ORGANIC
LETTERS

2009
Vol. 11, No. 12
2563−2566

New Oligothiophene-Pentacene Hybrids as Highly Stable and Soluble Organic Semiconductors

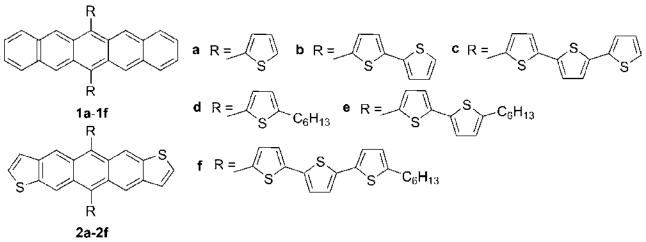
Jing Wang,[†] Ke Liu,[†] Yi-Yang Liu,[†] Cheng-Li Song,[†] Zi-Fa Shi,[†] Jun-Biao Peng,[‡] Hao-Li Zhang,*,[†] and Xiao-Ping Cao*,[†]

State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China, and Key Laboratory of Specially Functional Materials and Advanced Manufacturing Technology, South China University of Technology, Guangzhou 510640, China

Haoli.zhang@lzu.edu.cn; Caoxplzu@163.com

Received April 16, 2009

ABSTRACT



Two series of new oligothiophene-pentacene hybrid compounds were successfully synthesized and characterized, which consist of pentacene and anthradithiophene skeletons modified by different oligothienyl groups at 6,13 sites or 5,11 sites, respectively. Their optical, thermal, and electrochemical properties show regular variations with the length change of the side groups. These materials exhibit much higher solubility and significantly improved thermal and photooxidation stabilities compared with unmodified pentacene and anthradithiophene.

Organic field-effect transistors (OFETs) based on organic π-conjugated materials have attracted tremendous interest due to their potential applications in flexible and low cost electronics. Pentacene is one of the most well studied organic semiconductors,[1,2] manifesting to the highest mobility.[3] However, a significant drawback of pentacene is its low solubility in common solvents, which makes it incompatible with low-cost solution deposition methods. Many soluble pentacene derivatives have been reported, but most of them are highly susceptible to photooxidation in solution (typical half-life time under UV irradiation is around a few minutes),[4−6] practically precluding them from solution fabrication applications under ambient conditions. Much efforts have been made to tailor the properties of pentacene by changing the substitution pattern on the main aromatic skeleton.[5,7−9] For example, Anthony et al. reported that attaching various trialkylsilylethynyl moieties on the center ring not only imparted solubility to the pentacene derivatives but also enhanced π-stacking in the solid state.[10,11]

[†] Lanzhou University.

[‡] South China University of Technology.

(1) Dimitrakopoulos, C. D.; Mascaro, D. J. *Adv. Mater.* **2002**, *14*, 99.

(2) Katz, H.; Bao, Z.; Gilat, S. *Acc. Chem. Res.* **2001**, *34*, 359.

(3) Kelly, T. W.; Boardman, L. D.; Dunbar, T. D.; Muyres, D. V.; Pellerite, M. J.; Smith, T. P. *J. Phys. Chem. B* **2003**, *107*, 5877.

(4) Wolak, M. A.; Jang, B. B.; Palilis, L. C.; Kafafi, Z. H. *J. Phys. Chem. B* **2004**, *108*, 5492.

(5) Li, Y.; Wu, Y.; Liu, P.; Prostran, Z.; Gardner, S.; Ong, B. S. *Chem. Mater.* **2007**, *19*, 418.

(6) Allen, C. F.; Bell, A. *J. Am. Chem. Soc.* **1942**, *64*, 1253.

(7) Chen, J.; Subramanian, S.; Parkin, S. R.; Siegler, M.; Gallup, K.; Haughn, C.; Martin, D. C.; Anthony, J. E. *J. Mater. Chem.* **2008**, *18*, 1961.

(8) Stone, M. T.; Anderson, H. L. *J. Org. Chem.* **2007**, *72*, 9776.

(9) Lehnherr, D.; Tykwinski, R. R. *Org. Lett.* **2007**, *9*, 4583.

(10) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482.

(11) Payne, M. M.; Delcamp, J. H.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 1609.

(12) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138.

