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Synthesis of Highly Soluble and Oxidatively Stable Tetraceno[2,3-*b*]thiophenes and Pentacenes

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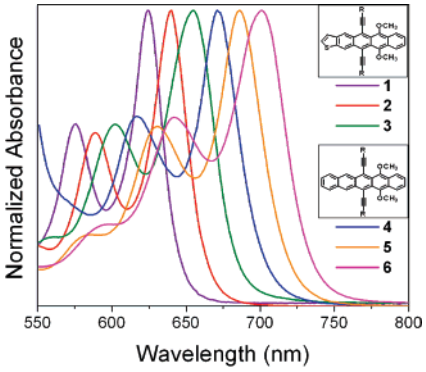

A comparative study of suitably functionalized, highly soluble tetraceno[2,3-*b*]thiophenes (**1**−**3**) and pentacenes (**4**−**6**) that show higher photoxidative stability than that of unfunctionalized corresponding acenes is reported. The absorption and emission of **1**−**3** (A_{max} = 624−656 nm, λ_{max} = 634−672 nm, $\Phi_F \approx 10\%$) and **4**−**6** (A_{max} = 672−704 nm, λ_{max} = 682−718 nm, $\Phi_F \approx 10\%$) were found to be systematically red-shifted by the substitution in the order of the *tert*-butylethynyl < triisopropylsilylethynyl < phenylethynyl groups. The oxidation potentials of these compounds were similar ($E_{1/2} \approx 0.70$ V), except for **4**, which showed lower oxidation potential ($E_{1/2} \approx 0.63$ V).

The design and synthesis of new π-conjugated organic semiconductors are currently at the forefront of research in order to realize stable and efficient organic electronic devices.[2] Linear polycyclic aromatic hydrocarbons are π-conjugated organic systems widely studied for electronic applications. Pentacenes, for example, are a current choice in superconductors, organic field-effect transistors (OFETs),[3] and organic light-emitting diodes (OLEDs).[4] Field-effect mobility greater than 1 $cm^2\ V^{-1}\ s^{-1}$ has been reported with pentacene as the active layer in OFET devices.[5] But practical applications of this class of compounds have been limited by their air (O_2) and light sensitivity and poor solubility in most common organic solvents.[6]

Modification of the molecular structure of acenes could lead to substantial changes in electronic and optical properties. Structural modification may also increase the stability, improve the solubility, and improve the thin film packing and mobility over the parent hydrocarbon. The electronic, physical, and photophysical properties of pentacenes, for example, can be easily modified by changing the substitution pattern on the main aromatic skeleton.[7−9] Anthony et al. showed that the solid-state packing of pentacene could be improved by substitution of various trialkylsilylethynyl functionalities at the 6 and 13 positions.[10,11] Such improved packing results in the enhanced intermolecular orbital overlap, which is a prerequisite for better OFET device performance.

Bao et al. recently showed that tetraceno[2,3-*b*]thiophene, an asymmetric sulfur containing acene, exhibited field effect mobility as high as 0.47 $cm^2\ V^{-1}\ s^{-1}$ with a decent on−off ratio (>10^5 at room temperature).[12] This compound seems quite interesting given that its OFET device performance is comparable to that of pentacene. However, tetraceno[2,3-*b*]thiophene also suffers from instability and decomposes within 60 min in solution.[12] We anticipated that its properties and performance could be improved by suitable substitution.

In this paper we report the synthesis, characterization, and photophysical properties of tetraceno[2,3-*b*]thiophenes (**1**−**3**) and pentacenes (**4**−**6**) (Chart 1). Compounds **1**−**3** are functionalized at the 6,11 and 5,12 positions with the methoxy and alkylethynyl and phenylethynyl groups, respectively, while **4**−**6** are substituted at the 5,14 and 6,13 positions with the same functionalities. Our goals were 2-fold: to understand the effect of substituents on the properties of the tetraceno[2,3-*b*]-thiophenes and to compare properties with analogous pentacenes. We observed a systematic shift in the optical band gap of the compounds. We show that **1**−**6** are highly soluble in common organic solvents and more stable than the corresponding parent hydrocarbons, tetraceno[2,3-*b*]thiophene (**7**) as well as pentacene (**8**).

