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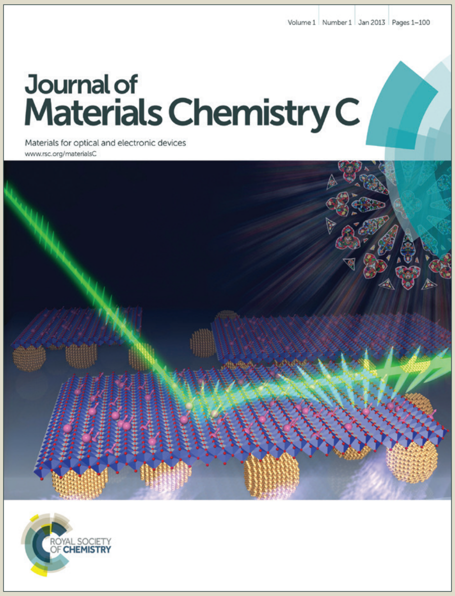

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ARTICLE TYPE

Position Effect of Ethynyl Spacer on Carrier Mobility of Anthracene Derivatives

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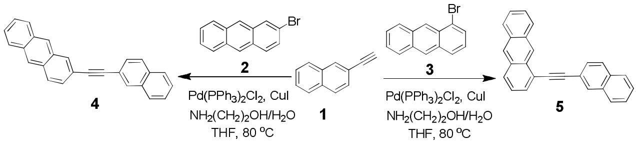
Two oxidation-stable naphthalenyl ethynyl anthracene derivatives have been synthesized via Sonogashiwa coupling. In contrast to 1-position substituted anthracene derivative with near zero mobility, the functionalization at 2-position of anthracene gives rise to a dense packing structure and a uniform film with mobility up to 1.6 cm^2 V^{-1} s^{-1}, which is one of the highest values for thin film transistors based on anthracene derivatives.

Acenes are excellent organic semiconductors for electronic devices because of high charge carrier mobility resulting from the intermolecular overlap of π–π systems.[1,2] Although the hole mobility of pentacene was found to be up to 40 cm^2 V^{-1} s^{-1},[3] the chemical instability have limited the application in electronics. Compared to pentacene, anthracene has a shorter electronic conjugation but much lower HOMO level, endowing with much higher stability. [4,5] In order to achieve high carrier mobility, the π-system of anthracenes has been enlarged by incorporation of other aromatic units via different types of carbon-carbon bonds.[6-23] Compared with double bonds suffering trans/cis-photoisomerization, triple bonds is more photochemically stable. Notably, the ethynyl spacer can effectively keep the planarity of π-system not only at end-positions (2,3,6,7-) but also at peri-positions (1,4,5,8,9,10-) of anthracene.[2] Until now, there are still scare studies on the relationship between ethynyl position and carrier mobility, which is important to shed light on the development of high performance alkynyl substituted anthracens. Herein, we designed and synthesized two new kinds of asymmetric anthracene derivatives by incorporation of 2-ethynylnaphthalene moiety. The modification at 2-position of anthracene endow the compound **4** with dense packing structure, good film forming ability and high hole mobility up to 1.6 cm^2 V^{-1} s^{-1} whereas 1-position substituted derivative **5** has a loose stacking arrangement and a discontinuous sphere-like film with near zero mobility.



Scheme 1 Synthetic route to compounds **4** and **5**.

The synthetic routes for the derivatives are shown in Scheme 1. The compound **1** was synthesized according to the reported literature[19,22]. Then compounds **4** and **5** were obtained in good yields by Sonogashiwa cross-coupling reaction, respectively.

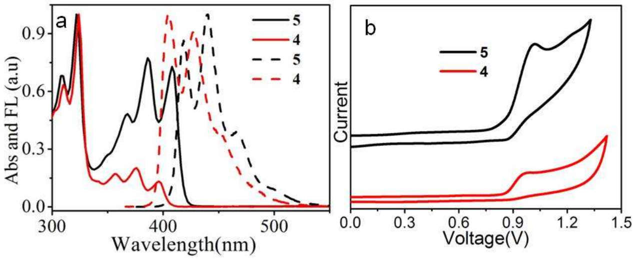


Fig. 1 (a) UV-vis absorption and fluorescence spectra of compounds **4** and **5**. (UV: solid curve; FL：dash curve); (b) Cyclic voltammograms of **4** and **5**.

UV-vis absorption spectra and fluorescent spectra of these two compounds are shown in Fig. 1a. The compounds exhibit similar absorption characteristics. The absorption peaks at around 322 nm attributed to anthracene backbone exhibit no obvious shift for them. The maximum absorption edges for compounds **4** and **5** are 405 nm and 420 nm, respectively, indicating their energy gaps are 3.06 eV and 2.95eV. All peaks of their fluorescence spectra range from about 400 nm to 450nm, giving blue-purple emission.