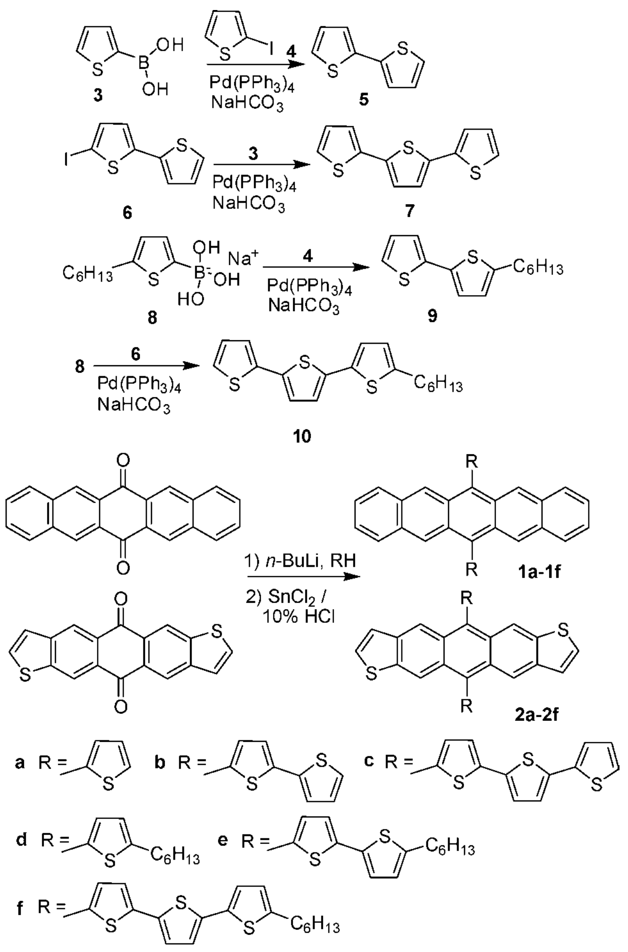
10.1021/ol900838a CCC: $40.75

Meanwhile, oligothiophene and polythiophene derivatives are also well-studied organic semiconductors and show excellent p-type carrier properties. They are currently under intense investigation for applications in electroluminescent diodes,[12] lasers,[13] sensors,[14] photovoltaic cells,[15] and fluorescent markers.[16]

We propose that joining thiophene moieties and pentacene structures may bring about new functionalities that combine the unique properties of the two excellent materials. This purpose could be achieved via two strategies. The first approach is to incorporate the thiophene units into the acene skeletons, such as linear anthradithiophene (ADT), which is structurally analogous to pentacene.[17] Another approach is to attach the oligothiophene structures to the acenes as side groups.

To explore both of the above approaches, we designed two series of oligothiophene-pentacene hybrids which contained different thienyl groups as substituents at the 6,13 postitions or 5,11 positions for pentacenes and anthradithiophenes, respectively (Scheme 1). Alkyl chains are incorporated to improve the solubility and tailor the molecular packing in solid state. By comparing these new compounds, we are aiming to understand the effects of systematic structural variation on their spectroscopic, electrochemical and thermal properties.

Scheme 1



The synthesis of six 6,13-oligothienyl-substituted pentacenes (**1a**−**1f**) and six 5,11-oligothienyl-substituted anthradithiophenes (**2a**−**2f**) was presented in Scheme 1. Compound **3** reacted with 2-iodothiophene (**4**) or 5-iodo-2,2′-bithiophene (**6**) by Suzuki cross coupling reaction produced 2,2′-bithiophene (**5**) or 2,2′:5′,2″-terthiophene (**7**) respectively. Compounds **9** and **10** were synthesized from 2-hexylthiophene by the similar method. The 5-hexyl-2,2′-bithiophene (**9**) and 5-hexyl-2,2′:5′,2″-terthiophene (**10**) were successfully obtained in the yields of 80% and 85%, respectively. 6,13-Di(2′-thienyl)pentacene (**1a**), 2-thienylboronic acid (**3**), 5-iodo-2,2′-bithiophene (**6**) and sodium (2-hexylthiophene-5-boronate) (**8**) were synthesized according to literature methods.[18−21] The target molecules were synthesized from 6,13-pentacenequinone or 5,11-anthradithiophenequinone by reacting with the corresponding thienyl lithium followed by reduction with 10% aqueous HCl/Tin (II) chloride, which induced deoxygenation and produced the desired target molecules.

Introducing thienyl moieties and alkyl chains significantly improved solubility, and the new materials generally have solubilities one order higher than pentachene and ADT (S-Table 1, Supporting Information). The ADT series is more soluble than the pentacene series, suggesting that incorporating thiophene unit into the fused rings helps to improve the solubility. In contrast, the number of thiophene units in the side chain tends to decrease the solubility. Meanwhile, the molecules with hexyl side chains have solubilities 2−3 times higher than their alkyl free analogs.