Compounds **1**−**6** were synthesized from 2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione (**9**), which was first methylated by using dimethyl sulfate in the presence of anhydrous potassium carbonate (Scheme 1).[13−15] Double aldol condensation of the product (2,3-dihydro-9,10-dimethoxy-1,4-anthracenedione, **10**) with 1 equiv of 2,3-thiophenedicarboxaldehyde or 1,2-benzenedicarbaldehyde produced 5,11-dimethoxy-5,12-tetracene-

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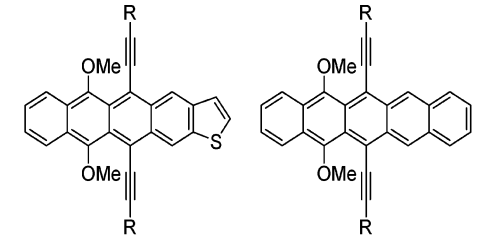
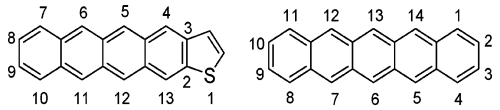
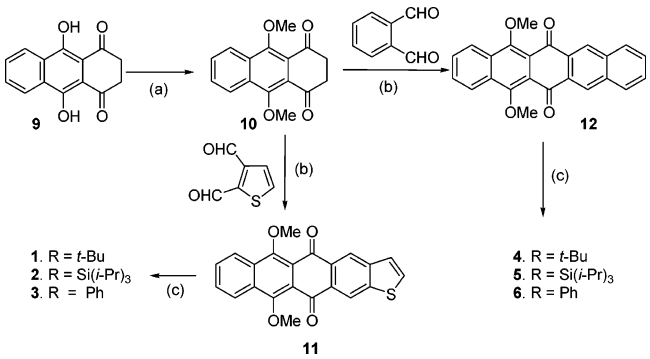
CHART 1





SCHEME 1 [a]



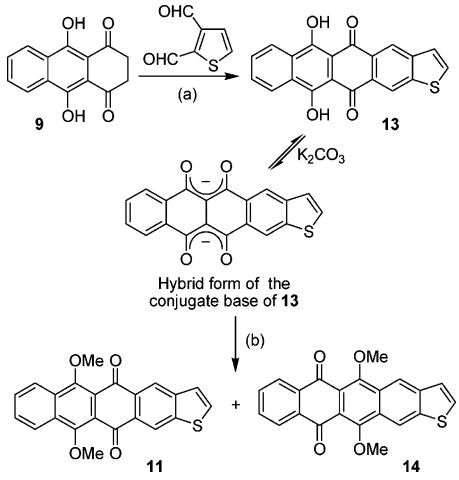
[a] Reagents and conditions: (a) anhydrous K_2CO_3, Me_2SO_4, acetone, dioxane, rt, 30 min, 55 °C, 12 h; (b) 5% KOH, tetrahydrofuran (THF), reflux, 12 h; (c) RC_2Li, rt, 12 h, then 10% HCl, $SnCl_2$, rt, 24 h.

quinone[2,3-*b*]thiophene (**11**) or 5,14-dimethoxy-6,13-pentacenequinone (**12**), respectively. The latter compounds were finally converted into **1**−**6** following known synthetic procedures.[15−17]

We initially attempted methylation after the aldol type of condensation between **9** and 2,3-thiophenedicarboxaldehyde. But the reaction of the aldol product (6,11-dihydroxy-5,12-tetracenequinone[2,3-*b*]thiophene, **13**) with dimethyl sulfate resulted in an inseparable isomeric mixture of the methylated products (**11** and **14**) (Scheme 2). This is because **13** undergoes tautomerization under the reaction conditions employed (anhydrous K_2CO_3, Me_2SO_4). However, an optimized reaction condition (Scheme 1) was used to accomplish the methylation of **9** in the first step, which afforded **10** in a good yield. The aldol-type condensation of **10** with 2,3-thiophenedicarboxaldehyde yielded only **11**.

