Position Effect of Ethynyl Spacer on Carrier Mobility of Anthracene Derivatives

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Experimental Section

Materials and Instrumentations

All reagents were used as received from commercial resources unless otherwise specified.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker ADVANCE 400 NMR Spectrometer. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) and CH_2Cl_2 (5.33 ppm). UV-vis absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. In this experimental setup, it is possible to measure the X-ray diffraction intensity data were collected at 173 K on a Saturn724 + CCD diffractometer with graphite monochromated Mo K\α radiation. And the structure and refinement were carried out using the Crystal Clear (Rigaku Inc., 2008).

Synthesis of compounds 4 and 5

Compound 4: A 100 mL flask was charged with 2-bromoanthracene (1.80 g, 7mmol), copper iodide (115 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (210 mg, 0.3 mmol), aqueous 2-aminoethanol (2 M, 20 mL), and THF (40 mL) under Ar. After the reaction mixture was degassed three times, 2-naphthylacetylene (1.52 g, 10 mmol) was added. The reaction solution was stirred overnight at 80 °C under Ar atmosphere. The aqueous layer was extracted with dichloromethane. The combined organic layer was evaporated under reduced pressure. The crude mixture was purified by recrystallization from toluene to provide compound **4** as yellow power (yield: 1.64 g, 71%).^{1}H NMR (400 MHz, CD_2C_2) δ (ppm): δ9.09 (s, 1H), 8.53 (s, 1H), 8.28 (s, 1H), 8.21 – 8.15 (m, 1H), 8.08 (d, J = 8.6 Hz, 2H), 7.97 – 7.88 (m, 3H), 7.86 (dd, J = 6.9, 1.0 Hz, 1H), 7.80 (dd, J = 8.5, 1.6 Hz, 1H), 7.59 – 7.47 (m, 5H).HR-MS (EI) for $C_{26}H_{16}$:Calculated: 328.1252; Found: 328.1450.

Compound 5: A 100 mL flask was charged with 1-bromoanthracene (1.80 g, 7mmol), copper iodide (115 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (210 mg, 0.3 mmol), aqueous 2-aminoethanol (2 M, 20 mL), and THF (40 mL) under Ar. After the reaction mixture was degassed three times, 2-naphthylacetylene (1.52 g, 10 mmol) was added. The reaction solution was stirred overnight at 80 °C under Ar atmosphere. The aqueous layer was extracted with dichloromethane. The combined organic layer was evaporated under reduced pressure. The crude mixture was purified by recrystallization from toluene to provide compound **4** as yellow power (yield: 1.49 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ8.42 (s, 2H), 8.28 (s, 1H), 8.13 (s, 1H), 8.00 (d, J = 8.8 Hz, 3H), 7.85 (d, J = 8.3 Hz, 3H), 7.65 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.53 – 7.47 (m, 4H). HR-MS (EI) for $C_{26}H_{16}$: Calculated: 328.1252; Found: 328.1053.

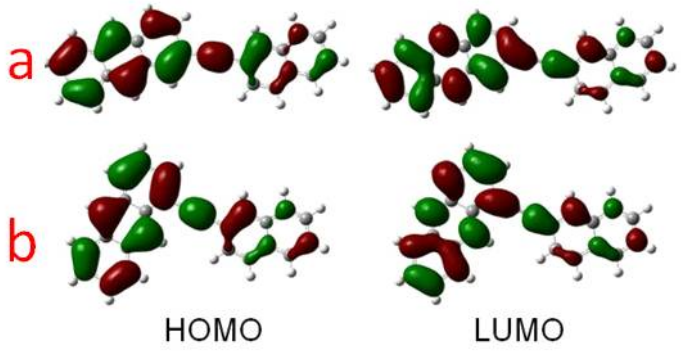


Fig. S1 HOMO and LUMO of **4** (a) and **5** (b) calculated at the B3LYP/6- 31G(d) level.

