

Recent advances in organic field effect transistors

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Abstract: We review the progress in the performance of organic field effect transistors that has been reported in the last 30 years, with a major emphasis on the last 10 years. We focus on the best performing organic semiconductors, and elucidate the underlying relations between the chemical and physical structures of the materials in the solid state and their electronic properties.

Key words: Organic semiconductors, mobility, organic transistors, large area electronics

1. Introduction

Organic semiconductors have been studied for the last 60 years [1]. They have already had a significant technological impact in optoelectronic applications such as xerography, organic electroluminescent devices [2–4], and organic photovoltaic cells [5–9]. Organic thin-film field-effect transistors (OTFTs), on the other hand, despite their great promise, have not found their way into commercial products by the time of writing. The main reason for this is likely the existence of competing inorganic semiconductor thin film technologies, such as the entrenched hydrogenated amorphous silicon (a-Si:H) thin film transistor (TFT) technology (field effect mobility between 0.1 and $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which is used in active matrix liquid crystal displays (AMLCDs) [10], and ZnO, which is a newer technology, exhibits higher mobility than a-Si:H (about $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [11], and can be compatible with some plastic substrates. However, in the last 3 years, tremendous progress in OTFT performance has been observed, and this can be a game changer, as it can enable applications previously unattainable by OTFTs, including AMLCDs and active matrix organic light emitting diode displays (AMOLEDs) on transparent plastics. AMOLEDs require TFT performance higher than that offered by a-Si:H TFTs, and closer to the performance of polycrystalline Si transistors. In this review we focus mainly on the extraordinary OTFT performance improvements that have taken place in the last few years. We restrict our review to transistors in which the organic active layer is a thin film. It has been shown that just a few complete monolayers of an organic semiconductor are sufficient for proper transistor operation [12,13]. We include representative examples from various classes of organic semiconductors, fabrication processes, and OTFT designs. Some older papers that, in the authors' opinion, played a pivotal role in shaping the OTFT field are also reviewed briefly, but the reader is encouraged to look up a number of previously published review papers that cover that period in more detail [14–25]. In addition, reported results from single crystal organic field effect transistors will be used to estimate the upper limits of mobility for the various organic semiconductors and to gain a better understanding of the underlying device physics.

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As with inorganic semiconductors, organic semiconductors can function as either p-type or n-type. In p-type semiconductors the majority carriers are holes, while in n-type the majority carriers are electrons. Interestingly, most organic semiconductors exhibit strong trapping of electrons but much weaker trapping behavior for holes. As a result, reported organic field-effect transistors (OFETs) typically show p-type, but not n-type conduction even with the necessary low work function electrodes, except for a few organic semiconductors that possess high-electron-affinity. An explanation for this behavior was provided in a paper by Chua et al., who demonstrated that the use of an appropriate hydroxyl-free gate dielectric can yield n-channel FET conduction in most conjugated polymers, which would exhibit exclusively p-type characteristics with a standard SiO₂ gate dielectric [26]. Based on this understanding, we will not make a specific classification of organic semiconductors as p-type or n-type in this paper—this had been traditionally the *modus operandi* in earlier OTFT reviews—since the same organic semiconductors can be rendered p-type or n-type with appropriate doping on an appropriate dielectric.

2. Progress in performance of OTFTs, 1984 to 2014

In 2 previous papers written more than a decade ago [19,27] we presented a semilogarithmic plot of each year's highest reported field-effect mobility value from TFTs based on various organic semiconductors. Herein, we include an updated version of that plot (Figure 1). The data of Figure 1 are represented in tabular form in the Table, which comprises the data in the referenced plot and also the highest field effect mobilities demonstrated using organic semiconductor thin films subsequent to the earlier report [19], namely during the last 12 years. The highest mobilities measured from OFETs with macroscopic, 3D single crystal channels are also included in Figure 1 (red plot) and the Table for comparison.