The tetraceno[2,3-*b*]thiophene derivatives (**1**−**3**) are deep blue while the new pentacene derivatives (**4**−**6**) are blue-green. Each is highly soluble in common organic solvents and thus easily processible. Figure 1 shows the absorption spectra of **1**−**6** recorded in dichloromethane. The $\pi-\pi^*$ band is highly sensitive to the substituents and showed significant bathochromic shifts

SCHEME 2 [a]



[a] Reagents and conditions: (a) 5% KOH, EtOH, reflux, 12 h; (b) anhydrous K_2CO_3, Me_2SO_4, acetone, dioxane, 55 °C, 36 h.

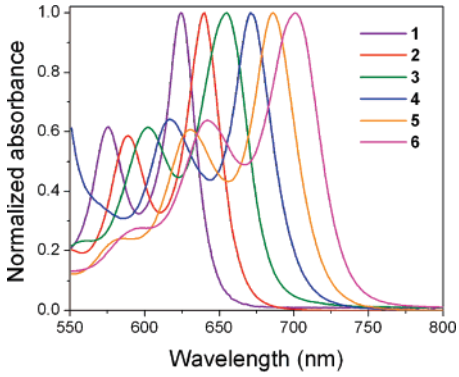


FIGURE 1. Normalized absorption spectra of **1**−**6** recorded in dichloromethane.

compared to that of unfunctionalized corresponding acenes. For example, the absorption maxima of **1** (624 nm) and **4** (672 nm) are more than 90 nm red-shifted than those of **7** (532 nm)[12] and **8** (578 nm), respectively. This huge red-shift in absorption can be attributed to the π-conjugation extending ethynyl group as well as the electron donating methoxy group. The latter is known to cause a red shift of about 25 nm in the absorption of several compounds.[15,18] Interestingly, the absorption maxima are also sensitive to the peripheral substituents attached to the ethynyl group. In the order of the *tert*-butyl < triisopropylsilyl < phenyl groups, the compounds in both series showed an increment of about 15 nm in absorption maxima.

Absorption maxima (A_{max}), extinction coefficients (ϵ), emission maxima (λ_{max}), and fluorescence quantum yields (Φ_F) of **1**−**6** recorded in dichloromethane are presented in Table 1. The tetraceno[2,3-*b*]thiophenes especially show very small Stoke's shift (∼9−16 nm). Compounds **1**−**3** are weakly fluorescent ($\Phi_F \approx 10\%$), similar to **8** and other linear hydrocarbon acenes. The Φ_F values of **1**−**6** were found to be similar (∼10%) in various solvents such as dichloromethane, tetrahydrofuran, and toluene. The absorptions of **1**−**6** were also recorded in thin films, which were made by casting 2−3 drops of concentrated dichloromethane solution of the compounds on a quartz plate and

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(18) The magnitude of this shift agrees with the empirical rules for absorption spectroscopy, each methoxy group inducing a red shift of ∼25 nm.

TABLE 1. Photophysical Properties of 1−6 Recorded in Dichloromethane

compd	A_{max} (nm)/ ϵ ($M^{-1}cm^{-1}$)	A_{max} (nm)[a]	λ_{max} (nm)	Φ_F	$E_{1/2}$ (V)[b]	optical E_G (eV)[c]
1	624 (10 100)	633	634	0.08	0.69	1.86
2	639 (13 300)	646	648	0.09	0.71	1.83
3	656 (13 400)	674	672	0.11	0.69	1.72
4	672 (10 300)	679	682	0.09	0.63	1.70
5	686 (14 200)	691	712	0.12	0.70	1.69
6	704 (13 500)	725	718	0.11	0.70	1.58

[a] Recorded in thin film. [b] $E_{1/2}$ values against the ferrocene/ferrocenium redox system (−4.8 V). [c] Optical band gap (E_G) determined from the onset of the thin film absorption peak.