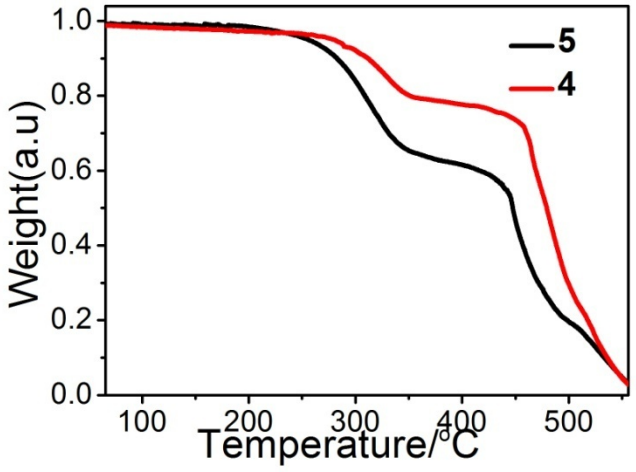


Fig. S2. TGA curves of compound**s 4** and **5**, measured with a heating rate of 10 °C /min in nitrogen.

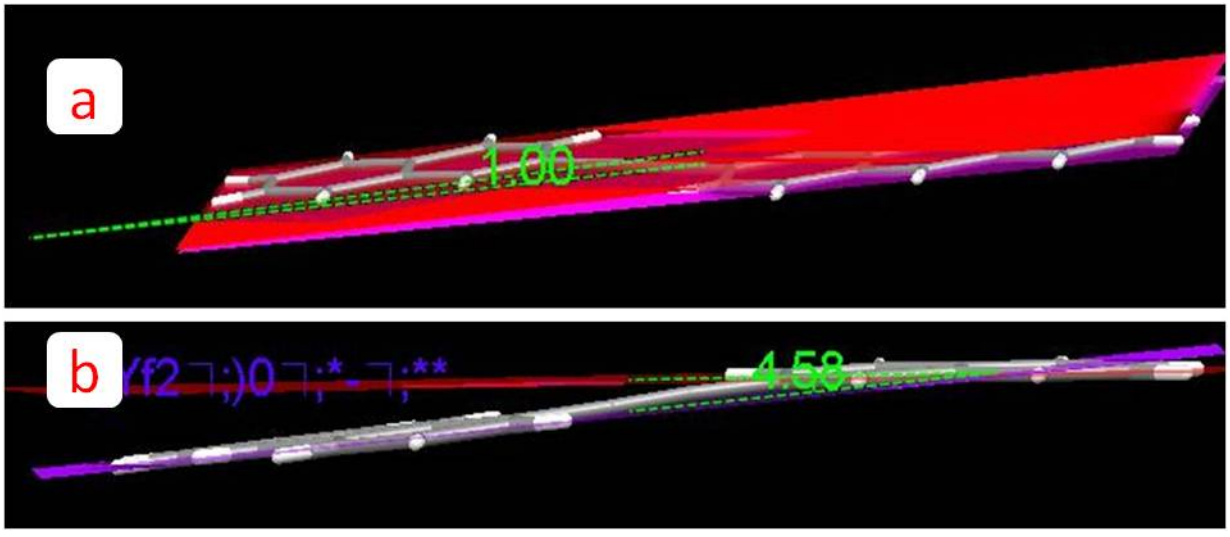


Fig. S3 The configuration and twist angle of **4** (a) and **5** (b).

Table S1 Single crystal diffraction data and structure refinement of compounds **4** (CCDC 1020805) and compounds **5** (CCDC 1004478).