The UV−vis absorption bands of new hybrid materials in toluene solution are similar to that of the parent pentacene and ADT, but show significant red shifts (Table 1), indicating an extended π-electron delocalization from the acene nucleus, brought about by the oligothienyl substituents. In each set of molecules with similar structures, the increase of thienyl number induces a shift of the absorption maxima toward long wavelength. This is consistent with the energy gaps between HOMO and LUMO, determined by extrapolating the long-wavelength absorption edges, decreases with the increase of side chain length (Table 1). The absorption maxima in the thin films of the compounds **1a**−**2f** exhibit 20 to 40 nm red shifts along with significant peak broadening (Table 1),

---

(13) Pisignano, D.; Anni, M.; Gigli, G.; Cingolani, R.; Zavelanirossi, M.; Lanzani, G.; Barbarella, G.; Favaretto, L. *Appl. Phys. Lett.* **2002**, *81*, 3534.

(14) Torsi, L.; Lovinger, A. J.; Crone, B.; Someya, T.; Dodabalapur, A.; Katz, H. E.; Gelperin, A. *J. Phys. Chem. B* **2002**, *106*, 12563.

(15) Hara, K.; Kurashige, M.; Danoh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *New J. Chem.* **2003**, *27*, 783.

(16) Barbarella, G. *Chemistry* **2002**, *8*, 5072.

(17) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Chem. Mater.* **1996**, *8*, 2542.

(18) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1340.

(19) Burrell, A. K. *J. Org. Chem.* **2003**, *68*, 8974.

(20) Hotta, S.; Kimura, H.; Lee, S. A.; Tamaki, T. *J. Heterocyclic Chem.* **2000**, *37*, 281.

(21) Cammidge, A. N.; Goddard, V. H. M.; Gopee, H.; Harrison, N. L.; Hughes, D. L.; Schubert, C. J.; Sutton, B. M.; Watts, G. L.; Whitehead, A. J. *Org. Lett.* **2006**, *8*, 4071.

Table 1. Optical Absorption Maxima (A_{max}), Fluorescence Emission Maxima (λ_{max}), Band Gap (E_g), Electrochemical Properties, and Decomposition Temperature for Compounds **1a**−**2f**

	A_{max} (nm)		λ_{max} (nm)	band gap[a]								
compound	film	soln	soln	E_g (eV) (film)	E_g (eV) (soln)	E_g[b] (eV)	$E_{g,\ DFT}$[c] (eV)	E_{HOMO}[b] (eV)	E_{LUMO}[b] (eV)	$E_{HOMO,\ DFT}$[c] (eV)	dec temp (°C)	half-life time[d] (min)
1a	622	604	620	1.91	1.97	2.02	2.18	−5.26	−3.24	−5.01	300	12
1b	625	609	635	1.80	1.94	1.98	2.07	−5.24	−3.26	−4.90	350	75
1c	633	611	639	1.77	1.93	1.75	1.93	−5.16	−3.41	−4.76	340	54
1d	633	607	628	1.86	1.96	2.08	2.02	−5.22	−3.14	−4.71	360	39
1e	673	611	638	1.69	1.93	1.89	1.90	−5.16	−3.27	−4.65	375	97
1f	686	612	643	1.68	1.92	1.79	1.89	−5.14	−3.35	−4.65	380	50
pentacene	670	577	–	1.85	2.15[26]	–	2.15	–	–	−4.82	330[27]	5
2a	529	515	531	2.22	2.33	2.34	2.56	−5.61	−3.27	−4.98	352	363
2b	535	520	550	2.20	2.29	2.31	2.45	−5.59	−3.28	−5.01	365	432
2c	541	523	557	2.07	2.26	2.26	2.40	−5.57	−3.31	−4.90	250	470
2d	524	516	535	2.27	2.33	2.49	2.56	−5.75	−3.26	−4.87	375	260
2e	531	521	552	2.06	2.29	2.38	2.45	−5.69	−3.31	−4.95	385	415
2f	552	522	562	2.04	2.27	2.32	2.39	−5.66	−3.34	−4.81	370	741
ADT	560	488	–	1.97	2.46[7]	–	2.69	–	–	−4.95	–	–

[a] Optical HOMO−LUMO gaps determined from the onset of lowest-energy visible absorption band. The onset is defined as the intersection between the baseline and a tangent line that touches the point of inflection. [b] $E_g = E_{LUMO} - E_{HOMO} = (E_{1/2}^{red} + 4.44) - (E_{1/2}^{ox} + 4.44)$. [c] HOMO and LUMO levels and energy gap were obtained by DFT calculation at B3LYP/6-31G (d) level using Gaussian 03 package. [d] Half-life times were obtained by fitting the data in Figure 1 according to a unimolecular first-order kinetics.