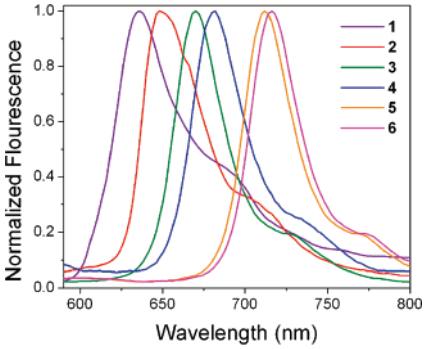

FIGURE 2. Normalized fluorescence spectra of **1**−**6** recorded in dichloromethane.

evaporating the solvent. The thin film absorptions (spectra provided in the Supporting Information) were expectedly red-shifted and broadened compared to those recorded in solution, apparently due to the strong electronic interactions in the film.[19] The thin films of these compounds were stable under laboratory conditions, at least for 3 weeks.

Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of **1**−**6**. The CV graphs were obtained with a scan rate of 100 mV/s and with the compounds in 0.1 M tetrabutylammonium perfluorate (Bu_4NPF_6) in anhydrous dichloromethane. The oxidation potentials of tetraceno-[2,3-*b*]thiophenes (**1**−**3**, $E_{1/2} \approx 0.70$ V) were found to be similar to that of pentacene ($E_{1/2} \approx 0.70$ V)[12] and its derivatives (**5** and **6**), indicating that the electrochemical HOMO levels of these compounds are similar (Table 1). Interestingly, **4** showed a lower $E_{1/2}$ value (0.63 V) and also turned out to be the most photounstable (vide infra). The optical band gaps estimated either in solution or in the solid state are higher for **1**−**3** (1.86−1.72 eV in solid) than for **4**−**6** (1.70−1.58 eV in solid). This indicates that the LUMO levels of tetraceno[2,3-*b*]thiophenes are higher than those of pentacenes, since their HOMO levels are similar. Furthermore, there is also a distinct trend of decreasing optical band gap going from **1** to **3** or from **4** to **6**. Thus, the LUMO levels of both series are similarly and considerably affected by the substitution pattern.

The photoxidative stability of **1**−**6** was studied by monitoring changes in the absorption of air-saturated solutions under ambient light (Figure 2). Compounds **5** and **6** were relatively stable, while compounds with the *tert*-butylethynyl function (**1** and **4**) were quite unstable, the long wavelength absorption of **1** and **4** decaying to almost zero within 5 and 10 h, respectively. On the other hand, there was comparatively little change (less than 20%) in the absorption of **5** and **6** even after 10 h of ambient light illumination. The corresponding tetraceno[2,3-*b*]-thiophene derivatives (**2** and **3**) showed intermediate stability with their absorption diminishing almost 80% in 10 h. Substitution seems to increase the photoxidative stability of these compounds, especially in the pentacene series, because **7** and **8** are not stable and disappear in less than 1 h under ambient light.[12]

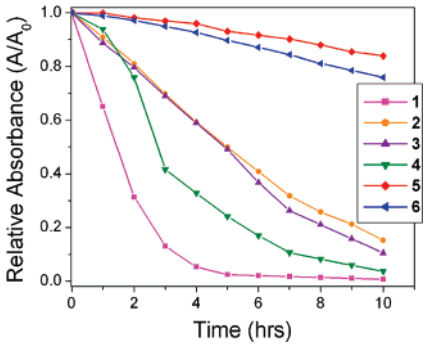

FIGURE 3. Photoxidative stability of **1**−**6** monitored through decrease in their absorption in toluene solution upon exposure to ambient light.