Parameters	**4**	**5**
Empirical formula	$C_{26}H_{16}$	$C_{26}H_{16}$
Formula weight	328.39	328.39
Temperature	173.1500K	296(2)K
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C1c1	Cc
Unit cell dimensions	a=38.26(3)Å , α =90 b= 5.862(4) Å, β= 92.456(9) c=7.489(6)Å, γ =90	a=4.8880(10)Å , α =90.00 b= 23.378(5) Å, β= 94.07(3) c=15.437(3)Å, γ =90.00
Z	4	4
Density (calculated)	1.300 g/cm^3	1.240 g/cm^3
Absorption coefficient	0.074	0.070
F(000)	688	688
Crystalsize(mm)	0.45×0.43×0.03	0.38×0.21×0.07
Thetarange for data collection	1.0655° to27.4694°	1.3224° to27.4696°
Indexranges	-49<=h<=49 -7<=k<=7 -9<=l<=9	-6<=h<=6 -30<=k<=30 -19<=l<=18
Reflections collected	6239	9745
Independent reflections	3537	2013
R_{int}	0.0352	0.0601
Completeness to theta	98.9%	99.3%
Absorption correction	multi-scan	multi-scan
Max. and min. transmission	1.0000 and 0.6993	1.0000 and 0.5409
Data/ restraints / parameters	3537/2/235	2013/2/235
Goodness-of-fiton F^2	1.120	1.276
FinalR indices [I>2sigma(I)]	R_1 = 0.0648 wR_2 =0.1608	R_1 = 0.0748 wR_2 =0.1599
Rindices (all data)	R_1 =0.0592, wR_2 =0.1757	R_1 =0.0667, wR_2 =0.1555
Largest diff. peak and hole	0.288 and -0.202e.Å^{-3}	0.138 and -0.100e.Å^{-3}

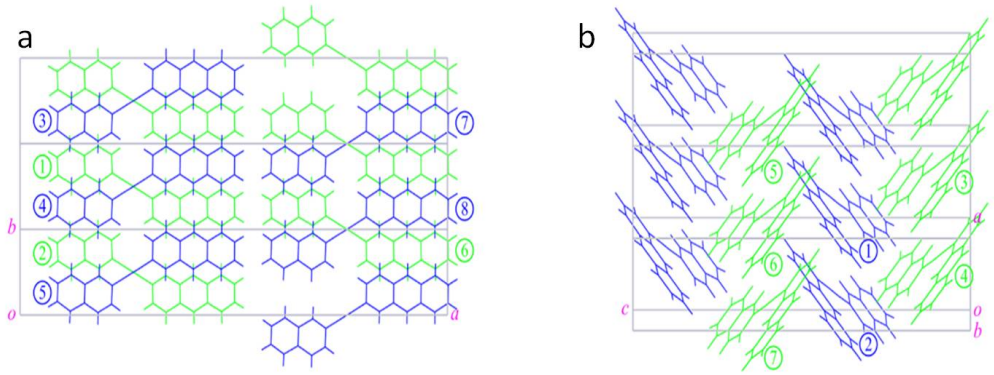


Fig. S4 Crystal structures of compounds **4** (a) and **5** (b) and illustrations for the nearest neighbouring molecular pairs considered in the transfer integral calculation.

Table S2 Hole and electron transfer integrals for the molecular pairs taken from compounds **4** and **5.**

		holes (meV)	electrons (meV)
4	t_{12}	57.733	65.911
	t_{13}	5.076	5.694
	t_{14}	99.835	78.646
	t_{15}	54.733	48.737
	t_{16}	0.833	2.529
	t_{17}	0.853	0.352
	t_{18}	0.645	0.744
5	t_{12}	42.604	9.433
	t_{13}	7.563	2.207
	t_{14}	2.974	1.588
	t_{15}	2.937	1.751
	t_{16}	0.651	8.603
	t_{17}	5.241	10.439

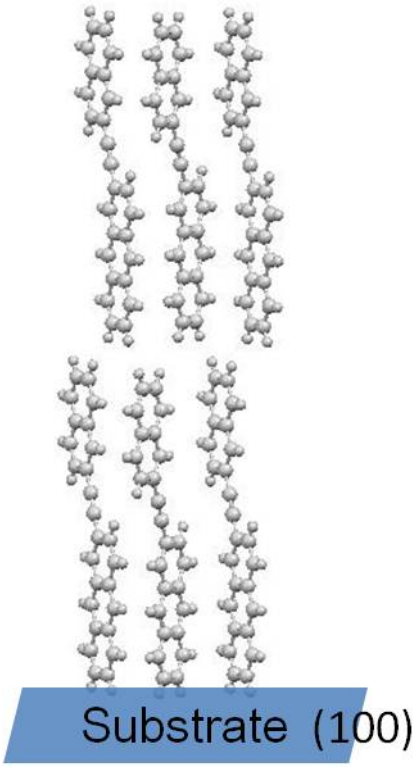


Fig. S5 The molecules of compound **4** were perpendicular to the substrate.