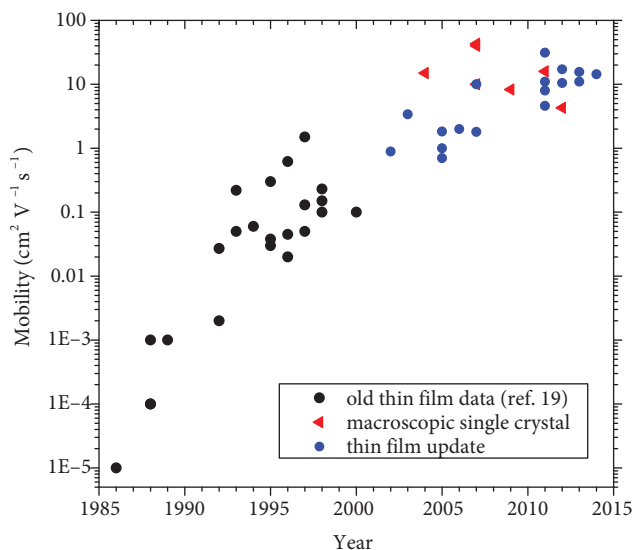


Figure 1. Semilogarithmic plot of each year's highest reported field-effect mobility value from TFTs based on various organic semiconductors. Pre-2002 data (black circles) from reference 19. Figure 1 includes updated data based on the contents of the Table that also comprises the highest field effect mobilities demonstrated using organic semiconductor thin films during the last decade (blue circles). The highest mobilities measured from OFETs with macroscopic, 3D single crystal channels are also included for comparison (red triangles).

Table. Compilation of the highest field effect mobilities demonstrated using various organic semiconductor thin films from 1984 to 2014. The highest mobilities measured from OFETs with macroscopic, 3D single crystal channels are also included for comparison.

Year	Mobility ^[*] (cm ² V ⁻¹ s ⁻¹)	Material (deposition method) (v) = vacuum deposition (s) = from solution (s.c.) = macroscopic single crystal OFET	Reference
1964	NR ^[†]	Cu-phthalocyanine (v) (first demonstration of field effect in small organic molecules)	28
1983	NR	Polyacetylene (s) (first demonstration of field effect in polymers)	10
1984	1.5×10^{-5}	Merocyanine	29
1986	10^{-5}	Polythiophene (s)	30
1988	10^{-4} 10^{-3} 10^{-4}	Polyacetylene (s) Phthalocyanine (v) Poly(3-hexylthiophene) (s)	31 32 33
1989	10^{-3} 10^{-3}	Poly(3-alkylthiophene) (s) α -sexithiophene (v)	34 35
1992	0.027 2×10^{-3}	α -sexithiophene (v) Pentacene (v)	36 36
1993	0.05 0.22	α - ω -dihexyl-sexithiophene (v) Polythienylenevinylene (s)	37 38
1994	0.06	α - ω -dihexyl-sexithiophene (v)	39
1995	0.03 0.038	α -sexithiophene (v) Pentacene (v)	13 40
1996	0.02 0.045 0.62	Phthalocyanine (v) Poly(3-hexylthiophene) (s) Pentacene (v)	41 42 43
1997	1.5 0.13 0.05 0.01	Pentacene (v) α - ω -dihexyl-sexithiophene (v) Bis(dithienothiophene) (v) <i>trans-trans</i> -2,5-Bis-[2-5-(2,2'-bithienyl)ethenyl]thiophene (BTET) (v)	44 27 45 46
1998	0.1 0.23 0.15	Poly(3-hexylthiophene) (s) α - ω -dihexyl-quaterthiophene (v) Dihexyl-anthradithiophene	47 48 49
2000	0.1	α - ω -dihexyl-quinquethiophene (s)	50
2002	0.89	Pentacene from precursor (s)	51,52
2003	3.4	Pentacene (v)	53
2004	15.0	Rubrene (s.c.)	54,55
2005	0.7	Rubrene (s)	56
2005	1.0	Triethylsilyl derivative of anthradithiophene (s)	57
2005	1.8	5,5'-bithiazole with trifluoromethylphenyl end groups (n-type) (v)	58
2006	2.0	2,7-Diphenyl[1]benzothieno[3,2-b]benzothiophene (or DPh-BTBT) (v)	59
2007	1.8	TIPS-pentacene (s)	60
2007	15.0 - 40.0	Pentacene (s.c.)	61
2007	43.0	Rubrene (s.c.)	62
2007	10.0	Hexamethylenetetrafulvalene (HMTTF) (s.c.)	63