It is noted that **1**−**6** are more photostable than their unsubstituted analogous, i.e., **7** and **8**. The π-electron delocalization through the ethynyl group may be the reason for the higher photostability of **1**−**6**. The formation of endoperoxide across the most reactive central ring is the reason for the photoinstability of linear acenes.[3,20] The enhanced photostability of **2**, **3**, **5**, and **6** compared to that of **7** and **8** may also be related to the bulkiness of the substituent at the central ring and the presence of the methoxy group, which may hinder the approach of O_2.

In conclusion, tetraceno[2,3-*b*]thiophenes (**1**−**3**) and pentacenes (**4**−**6**) substituted with the methoxy, alkylethynyl, and phenylethynyl groups were synthesized. The absorption and emission spectra of **1**−**3** (A_{max} = 624−656 nm, λ_{max} = 634−672 nm, $\Phi_F \approx 10\%$) and **4**−**6** (A_{max} = 672−704 nm, λ_{max} = 682−718 nm, $\Phi_F \approx 10\%$) were found to be systematically red-shifted by the substitution in the order of the *tert*-butylethynyl < triisopropylsilylethynyl < phenylethynyl groups. The oxidation potentials were similar ($E_{1/2} \approx 0.70$ V), except for **4**, which showed lower oxidation potential ($E_{1/2} \approx 0.63$ V). Compounds **1**−**6** are quite soluble in common organic solvents and more stable than unfunctionalized compounds. The derivatives containing the *tert*-butylethynyl functionality were relatively more unstable than the rest.

Experimental Section

General. All chemicals and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted. Moisture and air-sensitive reactions were carried out in a drybox. ^1H and ^{13}C NMR spectra were recorded with a Bruker 300 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and chemical shifts relative to TMS at 0.0 ppm are reported in parts per million (ppm) for ^1H NMR on the δ scale. UV−visible absorbance spectra were recorded with a Shimadzu UV−vis spectrometer. Fluorescence spectra were recorded with a

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Fluorolog fluorimeter. Thin layer chromatography was performed on MERCK Silica Gel 60 thick layer plates. Column chromatography was performed on Sorbent Technologies brand silica gel (40−63 um, Standard grade). High-resolution mass analyses were performed at University of Illinois SCS Mass Spectrometry Laboratory.

2,3-Dihydro-9,10-dimethoxy-1,4-anthracenedione (10). Compound **10** was prepared by a modified methylation method.[13] Compound **9** (2.5 g, 10.3 mmol) was added to a 500 mL oven dried round-bottomed flask equipped with a stir bar and acetone (200 mL) and dioxane (100 mL) were added. During stirring dimethyl sulfate (28 mL, 169 mmol) and anhydrous potassium carbonate (15 g, 118.2 mmol) were also added. The entire mixture was stirred under argon at room temperature for about 30 min and then refluxed for 12 h. The optimal formation of **10** was monitored with GC-MS. The reaction mixture was allowed to cool and filtered. The filtrate was concentrated and subjected to the next step without further purification.

6,11-Dimethoxy-5,12-tetracenequinone[2,3-*b*]thiophene (11). Thiophene-2,3-carboxaldehyde (1 equiv of **10** as estimated from the GC/MS profile) and THF (100 mL) were added to the concentrated solution of **10** and the mixture was stirred several minutes until all solids dissolved. Ethanolic KOH (5%, 5.75 mL) was then added. The mixture was refluxed overnight, following which it was cooled and poured into an ice cold water bath. The product precipitated then was filtered and dried. The brown crude solid product was purified by column chromatography with dichloromethane as solvent. Evaporation of the solvent yielded pure **11** in the form of an orange yellow solid (yield 20%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.75 (s, 1H), 8.45 (m, 2H), 7.77 (m, 3H), 7.60 (d, 1H), 4.18 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 183.06, 182.71, 156.00, 155.96, 144.53, 143.08, 132.88, 132.03, 131.45, 130.71, 129.91, 125.02, 124.83, 122.79, 122.04, 121.30, 121.27, 63.20; HRMS *m*/*z* $[M]^+$ calcd for $C_{22}H_{14}O_4S$ 374.0613, found 374.0614.