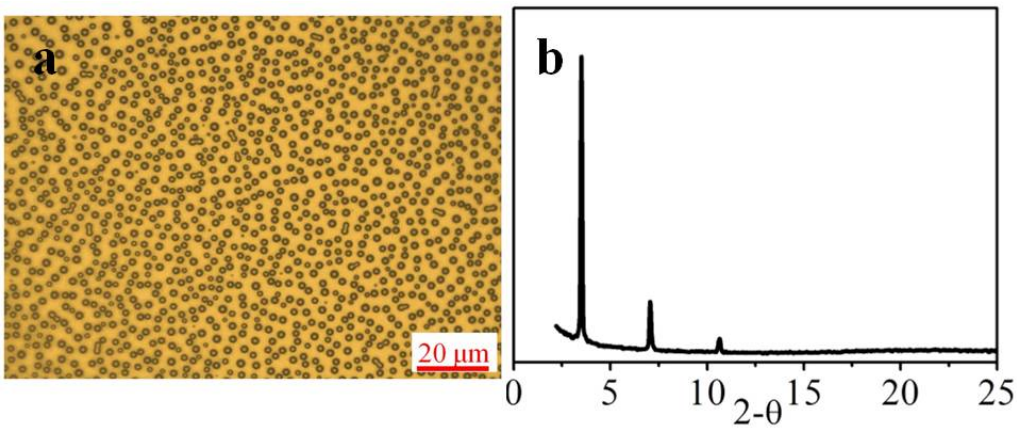


Fig. S6 (a) optical images of thin film of **5** on OTS treated Si/SiO_2 substrate; (b) thin film XRD analysis of compound **5.**