Table. Continued.

2007	10.0	titanyl phthalocyanine (TiOPc), α -phase (v)	64
2009	8.3	dinaphtho[2,3- <i>b</i> :2',3'- <i>f</i>]thieno[3,2- <i>b</i>]-thiophene (DNTT) (s.c.)	65
2011	31.3	2,7-dioctyl[1]benzothieno[3,2- <i>b</i>][1]benzothiophene (C ₈ -BTBT), (s.c.), (ink-jet printed), (s)	66
2011	4.6	TIPS-pentacene (s), with strained lattice	67
2011	8.0	C ₁₀ -DNTT (v)	68
2011	11.0	C ₁₀ -DNTT (s)	69
2011	16.0	dianthracen-[2,3- <i>b</i> :2',3' <i>f</i>]thieno[3,2- <i>b</i>]thiophene (DATT) (s.c.)	– 70
2012	4.3	Hexacene (s.c.)	71
2012	17.2	Asymmetric C ₁₃ -BTBT (v)	72
2012	10.5	Alternating D-A polymer with donor moiety, dithienylthieno[3,2- <i>b</i>]thiophene (DTT) and acceptor moiety, N-alkyl diketopyrrolo-pyrrole (DPP) (s)	73
2013	11.0	TIPS-pentacene (s), OTFTs with single crystal domains and nonequilibrium crystal structure.	74
2013	15.6	End-substituted <i>bis</i> (benzothieno)naphthalenes (BBTN) (v)	75
2014	14.4	(D-A) polymer semiconductor: poly(thienoisindigo-alt-naphthalene) (PTIIG-Np) (s)	76

[*] Measured at room temperature

[†] NR= Not reported

The Table lists the highest field-effect mobility (μ) values, as reported in the literature, annually from 1984 to the present time for each of several important organic semiconductors. For a specific organic semiconductor that already has an entry in the Table and Figure 1 for any previous year, a new mobility value is entered only if it is higher than the value of the preceding entry. Additionally, the Table provides information on the deposition method used to make the thin film channels in OTFTs ((v) = vacuum deposition, (s) = deposition from). In cases that the data refer to macroscopic single crystal OFET measurements, the designation “s.c.” is used. For specific protocols and methods for measuring the field effect mobility of organic semiconductors used as active channels in thin film transistors, the reader is directed to reference 19.

From the Table and Figure 1, we can observe that in the 12 years since our previous comprehensive review of the progress in organic thin film transistors [19] serious increases in mobility have taken place. While in 2002 organic semiconductor thin film mobilities rivalled the mobility levels of a-Si:H TFTs (mobility up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), today there are a few classes of organic semiconductors whose thin films exhibit field effect mobilities 1 order of magnitude higher. Such performance improvements are the result of several new scientific and technological developments: (i) Molecular design and synthesis of new organic semiconductor materials, in order to optimize the electronic properties of the individual molecules, and in addition facilitate the control of the molecular arrangement within the organic solid. The latter, in turn, allows the maximization of the molecular orbital overlap and the minimization the $\pi - \pi$ stacking distance of nearest neighbor (n.n.) molecules, and thus the enhancement of the electronic transport properties. (ii) Improved organic semiconductor deposition and/or growth processes and improved interfaces [44,77–79] that result in lower impurity levels, fewer structural defects

(vacancies, dislocations, stacking faults, grain boundaries), and better molecular packing and orientation. (iii) Better device configuration and/or design, component materials, and fabrication processes.

