C, as demonstrated by thermogravimetric analysis (Table 1). Thermal stability of these TBADTs was, however, lower than that of the previously reported PE-ADT (***E***). From differential scanning calorimetry (DSC) measurements, TBADTs **1** and **2** (decomposition temperatures of 215 °C and 210 °C, respectively) exhibited higher thermal stabilities than the analogous **3** (decomposition temperatures of 152 °C) and TESPE-ADT (**G**, decomposition temperature of 168 °C).[16] Note that compared to the PE and TE groups, TTE substituents decreased the thermal stability of the corresponding ADT. Concurrently, in order to improve the synthetic yield for compound **3**, a lower reaction temperature was required compared to compounds **1** and **2**; 0 °C for **3**, 40 °C for **2**, and 60 °C for **1**.

With arylethynyl substituents, TBADTs **1**–**3** exhibited significantly red-shifted optical absorption spectra with λ_{max} values of >577 nm compared to ADT (λ_{max} = 490 nm; Figure 3). As expected, TTE-TBADT (**3**) with more conjugated TTE substituents afforded highest absorption maximum at λ = 604 nm, demonstrating the most extended π-electron delocalization between the main core and the arylethenyl substituents among three TBADTs. Calculated from the onset of the optical absorption, compound

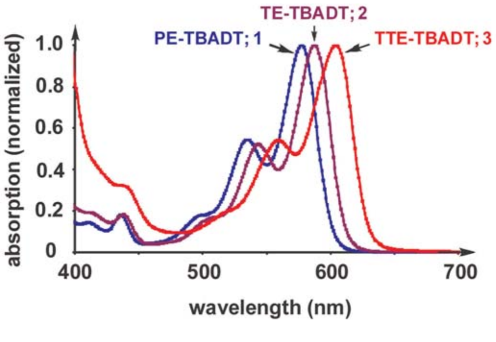
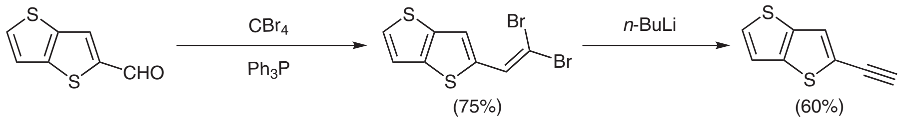


Figure 3 Optical absorption spectra of TBADT **1**–**3** in chlorobenzene solution



Scheme 4 Synthesis of 2-ethynylthieno[3,2-*b*]thiophene (TTE)

Table 1 Thermal, Optical Absorption/Emission, and Electrochemical Data for TBADTs **1**–**3**

Compound	Decomp temp (T_d; °C)	TGA (°C; 5%)	Optical λ_{max} (nm)[b]	Reductive potential (V)[c]	Oxidative potential (V)[c]	ΔE_{gap} (eV)	
						(UV)[b]	(DPV)[c]
PE-ADT[a]	339	320	571	–1.14[d]	0.948[d]	2.06	2.09
TESPE-ADT[a]	168	239	576	–1.14[d]	0.956[d]	2.05	2.10
PE-TBADT (**1**)	215	400	577	–1.21	0.84	2.05	2.05
TE-TBADT (**2**)	210	400	587	–1.17	0.83	2.01	2.00
TTE-TBADT (**3**)	152	372	604	–1.12	0.82	1.95	1.94

[a] From ref. 9.

[b] In chlorobenzene.

[c] In 1,2-dichlorobenzene at 25 °C (Fc/Fc$^+$ as an internal standard at +0.6 V).

[d] In 1,2-dichlorobenzene at 100 °C.

3 exhibited smaller HOMO–LUMO energy gaps than compounds **1** and **2**, consistent with the electrochemically derived energy gap values (vide infra, Table 1).

The photooxidative stability of compounds **1**–**3** was investigated by monitoring the absorbance decay at λ_{max} in aerated chlorobenzene solutions under the exposure of white light (fluorescent lamp) at room temperature (Figure S1, see Supporting Information). Decomposition of the corresponding compounds was observed for all three TBADTs over the course of hours. Of particular note, the compound with a lower LUMO level (vide infra) was more stable than the others.[17] TTE-substituted **3** exhibited longer half-lives than **1** and **2**, demonstrating enhanced photooxidative stability via arylethynyl substitution, as observed in the other PEN or ADT derivatives.[18]

To further investigate the decomposition mechanism more detailed experiments were carried out. First, under ambient conditions (O_2 and H_2O present) but in the absence of white light, no decomposition was observed for all three compounds over the course of 24 hours.