compared with the absorptions in solution, due to the increased intermolecular $\pi-\pi$ interactions in the solid state.[22]

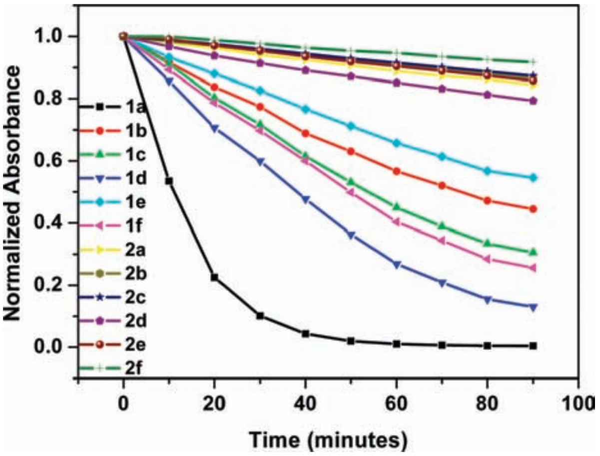


Figure 1. Photooxidative stability of **1a**−**2f** monitored through decrease in their absorption in THF solution upon exposure to ambient light and air at 22 °C.

The photooxidative stabilities of **1a**−**2f** were investigated by monitoring the reduction in the absorbances at λ_{max} in an air-saturated 1.0×10^{-4} M THF solution under ambient light at 22 °C. The half-life of "dilute" pentacene in o-dichlorobenzene under the identical photooxidative conditions was found to be around 5 min. In contrast, the absorption of the compounds **1a**−**2f** are still detectable after more than one hour exposure, showing much higher stabilities. The compound **2f**, whose absorption band diminished only 10% in 90 min ($t_{1/2} = 741$ min), possessed the highest stability. The observed stability order is: **2f** > **2c** > **2b** > **2e** > **2a** > **2d** > **1e** > **1b** > **1c** > **1f** > **1d** > **1a** > pentacene. It can be seen that the ADT derivatives are more stable than pentacene derivatives because the incorporation of fused thiophene units in heteroacenes widens the HOMO−LUMO gap and stabilizes the HOMO level due to the formation of kinked substructures.[23,24] The formation of endoperoxide across the most reactive central ring is the main reason for the photooxidation of linear acenes.[25] The thienyl groups on the new compounds successfully blocked the most reactive sites on the center ring, therefore the photooxidative resistances are also influenced by both steric and electronic factors.[28] The increased stability is also attributed to their lower LUMO orbital energy compared to that of pentacene (Table 1), as the lower LUMO energy hinders photooxidation by reducing the rate of electron transfer from photoexcited species to oxygen.[29]

The thermal stabilities were studied by thermogravimetric analysis (TGA). All the new hybrid materials show higher

---

(22) Ostroverkhova, O.; Shcherbyna, S.; Cooke, D. G.; Egerton, R. F.; Hegmann, F. A.; Parkin, S. R.; Anthony, J. E. *J. Appl. Phys.* **2005**, *98*, 33701.

(23) Zhang, X.; Matzger, A. J. *J. Org. Chem.* **2003**, *68*, 9813.

(24) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224.

(25) Ono, K.; Totani, H.; Hiei, T.; Yoshino, A.; Saito, K.; Eguchi, K.; Tomura, M.; Nishidad, J.; Yamashitad, Y. *Tetrahedron.* **2007**, *63*, 9699.

(26) Xiao, K.; Liu, Y.; Qi, T.; Zhang, W.; Wang, F.; Gao, J.; Qiu, W.; Ma, Y.; Cui, G.; Chen, S.; Zhan, X.; Yu, G.; Qin, J.; Hu, W.; Zhu, D. *J. Am. Chem. Soc.* **2005**, *127*, 13283.

(27) Hong, W.; Wei, Z.; Xi, H.; Xu, W.; Hu, W.; Wang, Q.; Zhu, D. *J. Mater. Chem.* **2008**, *18*, 4814.

(28) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGruer, N. E.; Miller, G. P. *J. Am. Chem. Soc.* **2008**, *130*, 16274.