Based on the semiclassical Marcus electron transfer theory [80,81] and further theoretical work [82–85], charge transfer in defect-free organic semiconductors depends mainly on electron–electron and electron–phonon interactions. According to the formalism in these works, there are 2 main parameters describing the charge transfer rate k_{ET} : the transfer integral (t) and the reorganization energy (λ), as expressed by the following equation [86]:

$$k_{ET} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} t^2 \exp\left(-\frac{\lambda}{4k_B T}\right),$$

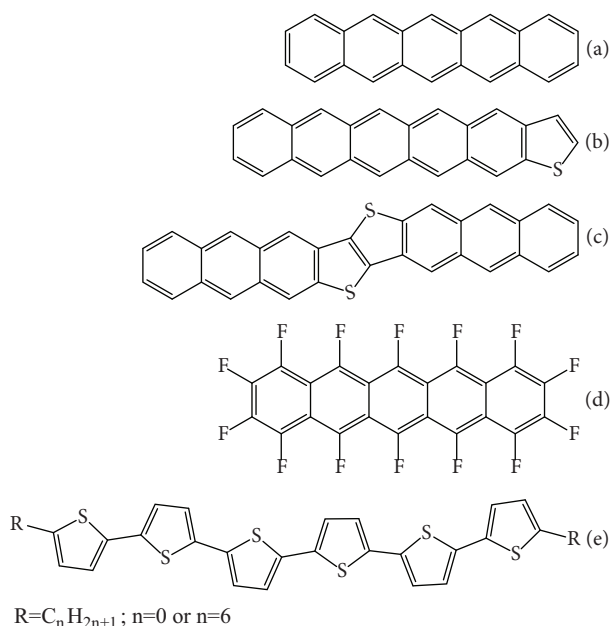
where T is the temperature, h is the Planck constant, and k_B is the Boltzmann constant. t represents the extent of electronic coupling and thus the molecular orbital overlap between n.n. molecules, and depends strongly on the $\pi - \pi$ stacking distance and the orientation of the n.n. molecules relative to each other. The term λ represents the amount of energy required to impose the geometrical reorganization of the molecular structure resulting from the transfer of a single charge to the molecule (internal contribution), as well as the change in polarization of the surrounding medium (external contribution) [86]. An organic semiconductor exhibiting a large transfer integral and small reorganization energy is a promising candidate for producing high electron or hole mobility.

Organic semiconductors can be small molecules, oligomers, or polymers. What these 3 molecular systems have in common is a long π -conjugated section or sections, often called the conjugated core(s). The conjugated core can extend from one end to the other in small molecules or oligomers, or can be a major portion of the repeat unit (monomer) in a polymer. The π -conjugated core is the structure that is responsible and necessary for carrier delocalization along the long axis of the molecules, and thus intramolecular charge transport. Intermolecular charge transfer between n.n. molecules is enhanced by increasing the overlap of the π -orbitals of n.n. conjugated cores. A typical conjugated core can consist of a number of fused benzene rings arranged in a linear fashion as for example in the acene series (Scheme 1a). Modified conjugated cores have been designed starting with an acene and replacing 1 or more of the fused benzene rings with 1 or more 5-member heterocyclic systems rings, respectively, containing a heteroatom (e.g., S, Se, and N). Two examples of such substitution are pentaceno[2,3-b]thiophene (Scheme 1b) [87], where 1 end ring of hexacene is replaced by a thiophene ring, and dianthra[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DATTT, Scheme 1c), a heteroarene with 8 fused aromatic rings from which the 2 central rings are thiophene [70,88]. Such heteroatoms can strongly affect the electronic properties of an organic semiconductor (conduction and valence band levels, band gap, etc.) as well as n.n. intermolecular interactions. A review of the effect of heteroatom substitution on crystal structure and n.n. intermolecular interactions can be found in a recent paper by Dong et al. [89].