5,14-Dimethoxy-6,13-pentacenequinone (12). Compound **10** was caused to react with 1,2-bezenedicarbaldehyde to obtain **12** following the same procedure employed for **11**. Pure **12** was isolated as yellow solid (yield 21%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (s, 2H), 8.44 (m, 2H), 8.12 (m, 2H), 7.79 (m, 2H), 7.70 (m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 182.98, 156.04, 135.16, 132.37, 131.42, 129.93, 129.91, 129.06, 128.74, 124.83, 121.68, 63.28; HRMS *m*/*z* $[M]^+$ calcd for $C_{24}H_{16}O_4$ 368.1048, found 368.1049.

General Procedure for the Synthesis of 1−6. Compounds **1**−**6** were synthesized starting from either **11** or **12** following a general method. The synthesis of **1** is detailed as an example. An oven dried 100 mL round-bottomed flask equipped with a stir bar was clamped in a dry box. *tert*-Butylacetylene (0.13 mL, 1.06 mmol) was added to the flask and dissolved in dry dichloromethane (10 mL). To this stirring solution was added *n*-BuLi (0.44 mL of a 2.5 M solution in hexane) dropwise. The mixture was stirred for about 30 min at room temperature. In a separate flask a solution of **11** (0.1 gm, 0.27 mmol) in dry dichloromethane (5 mL) was prepared, and was slowly added to the lithiated *tert*-butylacetylene solution. The whole mixture was allowed to stir at room temperature overnight. Then it was taken out of the dry box and was quenched with 10% HCl (1 mL). To this was added $SnCl_2$ in 10% HCl (1 mL) and the mixture was stirred at room temperature under dark and argon for 24 h. The progress of the reaction was monitored by thin layer chromatography (TLC). After the reaction was complete, the solution was dried with anhydrous Na_2SO_4 and the filtrate was evaporated to obtain crude **1**. The product was purified in the dark by column chromatography over silica gel with a mixture of hexane and dichloromethane (1:1) as the eluent.

5,12-Bis(*tert*-butylethynyl)-6,11-dimethoxytetraceno[2,3-*b*]-thiophene (1). Yield 34%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.31 (s, 1H), 9.26 (s, 1H), 8.30 (m, 2H), 7.53 (d, 1H), 7.42 (m, 3H), 4.10 (s, 6H), 1.64 (s, 18H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.05, 140.00, 139.50, 131.00, 129.75, 125.47, 124.95, 124.85, 124.76, 124.63, 123.88, 123.04, 121.49, 120.01, 115.55, 114.00, 112.00, 111.55, 80.44, 80.36, 63.71, 31.02, 29.33; HRMS *m*/*z* $[M]^+$calcd for $C_{34}H_{32}O_2S$ 504.2123, found 504.2120.

5,12-Bis(triisopropylsilylethynyl)-6,11-dimethoxytetraceno-[2,3-*b*]thiophene (2). 2 was prepared by the reaction between triisopropylsilylacetylene and **11** and purified by column, using a mixture of hexane and dichloromethane (2:3) as the eluent. Yield 41%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.53 (s, 1H), 9.47 (s, 1H), 8.32 (m, 2H), 7.54 (d, 1H), 7.45 (m, 2H), 7.38 (d, 1H), 4.10 (s, 6H), 1.33 (s, 42H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.55, 140.40, 140.02, 131.68, 130.19, 125.77, 125.72, 125.16, 125.07, 124.76, 124.68, 123.68, 123.09, 121.89, 120.48, 115.62, 114.30, 107.34, 106.63, 106.33, 94.73, 63.78, 18.94, 18.44, 11.61, 11.02; HRMS *m*/*z* $[M + H]^+$ calcd for $C_{44}H_{57}O_2Si_2S$ 705.3617, found 705.3621.

