

High performance, acene-based organic thin film transistors†

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1,4,8,11-Methyl-substituted 6,13-triethylsilylthynylpentacene shows extended π – π overlap when deposited from solution, yielding organic thin film transistors with high and reproducible hole mobility with negligible hysteresis.

New molecular structure plays a key role in optimising the performance of organic electronics whether they are small molecules or oligomeric semiconductors. In the case of acene-based small molecules, the effects of conjugation length and side chain type on solubility and thin film electronic properties have been extensively studied.^{1,2} Organic thin film transistors (OTFTs) based on pentacene exhibit some of the best performance to date with field effect hole mobilities (μ_{FET}) of $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for vacuum deposited³ and $35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for single crystal devices,⁴ respectively. 6,13-substituted pentacene derivatives have been the subject of intensive recent investigation attempting to combine good low cost solution processability with high performance.⁵ Substitution with either alkylthynyl or trialkylsilylthynyl has been shown to both improve solvent solubility whilst disrupting the herringbone packing in pentacene resulting in improved π – π interaction and improved hole mobilities.⁶

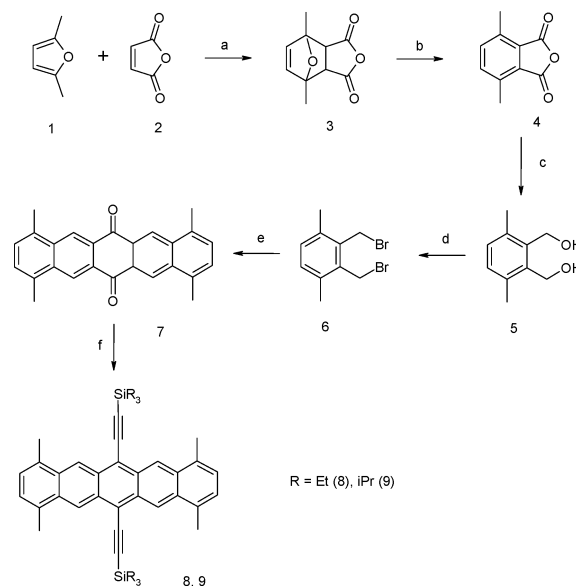
Although 6,13-triisopropylsilylthynylpentacene (TIPSP) has been shown to exhibit hole mobility up to $1.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from solution, extreme care has to be taken with respect to thin film processing conditions with variability in measured mobility values across a single substrate.⁵ Other processes including nanoribbon⁷ or evaporation⁸ permit high mobility devices but move further away from the concept of cheap and large area device fabrication.

In this work we present the first reported study on the synthesis and characterisation of 1,4,8,11-methyl-substituted 6,13-trialkylsilylthynylpentacene. We present two molecules 1,4,8,11-tetramethyl-6,13-triethylsilylthynylpentacene **8** and 1,4,8,11-tetramethyl-6,13-triisopropylsilylthynylpentacene **9** where **8** has a maximum μ_{FET} of $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in air when processed from solution at 70°C with no post-thermal

annealing. Importantly the variability in mobility values across a single substrate is lower than for previously reported 6,13-substituted pentacene derivatives, which is important in the commercialisation of such technology.

Scheme 1 shows the synthetic strategy used. Reduction of 1,4-dimethyl-7-oxobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, **3**, resulted in 50–60% yields similar to those reported in the literature⁹ with the further reduction of 3,6-dimethylphthalic anhydride, **4**, by standard methods¹⁰ to give 3,6-dimethylphthalyl alcohol, **5**. A high yielding route to 6,13-pentacenequinone has been reported *via* 1,2-benzenedicarboxaldehyde.¹¹ We attempted the oxidation of **5** to 3,6-dimethylphthalaldehyde by several literature methods^{12–14} but in all cases a mixture of **5** and 4,7-dimethyl-isobenzofuranone was obtained. Therefore we proceeded *via* the reaction of 3,6-dimethyl-1,2-bis(bromomethyl)benzene, **6**, which was obtained in high yield from **5**, with *p*-benzenequinone to give 1,4,8,11-tetramethyl-6,13-pentacenequinone, **7**, in low yield. **8** and **9** were synthesised by reported methods⁶ and purified using a silica plug.

Single crystals of **8** and **9** were obtained showing the molecules crystallise in a low symmetry $P\bar{1}$ group† with the molecules packed in the highly desirable 2D slip stack structure with an average π – π stacking distance between the



Scheme 1 Synthetic route to molecules **8** and **9**. Reagents and conditions: (a) Et_2O , rt, 60%; (b) H_2SO_4 , -6°C , 50%; (c) LiAlH_4 , THF, 70%; (d) PBr_3 , toluene, 95%; (e) NaI , *p*-benzoquinone, 90°C , DMA 25%; (f) (1) BuLi , trialkylsilylacetylene, (2) SnCl_2 , HCl , THF, 50%.