Further modification of the conjugated core can take place by changing the core substituents, for example from a typical hydrogen substitution in pentacene to a substitution with electron withdrawing groups, such as halogen atoms or CN. Such substitution usually leads to more environmentally stable organic semiconductors and often a conversion from p-type dominant character to n-type. Both of these consequences are the result of the increase in both the electron affinity and ionization potential of the core-substituted molecule. A representative case is the core substitution of pentacene H with F to form perfluoropentacene, which converts p-type pentacene to n-type perfluoropentacene (Scheme 1d) [90].

Side chains attached on conjugated cores increase the solubility of the organic semiconductor, and more importantly they influence strongly the molecular packing and orientation in the solid (thin film or 3D crystal). As a result they have a substantial impact in the processability and performance of organic semiconductors. The

synthesis and fabrication of OTFTs based on polycrystalline, vapor deposited α sexithiophene (6T, Scheme 1e with $n = 0$) [35,36] and its derivative with insulating end-attached alkyl side chains $\alpha - \omega$ -dihexyl-sexithiophene (DH6T, Scheme 1e with $n = 6$) [37] films reported by Garnier et al. played an important role in the evolution of the field of organic transistors. These publications delineated the strategies that should be followed as far as molecular orientation and packing are concerned in order to increase the performance of OTFTs. In the case of chain- or rod-like molecules, such as thiophene oligomers, large π -conjugation lengths along the long axis of the molecule and close molecular packing of the molecules along at least 1 of the short molecular axes (π -stacking) were shown to be 2 important conditions for high carrier mobility. These principles also operate in OTFTs based on polycrystalline, vapor deposited pentacene thin films, which does not have side-chain substitution [19,40,44].

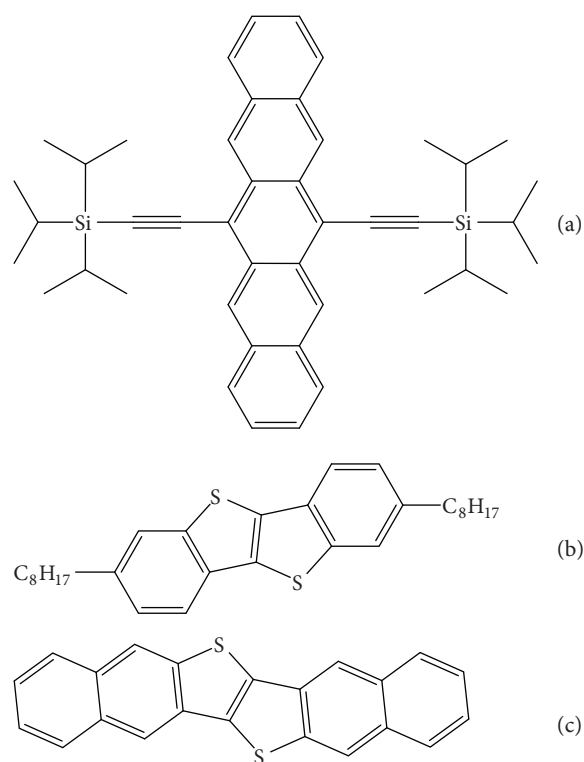


Scheme 1

Alkyl or aryl substitution at peri-positions of the archetypal pentacene and tetracene molecules has also been studied [91,92]. The 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-PEN, Scheme 2a) not only is solution processable but also changes its packing arrangement from the standard herringbone pattern of pentacene to a face to face 2D-bricklayer arrangement that increases molecular orbital overlap and enhances mobility. Mobilities up to $1.8 \text{ cm}^2/\text{Vs}$ were measured from drop cast films in 2007 [60], which was later increased to $4.6 \text{ cm}^2/\text{Vs}$ in a strained metastable thin film that exhibited a reduced $\pi - \pi$ stacking distance compared to unstressed films. Recently, Diao et al. reported OTFTs with mobility up to $11 \text{ cm}^2/\text{Vs}$ by using a micropillar-patterned printing blade to induce recirculation in the TIPS-pentacene solution to enhance crystal growth and engineer the curvature of the solution meniscus to control crystal nucleation, an impressive performance for solution processed transistors potentially compatible with large-area, roll-to-roll fabrication.