The redox properties of these compounds are shown in Fig. 1(b). The highest occupied molecular orbital (HOMO) levels for compound **4** and **5** were respectively calculated to be -5.64 eV and -5.66 eV by the onsets of oxidation peak, while their lowest unoccupied molecular orbital (LUMO) levels were respectively calculated to be -2.69 eV and -2.60 eV by HOMO levels and their energy gaps. The summarized results are shown in Table 1. Density functional theory (DFT) was used to calculate their HOMO and LUMO levels in theory. As shown in Fig S1, introduction of 2-ethynylnaphthalene group significantly increases the conjugation area of both **4** and **5**.

Table 1. HOMO-LUMO levels and energy gaps of compounds **4** and **5**.

	TGA (°C)	$E_{ox,onset}$ [eV]	HOMO [eV]	LUMO [eV]	E_g [eV]
4	285	0.86	-5.66	-2.60	3.06
5	258	0.84	-5.64	-2.69	2.95

HOMO levels were estimated by onsets of oxidation peaks vs. Fc/Fc^+ from CV, HOMO = $-4.8-E_{ox,onset}$.

The thermal stability of the two compounds was measured (see Fig. S2). The onset decomposition temperature of compound **4** is 285 ˚C, higher than that of compound **5** (258 ˚C). Different from compound **4** sublimated directly, compound **5** melted first at about 112 ˚C and then evaporated.

Single crystals of these two compounds were obtained from a mixture solvents (toluene-CH_2Cl_2 = 1:2 v/v) through slow evaporation at room temperature (CCDC 1020805 for compound **4** and CCDC 1004478 for **5**, Table S1in ESI†). As shown in Fig. 2 and Fig. S3, the compound **4** forms a usual herringbone packing structure, which belongs to the monoclinic *Cc* space group with lattice constants a = 38.26 Å, b = 5.86 Å, c = 7.49 Å, β = 92.46°. Each molecule has four short naphthalenyl-naphthalenyl C-H···π contacts with four adjacent molecules and two short anthracenyl-anthracenyl C-H···π contacts with two neighbour molecules respectively. Compound **5** also belongs to the monoclinic *Cc* space group with a = 4.89 Å, b = 23.34 Å, c = 15.44 Å, β = 94.07°. Each molecule has only two short naphthalenyl-anthracenyl C-H···π contacts with two nearest molecules. Coplanarity plays an important role in charge transporting behaviours of organic semiconductors.[24, 25] The dihedral angle between anthracene core and naphthalene unit for compound **4** is 1.0 ° while that of compound **5** is 4.6 ° (see Fig. S3), hence the molecular conformation of compound **4** is much planar than that of compound **5**.

Hole transfer integrals for the molecular pairs and intramolecular reorganization energies[26-29] were calculated from the crystals of compounds **4** and **5**. As shown in Fig. S4 and Table S2, the strong transfer integrals of compound **4** are estimated to be 57.73, 99.84 and 54.73 meV for three pairs while only one moderate electronic coupling of 42.60 meV was found in compound **5**. On the other hand, the reorganization energies of **4** and **5** are calculated to be 134 and 144 meV respectively. The results indicate that compound **4** is expected to have higher mobility than **5** due to the much stronger electronic couplings and smaller reorganization energy.

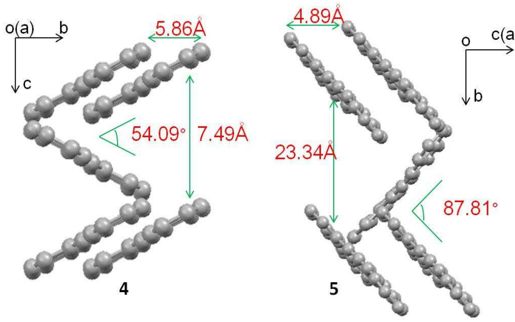


Fig. 2 The packing structure of compound **4** and **5**.

Morphology is a key factor for the performance of organic thin film transistors (OTFTs).[30] To examine the film forming ability of these two compounds, the morphologies of vacuum-deposited thin films both on OTS treated Si/SiO_2 substrate and bare Si/SiO_2 substrate were investigated by optical microscopy. Fig. 3 and Fig. S6-S7 show the optical images of thin films of compound **4** and compound **5** on OTS treated Si/SiO_2 substrate and bare Si/SiO_2 substrate at 20 °C under vacuum deposition conditions, respectively. Together with the thin film XRD analysis,[31] compound **4** formed a leaf-shaped polycrystalline thin films both on OTS treated Si/SiO_2 substrates and bare Si/SiO_2 substrates. Diffraction peaks at 2θ = 4.72°, 9.43°, 13.27°, 14.02°, 18.56°, 23.38° (Fig. 3), correspond to the diffractions of (2,0,0), (4,0,0), (6,0,0), (8,0,0) and (10,0,0) lattice planes of **4**, respectively. The results indicated that the molecules stand nearly perpendicular to the substrate and formed a perfectly packed structure (Fig S5). This orientation is favourable for achieving high mobility, because the stacking direction is consistent with the direction of current flow. On the other hand, compound **5** formed discontinuous sphere-like polycrystalline film. We also have checked different substrate temperature for vacuum-deposition, similar results were obtained. So we can concluded that the film forming ability of compound **4** is much better that that of compound **5**.