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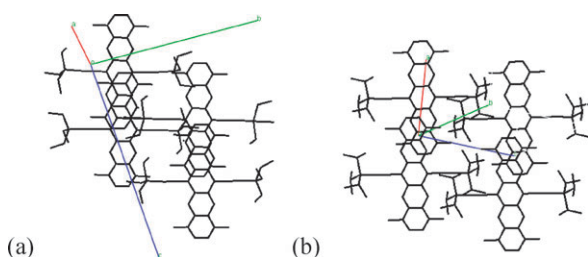


Fig. 1 Molecular packing of **8** (a) and **9** (b) illustrating the packing and π - π overlap.

conjugated pentacene backbones of 3.48 Å similar to TIPSP.^{5,6} Although the interplanar distances are similar for both **8** and **9**, there is significant difference in the extent of fused rings backbone overlap, with **9** being similar to TIPSP whereas **8** shows a significantly greater overlap (Fig. 1). AFM confirms the large difference in packing between **8** and **9** (ESI†). **8** is able to form a nearly continuous film when drop cast from toluene solution onto an OTS modified silica surface, whereas **9** wets only partially. Tapping mode of a thin film of **8** reveals atomic steps of about 1.77 nm, indicating that the molecule packs almost vertically to the substrate in an atomic layer.

Molecular orbital levels of **8** and **9** were measured using cyclic voltammetry in acetonitrile, and UV-vis performed in solution and of thin films (ESI†). Whilst the limitations of this methodology are recognised, we are unable to determine the reduction onset by CV since both materials undergo decomposition on reduction. Results are summarised in Table 1.

It is known that charge transport in disordered crystalline semiconductor obeys a semi-classical hopping charge transfer theory,¹⁵ with factors such as translation along the short axis and ring orientation influencing dramatically the electronic performance of the electronic semiconductor.¹⁶ It has been shown that increasing the extent of π - π overlap can result in an increase in hole mobility at the same π - π stacking distance.¹⁷ Since **8** shows a higher degree of π - π overlap and the same π - π stacking distance of the conjugated backbone as both **9** and TIPSP then a higher hole mobility would be anticipated.

Discrete bottom-gate, top-contact organic field effect transistor (OFET) devices were fabricated on OTS treated heavily *n*-doped silicon wafers comprising a 3000 Å thermally grown gate oxide layer. **8** and **9** were drop cast from 0.5 wt% toluene solution and dried under ambient atmosphere at 70 °C in an open laboratory with no post-thermal annealing. Gold source and drain channel electrodes, 60 µm width and 2 mm

Table 1 Oxidation potentials of **8** and **9** versus SCE reference by comparison to ferrocene and their optical band gap from thin film, determined at an onset absorption peak. Gap is determined from UV absorption edge in liquid state

Compound	8	9
$E_{\text{onset}}/\text{V}$	0.50	0.59
HOMO/eV	5.19	5.39
E_G/eV	1.87	1.87
LUMO/eV	3.32	3.52

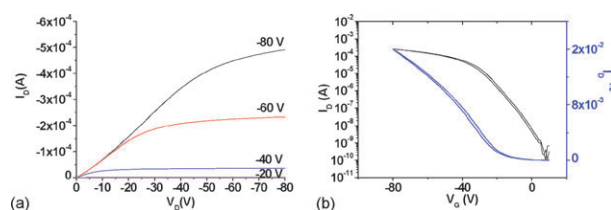


Fig. 2 Typical (a) output and (b) transfer curves for **8** solution deposited from 0.5% w/w toluene at RT on OTS-treated SiO₂.

long, were thermally evaporated, at 10^{-6} mBar, until a layer thickness of 50 nm was obtained, yielding 9 transistors per substrate. Gold was chosen since its work function, 5.1 eV, closely matches the HOMO level of **8** and **9**.

Compound **8** shows very high on/off ratios in excess of 10^7 , with maximum $\mu_{\text{SAT}} = 2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Fig. 2) and with negligible hysteresis and stable low threshold voltage. This device was one of the group of 9 OTFTs fabricated, the mobility range being 0.6 to $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, with an average mobility of $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a standard deviation of $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Compound **9** exhibits a maximum μ_{SAT} of about $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, due to poor film quality and less favourable charge injection. Under equivalent conditions TIPSP¹⁸ drop cast devices exhibit discontinuous film structures and gave maximum μ_{SAT} of $\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

To conclude, we have shown that 1,4,8,11-tetramethyl-6,13-triethylsilyl ethynylpentacene can make excellent OFETs, with high mobilities and on/off ratios when solution processed in air with improved device to device reproducibility as a consequence of the extended π - π overlap. With optimisation of formulation¹⁸ and device architecture it is believed that this new family of compounds will enable all solution processed devices with high performance and excellent reproducibility to be fabricated.