A longer conjugated core results in higher mobility, as shown clearly by comparison of the experimentally measured single crystal mobilities of the members of the acene series anthracene, tetracene, and pentacene, which are 0.02 (at low temperature), 0.4 [93] to 2.4 [94], and 15 to 40 cm^2/Vs [61], respectively. The same trend was also demonstrated by theoretical modelling, for all the members of the acene series from naphthalene

to hexacene, in which the mobility increases monotonically from 0.0511 to 1.461 cm^2/Vs [71]. Unfortunately, the increased mobility with longer conjugation lengths is accompanied by reduced environmental stability and solubility of the longer acenes. The former is a consequence of the increase of the HOMO level of the acene molecules with conjugation length. Going from anthracene to hexacene the HOMO level rises from -5.7 eV to -4.7 eV [71,95], which makes the longer acenes more prone to oxidation. The use of heterocyclic rings in place of one or more benzene rings in fused ring conjugated systems (e.g., heteroacenes) has proven to be a successful strategy for increasing their stability as well as their charge transport performance. The degree of aromaticity of the heteroacenes is lower than that of the corresponding acene compounds, due to the increased charge localization induced by the heteroatoms. Thus, while the conjugation length remains extended, the HOMO levels remain high (higher than the corresponding acenes with equal conjugation length), which results in an improved environmental stability without compromising performance [59,95].

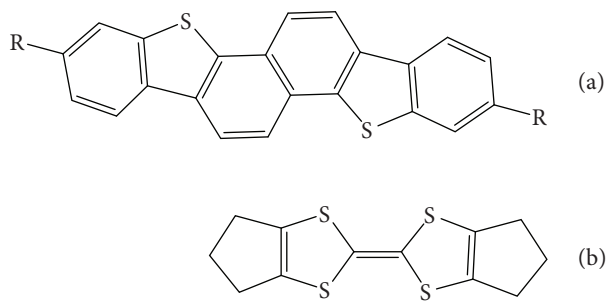


Scheme 2

Inserting 2 fused thiophene rings in the middle of acene molecules has shown very promising performance and stability. In 2006 vacuum deposited films of 2,7-diphenyl[1]benzothieno[3,2-b]benzothiophene (or DPh-BTBT) exhibited a mobility value of $2.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [59], and in 2011 ink-jet printed single crystals of another BTBT side chain derivative (2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene or C_8 -BTBT, Scheme 2b) exhibited unprecedented mobilities for a solution processed organic semiconductor channel, up to $31.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [66]. Vacuum deposited films of asymmetrically substituted C_{13} -BTBT (1 sided end substitution) exhibited mobility up to $17.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in 2012 [72], another very high mobility value that a few years ago was practically unthinkable for organic semiconductor thin films. Another promising molecule of this class, dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]-thiophene (DNTT, Scheme 2c) exhibited single crystal mobility of

8.3 cm² V⁻¹ s⁻¹ in 2009 [65], while the mobility of vacuum deposited films of DNNT was 3.1 cm² V⁻¹ s⁻¹ [87]. In a demonstration of the effectiveness of end substitution of the conjugated core in enhancing charge transport performance, the mobility of vacuum deposited films of alkyl end-substituted C₁₀-DNNT was increased to 8.0 cm² V⁻¹ s⁻¹ [68], and that of solution processed films of the same molecule reached a value of 11.0 cm² V⁻¹ s⁻¹ [69]. Such performance, coupled with the enhanced stability of this class of organic semiconductors, is very promising for the future of large area flexible electronics. A derivative of DNNT, dianthra-[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene (DATT, Scheme 1c), which was predicted by computational studies to have high mobility characteristics [70], was synthesized, and single crystal OFETs were fabricated that indeed exhibited very high mobilities (16 cm² V⁻¹ s⁻¹ in the linear regime) [70].