(29) Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, E.; Siegrist, T. *Chem. Mater.* **2004**, *16*, 4980.

decomposition temperatures than pentacene, except **2c** (Table 1). The thermal stability of the hybrids appears to be related to the substitutions in a complicated manner. With increasing number of thienyl moieties, the decomposition temperature first increases then decreases. Similar trend is also observed in the photostability of the **1a**−**1f** series but not on the **2a**−**2f** series. Meanwhile, the alkyl group is found to improve the thermal stability.[30]

In the case of organic p-type semiconducting materials where charge transport occurs predominantly by hopping through HOMOs, the relative HOMO energetic positions are crucial in determining hole injection from the electrodes to the active layer, consequently affecting the threshold voltage and contact resistance of the OFET devices.[31,32] Cyclic voltammetry (CV) was recorded in THF to investigate the LUMO and HOMO positions (Table 1).[33] The energy gaps calculated from CVs are consistent with that obtained from UV−vis spectroscopy. The HOMO levels of compounds **1a**−**1c** or **1d**−**1f** gradually increase with the lengthening of thienyl chains, consistent with a more effective conjugation with the acene cores.[31] The ADT derivatives show the same trend. The theoretical values of HOMO and LUMO have been calculated by density functional theory (DFT) method at B3LYP/6-31G (d) level. The calculation suggested that the HOMO of the ADT derivatives are generally lower than that of the pentacene derivatives, which is confirmed by the CV results. The HOMO−LUMO gaps predicated by DFT calculation are in good agreement with the experimental results, showing a decreases of band gap with the increase of π-electron delocalization.

X-ray single-crystal analysis revealed the exact packing structure of the planar **1d** molecule (Figure 2). **1d** forms a triclinic unit cell that belongs to the P-1 space group with the unit cell parameters $a = 7.7299$ Å, $b = 9.2123$ Å, $c = 12.4220$ Å, $\alpha = 69.112°$, $\beta = 81.845°$, $\gamma = 85.655°$. Figure 2b and c show the stacking pattern of molecule **1d** in the crystal. As expected, there is significant π-overlap with face-to-face interactions of 3.410 Å between stacks.[18]

In conclusion, we have synthesized and characterized two series of new oligothiophene-pentacene hybrid materials. These materials exhibit much higher solubility and significantly improved thermal and photooxidation stabilities compared with the unmodified pentacene and anthradithiophene, and, therefore are promising for high performance solution processed organic electronic applications. Further investigations including OFET device fabrication using the newly synthesized materials are under way.

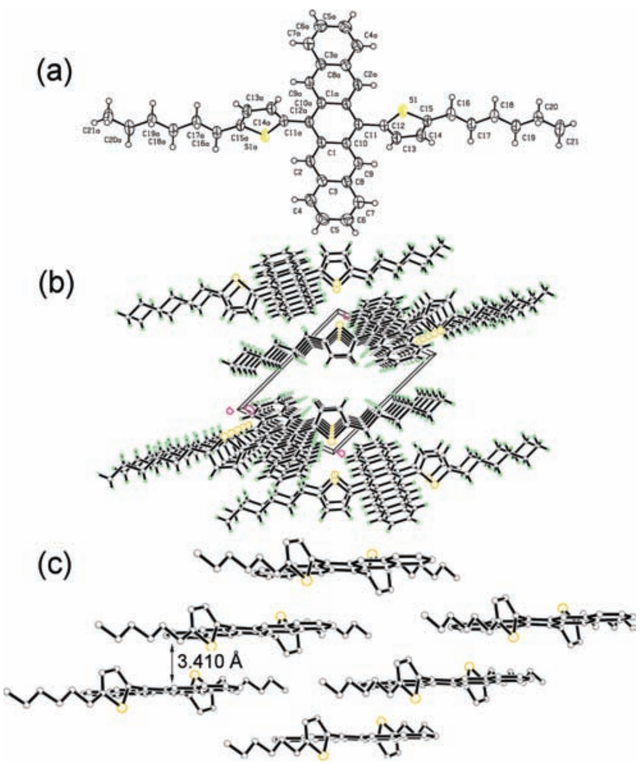


Figure 2. X-ray crystal structure of compound **1d**: (a) molecular structure of **1d**, (b) column stacking of **1d** view along the *c*-axis, and (c) face to face stacking of **1d** in the crystal.

Acknowledgment. This work is supported by Program for New Century Excellent Talents in University (NCET), National Natural Science Foundation of China (NSFC. 20621091, 20872055).

Supporting Information Available: Experimental procedures, solubility data, spectroscopic data, ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL900838A

---

(30) Gao, J.; Li, L.; Meng, Q.; Li, R.; Jiang, H.; Li, H.; Hu, W. *J. Mater. Chem.* **2007**, *17*, 1421.

(31) Yan, Q.; Zhou, Y.; Ni, B.; Ma, Y.; Wang, J.; Pei, J.; Cao, Y. *J. Org. Chem.* **2008**, *73*, 5328.

(32) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296.

(33) Tang, M. L.; Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2006**, *128*, 16002.