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Notes and references

† Single crystals of compounds **8** and **9** were obtained by solvent diffusion (solvent was 1,2,4-trichlorobenzene and antisolvent was acetonitrile), mounted in inert oil and transferred to the cold gas stream (150 K) diffractometer.

Crystal determination of compound **8**: $\text{C}_{42}\text{H}_{50}\text{Si}_2$, $M = 611.00$, triclinic, $a = 7.3024(2)$, $b = 10.9762(3)$, $c = 12.1090(4)$ Å, $\alpha = 74.402(3)^\circ$, $\beta = 89.953(2)^\circ$, $\gamma = 73.746(2)^\circ$, $U = 894.55(5)$ Å³, $T = 100$ K, space group $P1$ (no. 2), $Z = 1$, 13 549 reflections measured, 3297 unique ($R_{\text{int}} = 0.077$) which were all used in the calculations. The final $wR(F_2)$ was 0.1991 (all data) and R_1 0.0771 ($I > 3\sigma(I)$).

Crystal determination of compound **9**: $\text{C}_{48}\text{H}_{62}\text{Si}_2$, $M = 695.16$, $a = 9.0135(6)$, $b = 10.2107(5)$, $c = 11.7743(8)$ Å, $\alpha = 70.694(2)^\circ$, $\beta = 84.900(2)^\circ$, $\gamma = 82.342(5)^\circ$, $U = 1012.41(11)$ Å³, $T = 100$ K, space group $P1$ (no. 2), $Z = 1$, 5600 reflections measured, 3548 unique ($R_{\text{int}} = 0.098$) which were all used in the calculations. The final $wR(F_2)$ was 0.2784 (all data) and R_1 0.1180 ($I > 3\sigma(I)$).

- M. M. Payne, S. R. Parkin, J. E. Anthony, C.-C. Kuo and T. N. Jackson, *J. Am. Chem. Soc.*, 2005, **127**, 4986.
- J. E. Anthony, J. S. Brooks, D. L. Eaton and S. R. Parkin, *J. Am. Chem. Soc.*, 2001, **123**, 9482.
- H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik and W. Weber, *J. Appl. Phys.*, 2002, **92**, 5259.

- 4 O. D. Jurchescu, J. Baas and T. M. Palstra, *Appl. Phys. Lett.*, 2004, **84**(16), 3061.
- 5 S. K. Park, T. N. Jackson, J. Anthony and D. A. Mourey, *Appl. Phys. Lett.*, 2007, **91**, 063514.
- 6 J. E. Anthony, D. L. Eaton and S. R. Parkin, *Org. Lett.*, 2002, **4**, 15.
- 7 D. H. Kim, D. Y. Lee, H. S. Lee, W. H. Lee, Y. H. Kim, J. I. Han and K. Cho, *Adv. Mater.*, 2007, **19**, 678.
- 8 D. Sheraw, T. N. Jackson, D. L. Eaton and J. E. Anthony, *Adv. Mater.*, 2003, **15**, 2009.
- 9 T.-L. Chan, T. C. W. Mak, A.-D. Poon, H. N. C. Wong, J. H. Jia and L. L. Wang, *Tetrahedron*, 1986, **42**, 655.
- 10 G. M. Rubottom and J. E. Way, *Synth. Commun.*, 1984, **14**, 507.
- 11 N. Vets, M. Smet and W. Dehaen, *Tetrahedron Lett.*, 2004, **45**, 7287.
- 12 O. Farooq, *Synthesis*, 1994, **10**, 1035.
- 13 R. A. Fernandes and P. Kurman, *Tetrahedron Lett.*, 2003, **44**, 1275.
- 14 Y.-Y. Ming, T. C. W. Mak and H. N. C. Wong, *J. Org. Chem.*, 1990, **55**, 3214.
- 15 C. Reese and Z. Bao, *J. Mater. Chem.*, 2006, **16**, 329.
- 16 J. L. Bredas, J. P. Calbert, D. A. da Silva Filho and J. Cornil, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5804.
- 17 H. Moon, R. Zeis, C. Besnard, A. J. Lovinger, T. Siegrist, C. Kloc and Z. Bao, *J. Am. Chem. Soc.*, 2004, **126**, 15322.
- 18 M.-B. Madec, D. C. Crouch, G. R. Llorente, T. J. Whittle, M. Geoghegan and S. G. Yeates, *J. Mater. Chem.*, 2008, **18**, 3230.