5,12-Bis(phenylethynyl)-6,11-dimethoxytetraceno[2,3-*b*]thiophene (3). 3 was prepared by the reaction between phenylacetylene and **11** and purified by column, using a mixture of hexane and dichloromethane (9:1) as the eluent. Yield 35%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 9.45 (s, 1H), 8.41 (m, 2H), 7.85 (m, 4H), 7.91 (d, 1H), 7.72 (d, 1H), 7.62−7.45 (m, 8H), 4.21 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.05, 141.00, 140.05, 131.54, 131.50, 130.99, 130.88, 130.33, 128.76, 128.64, 125.98, 125.93, 125.39, 125.30, 124.78, 124.69, 124.49, 124.41, 123.88, 123.03, 121.39, 120.07, 115.32, 114.04, 103.41, 103.02, 91.48, 63.73; HRMS *m*/*z* $[M]^+$ calcd for $C_{38}H_{24}O_2S$ 544.1497, found 544.1509.

6,13-Bis(*tert*-butylethynyl)-5,14-dimethoxypentacene (4). 4 was prepared by the reaction between *tert*-butylacetylene and **12** and purified by column, using a mixture of hexane and dichloromethane (1:1) as the eluent. Yield 40%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (s, 2H), 8.26(m, 2H), 7.95 (m, 2H), 7.39 (m, 4H), 4.10 (s, 6H), 1.66 (s, 18); ^{13}C NMR (300 MHz, $CDCl_3$) δ 132.19, 131.37, 128.76, 126.47, 125.73, 125.55, 124.91, 123.08, 115.11, 113.00, 80.84, 63.66, 31.34, 29.42; HRMS *m*/*z* $[M]^+$ calcd for $C_{36}H_{34}O_2$ 498.2559, found 498.2553.

6,13-Bis(triisopropylsilylethynyl)-5,14-dimethoxypentacene (5). 5 was prepared by the reaction between triisopropylsilylacetylene and **12** and purified by column, using a mixture of hexane and dichloromethane (2:3) as the eluent. Yield 47%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 2H), 8.30 (m, 2H), 7.99 (m, 2H), 7.43 (m, 4H), 4.12 (s, 6H), 1.39 (s, 42H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.58, 132.49, 131.81, 128.56, 126.83, 126.11, 125.83, 125.30, 125.18, 123.15, 115.38, 107.61, 107.38, 63.73, 18.92, 12.31; HRMS *m*/*z* $[M]^+$ calcd for $C_{46}H_{58}O_2Si_2$ 698.3975, found 698.3984.

6,13-Bis(phenylethynyl)-5,14-dimethoxypentacene (6). 6 was prepared by the reaction between phenylacetylene and **12** and purified by column, using a mixture of hexane and dichloromethane (3:7) as the eluent. Yield 38%; ^{1}H NMR (300 MHz $CDCl_3$) δ 9.56 (s, 2H), 8.35 (m, 2H), 8.10 (m, 2H), 7.92 (m, 4H), 7.57−7.28 (m, 10H), 4.23 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.59, 132.52, 131.54, 131.12, 128.79, 128.68, 128.49, 126.42, 126.20, 126.03, 125.80, 125.40, 124.55, 123.07, 115.06, 104.16, 91.92, 63.67; HRMS *m*/*z* $[M]^+$ calcd for $C_{40}H_{26}O_2$ 538.1933, found 538.1931.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR of **1**−**6**, **11**, and **12**, details about formation of isomeric mixture of **11** and **14**, thin film absorption of **1**−**6**, CV graphs, the Φ_F values of **1**−**6** recorded in different solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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