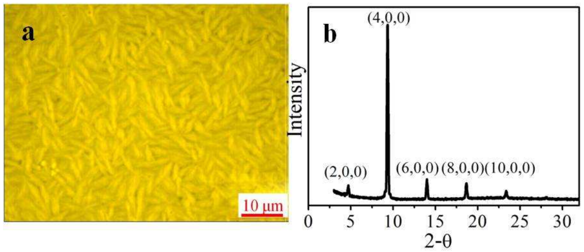


Fig. 3 Thin film optical microscopy (a) and XRD analysis of compound **4** (b) on OTS treated Si/SiO_2 substrate at room temperature.

To investigate the field-effect properties of compounds **4** and **5**, top-contact, bottom-gate of OFETs were fabricated by vacuum-deposition (50 nm) on bare-Si/SiO_2 (300 nm SiO_2) or OTS treated Si/SiO_2 substrates at different temperatures.[32] Representative transfer and output curves at room temperature were shown in Fig. 4 and the others are shown in Table 2.

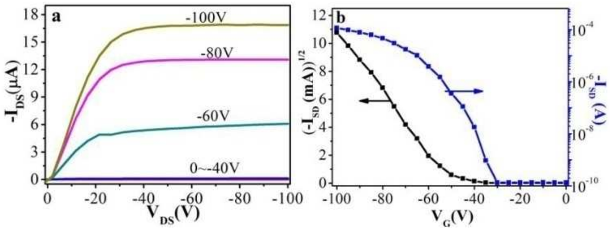


Fig. 4 Typical output (a) and transfer curve (b) of top-contact field-effect transistors based on vacuum-evaporated thin film of compound **4** on OTS treated Si/SiO_2 substrates

The average hole mobility based on 20 devices for compound **4** is 0.5 $cm^2 V^{-1} s^{-1}$ on bare-Si/SiO_2 substrate and 1.2 $cm^2 V^{-1} s^{-1}$ on OTS treated Si/SiO_2 substrates. Substrate temperature has a small effect on the performance. The best field-effect mobility is 1.6 $cm^2 V^{-1} s^{-1}$, current on/off ratio (I_{on}/I_{off}) is about 1.0×10^6, and threshold voltage (V_T) is -48 V, which is among the highest mobility anthracene derivatives. Consistent with poor film morphology of compound **5**, the devices exhibit almost no mobility.

Table 2. Hole mobility of compound **4** and **5**.

	Substrate	Temp(°C)	Average mobility ($cm^2 V^{-1} s^{-1}$)	Highest mobility ($cm^2 V^{-1} s^{-1}$)
4	OTS	20	1.2	1.6
		60	1.1	1.4
		90	1.0	1.2
		120	1.0	1.3
	Bare	20	0.3	0.7
		90	0.3	0.5
5	OTS	20,90	-	-
	Bare	20,90	10^{-5}	10^{-5}

In summary, the effect of ethynyl position on carrier mobility of anthracene derivatives was investigated by synthesis of two naphthalenyl ethynyl substituted derivatives. Compared with the modification at 1-position, the functionalization at 2-position of anthracene afford a much denser packing structure, stronger electronic couplings and better film morphology, leading to high hole mobility up to 1.6 $cm^2 V^{-1} s^{-1}$, which is to the best of our knowledge one of the highest values for thin film transistors based on anthracene derivatives. This work provides insight into the development of high-performance and oxidation-stable alkynyl substituted anthracenes for applications in electronic devices.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis detail of compounds **4** and **5**, TGA of compounds **4** and **5**. CV curve of compounds **4** and **5**, optical image of thin film vacuum-deposited on bare Si/SiO_2 substrates of compounds **4** and **5**, and thin film XRD analysis at different temperatureof compounds **4**. For ESI or other electonic format see DOI: 10.1039/b000000x.

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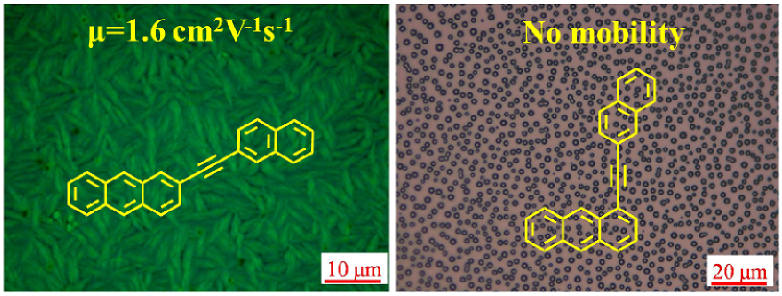
Graphical and textual abstract for “Position Effect of Ethynyl Spacer on Carrier Mobility of Anthracene Derivatives”:



The naphthalenyl ethynyl substitution at 1- and 2- position of anthracene exhibits totally different film forming ability and hole mobility.