In a very recent paper, Kurihara et al. [75] synthesized end substituted bis(benzothieno)naphthalenes (BBTNs, Scheme 3a), a heterocyclic system with 6 fused rings, of which 4 are benzene and 2 thiophene rings (second and fifth ring). Thus the central part of the BBTN molecule is a naphthalene moiety. The highest mobility of 15.6 cm² V⁻¹ s⁻¹ was exhibited by vacuum deposited thin films of the C₇-BBTN molecule. The molecular arrangement in the solid state was a typical herringbone structure with the long axis of the molecules being almost perpendicular to the substrate, a typical effect of the alkyl chain end substitution [37].



Scheme 3

Hexamethylene tetrathiafulvalene [96] (HMTTF, Scheme 3b) single crystals showed mobility of 10 cm² V⁻¹ s⁻¹ [63], which is the highest mobility among the promising class of organic semiconductors based on derivatives of the widely studied TTF molecule. HMTTF crystallizes in a ‘bricklayer’ packing motif (like TIPS-PEN), in which the molecules are stacked along the short b-axis with strong $\pi - \pi$ stacking interactions [57]. As a result, each molecule has large co-facial overlaps ($\pi - \pi$ interactions) with 2 molecules in the layer above it and 2 molecules in the layer below it. Furthermore, it has edge-to-edge interactions with the nearest neighbor molecules within its own layer (Figure 2).

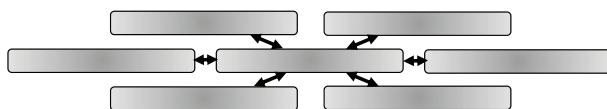


Figure 2. Bricklayer molecular stacking motif along the short axis of an organic semiconductor molecule that crystallizes in this way (e.g., TIPS-PEN or HMTTF).

Titanyl phthalocyanine (TiOPc), an approximately 2D molecule crystallizing in its α -phase structure, also adopts a ‘bricklayer’ packing configuration that leads to strong $\pi - \pi$ interactions, and resulted in mobilities up to 10 cm² V⁻¹ s⁻¹, measured in vacuum deposited thin films.

In the class of polymeric organic semiconductors, there has been tremendous progress in performance recently. Li et al. [73] reported that through synthesis and processing optimization of a conjugated, alternating donor–acceptor (D–A) polymer comprising a relatively strong donor, dithienylthieno[3,2-b]thiophene (DTT), and a weaker acceptor, N-alkyl diketopyrrolo-pyrrole (DPP), a simple DPP-DTT-based conjugated polymer could be produced, which exhibited very high hole mobility for a solution-processable polymer (up to $10.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [73] together with a high current on/off ratio of 10^6 . Excellent shelf-life and operating stability under ambient conditions is another important positive attribute of these D-A polymers.

Very recently, Kim et al. [76] reported the synthesis of another (D–A) polymer semiconductor: poly(thienoindigo-alt-naphthalene) (PTIIG-Np) exhibiting an unprecedented mobility, of $14.4 \text{ cm}^2/\text{Vs}$, for a polymer film. The authors used PTIIG-Np with a high- k gate dielectric, poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TFE)). The mobility was improved more than 2-fold by the use of a high- k gate dielectric [76], while it reduced the operating voltage of the device, at the same time [97]. This demonstrates the importance of optimizing all the components of an OTFT in order to extract the maximum performance from an organic semiconductor channel. Solution-processable polymer semiconductors with such high field effect mobility are ideal for low-cost large-area electronics fabrication using continuous R2R processing.