Furthermore, under fluorescent light but without O_2 (N_2 degassed from the solution, trace water present), no decomposition was observed over 24 hours. Therefore, the three new TBADT derivatives investigated in this study show promise as candidates for solution-processable organic semiconductors under ambient conditions in the absence of O_2 or light. Note that unsubstituted PEN and **ADT** suffer photooxidative decomposition.[19]

Differential pulse voltammograms (DPV; using ferrocene/ferrocenium as internal standard at +0.6 V) of **1**–**3** were recorded in dichlorobenzene at 25 °C, and the resulting oxidation and reduction potentials are summarized in Table 1.[20] As expected, the DPV spectra of compounds **1**–**3**, exhibited oxidative peaks at +0.82 V to +0.84 V, which are lower than that determined for ADT (+0.94 V; see Supporting Information, Figure S2). Therefore, the HOMO levels of the TBADTs are slightly higher than that of ADT (Figure 4; assuming ferrocene/ferrocenium oxidation at 4.8 eV). By contrast, the reductive peaks of compounds **1**–**3** at –1.12 V to –1.21 V are shifted to higher values than that of ADT (–1.67 V). Hence, the LUMO levels of the new compounds lie significantly lower than that of the unsubstituted ADT. Note that TTE-TBADT with more conjugation than the others afforded the highest HOMO and the lowest LUMO, which can be attributed to more extensive π-electron delocalization.[21] Overall, the electrochemically-derived HOMO–LUMO energy gaps are ranked in the order of **3** < **2** < **1** < ADT (Figure 4), in agreement with the values obtained from optical spectroscopy (Table 1).

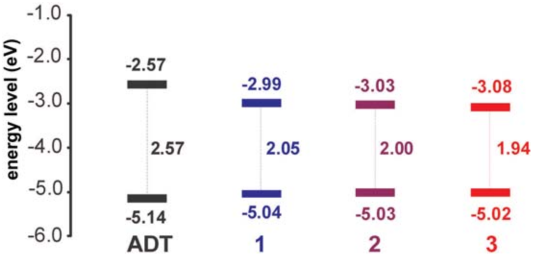


Figure 4 Electrochemically derived HOMO and LUMO energy levels of compounds **1**–**3** and ADT

The newly synthesized compounds were also tested as organic semiconductors for organic thin-film transistors (OTFT). Preliminary top-contact/bottom-gate OTFT were fabricated by drop-casting films of compounds **1**–**3** onto bare p^{++}-Si/SiO$_2$ (300 nm SiO$_2$ as dielectric) substrates, followed by Au deposition through a shadow mask to define the source and drain electrodes. OTFT characterization was performed under ambient conditions, and the corresponding device characteristics are summarized in Table 2 (see also Supporting Information, Figure S3).

The devices fabricated with compounds **1**–**3** all exhibited TFT activity as p-channel semiconductors (see Supporting Information, Figure S3). All the compounds employed in this study were sufficiently soluble in common solvents (toluene, chlorobenzene, and dichlorobenzene) at room temperature,[22] and drop-casting of the corresponding solutions was found to be a reliable semiconductor film-growth procedure for OTFT. Preliminary devices from

Table 2 Charge Carrier Mobility (μ, cm^2/Vs),[a] Current On/Off Ratio (I_{on}/I_{off}), and Threshold Voltage (V_T, V) Data for OTFT Fabricated with Compounds **1**–**3** on Bare p^{++}-Si/SiO$_2$ Substrates

Compd	Solvent	μ	I_{on}/I_{off}	V_T
1	1,2-dichlorobenzene	1.5×10^{-3}	10^4	− 8.0
2	1,2-dichlorobenzene	5.0×10^{-4}	10^3	+ 4.0
3	chlorobenzene	1.0×10^{-3}	10^2	+13.0

[a] Calculated in the saturation regime.

drop-casted films showed similar carrier mobility values of ca. 0.001 cm^2/Vs. Compound **1** exhibited the highest device performance with a carrier mobility of 1.5×10^{-3} cm^2/Vs and a current on/off ratio of 10^4. Compounds **2** and **3** showed slightly lower device performance compared to compound **1**, with a carrier mobility of 5×10^{-4} to 1×10^{-3} cm^2/Vs and a current on/off ratio of 10^2–10^3.

In summary, three new solution-processable tetrabutylanthradithiophene (TBADT) derivatives have been synthesized and characterized. The four butyl substituents and the arylethynyl substituents are found to be effective in increasing both the solubility and the environmental stability of the corresponding semiconductors. Preliminary tests of the TBADT-based compounds for organic thin-film transistors showed TFT activity as p-channel semiconductors with carrier mobilities of ca. 0.001 cm^2/Vs. Further studies on device fabrication and characterization under different conditions (e.g., solvent, concentration, substrate) using different solution process (e.g., spin-coating, printing) are under way. These results provide new information about the structural characteristics of TBADT-based semiconductors and the benefits of using these cores for the design and fabrication of solution-processable OTFT materials.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett. It contains all experimental sections and Figures S1–S26.

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(22) The solubility of TBADT derivatives was ca. 20 (for **3**) to 40 (for **1** and **2**) mg/mL in $CHCl_3$.