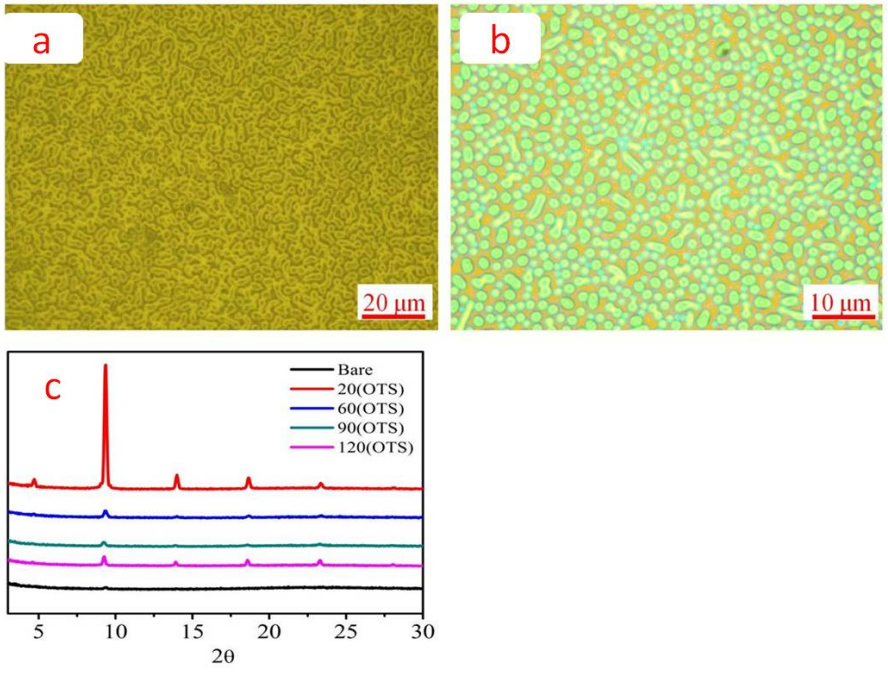
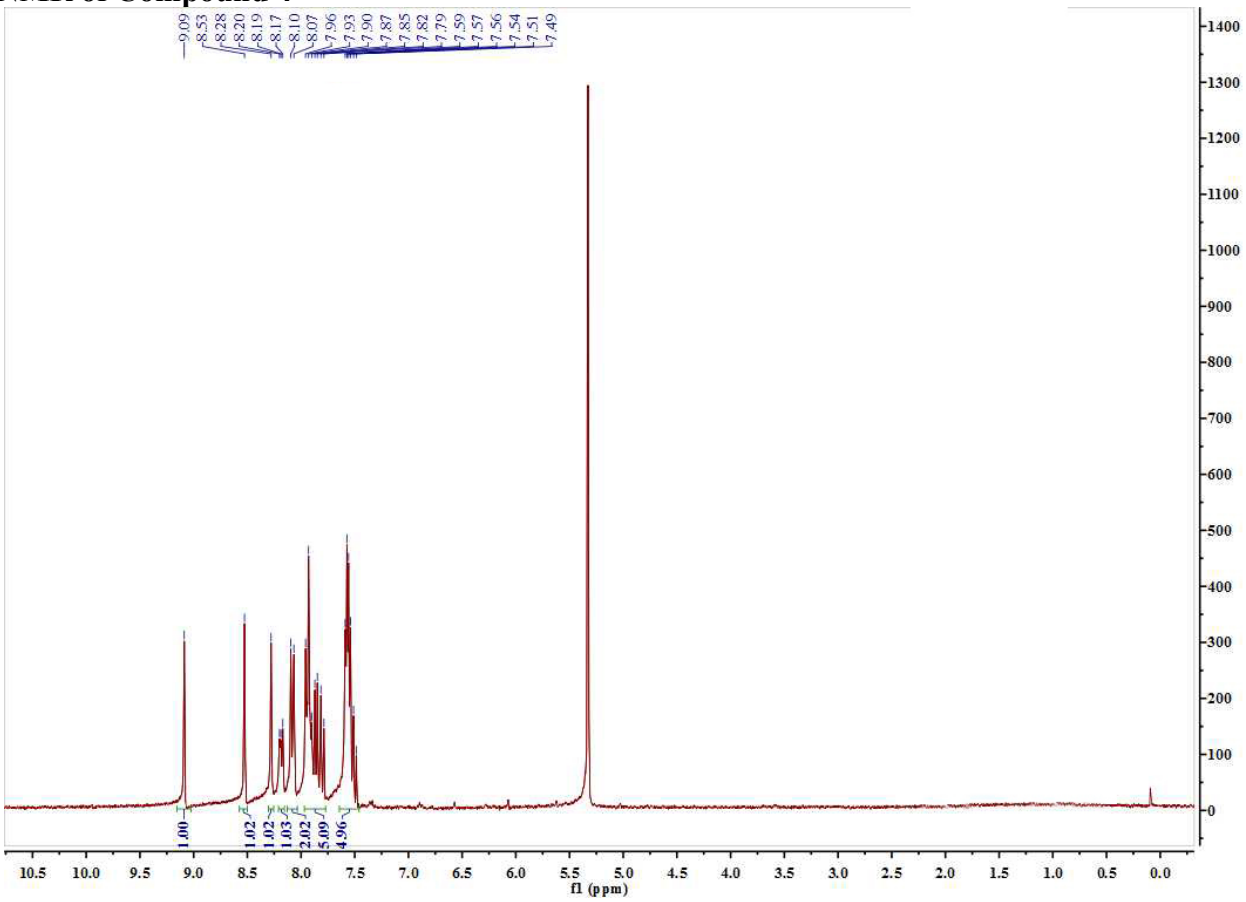


Fig. S7 Optical images of thin film of **4** and **5** on bare Si/SiO_2 substrate, and thin film XRD analysis of compound **4** at different conditions. (a) thin film of **4** on bare Si/SiO_2 substrate; (b) thin film of **5** on bare Si/SiO_2 substrate; (c) thin film XRD analysis of compound **4.**

^{1}H NMR of Compound 4



^{1}H NMR of Compound 5