3. Conclusions

There has been serious progress in OTFT performance during the last decade. Our understanding of the properties of organic semiconductors and the operation of OTFT devices has improved substantially, and this has paved the way towards better OTFT performance. Advances in device performance are the result of the introduction of newly designed materials obtained either by chemical modification of existing ones or by the synthesis of completely new structures, followed by optimization of the deposition processes in order to perfect their morphology and structural order. At present, we have reached the point where an initial product application of OTFTs can be seriously considered and be commercially competitive. The research phase has progressed enough to enable the initiation of the long development phase. In the latter phase, process control, repeatability, and device yields are the deliverables of the development team. Of course the commencement of the development phase does not mean that the quest for new and better organic semiconductors will cease. It just means that the performance of the current crop of organic materials is good enough for the industry to seriously consider investing in product applications based on organic semiconductors.

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References

- [1] Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*, 2nd ed.; Oxford University Press: Oxford, UK, 1999.
- [2] Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913–915.
- [3] Burroughes, J. H.; Bradley, D. D.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541.
- [4] Baldo, M. A.; Thompson, M.E.; Forrest, S. R. *Nature* **2000**, *403*, 750–753.
- [5] Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 183–185.

- [6] Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474–1476.
- [7] Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338.
- [8] Liu, P.; Zhang, K.; Liu, F.; Jin, Y.; Liu, S.; Russell, T. P.; Yip, H. L.; Huang, F.; Cao, Y. *Chem. Mater.* **2014**, *26*, 3009–3017.
- [9] You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C. C.; Gao, J.; Li, G.; Yang, Y. *Nature Communications* **2013**, *4*, 1446–1455.
- [10] R. L. Wisniew, J. J. Ritsko, *IBM Journal of Research and Development* **2000**, *44*, 409–422.
- [11] Levy, D. H.; Freeman, D.; Nelson, S. F.; Cowdery-Corvan, P. J.; Irving, L. M. *Appl. Phys. Lett.* **2008**, *92*, 192101-1–192101-3.
- [12] Ostojica, P.; Guerri, S.; Rossini, S.; Servidori, M.; Taliani, C.; Zamboni, R. *Synth. Met.* **1993**, *54*, 447–452.
- [13] Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *268*, 270–271.
- [14] Greenham, N.; Friend, R. H. In *Solid State Physics; Advances in Research and Applications*, Ehrenreich, H.; Spaepen, F., Eds. Vol. 49, Academic Press: San Diego, CA, USA, 1995, pp. 1–149.
- [15] Lovinger, A. J.; Rothberg, L. J. *J. Mater. Res.* **1996**, *11*, 1581–1588.
- [16] Brown, A. R.; Jarrett, C. P.; de Leeuw, D. M.; Matters, M. *Synth. Met.* **1997**, *88*, 37–55.
- [17] Horowitz, G. *Adv. Mater.* **1998**, *10*, 365–377.
- [18] Katz, H. E.; Bao, Z. *J. Phys. Chem. B.* **2000**, *104*, 671–678.
- [19] Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99–117.
- [20] Newman, C. R.; Frisbie, C. D.; da Silva, D. A.; Bredas, J. L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436–4451.
- [21] Katz, H. E. *Chem. Mater.* **2004**, *16*, 4748–4756.
- [22] Malliaras, G.; Friend, R. *Phys. Today* **2005**, *58*, 53–58.
- [23] Facchetti A. *Materials Today* **2007**, *10*, 28–37.
- [24] Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; X. Zhan, W. *Adv. Mater.* **2010**, *22*, 3876–3892.
- [25] Wang, C. L.; Dong, H. L.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. *Chemical Reviews* **2012**, *112*, 2208–2267.
- [26] Chua, L. L.; Zaumseil, J.; Chang, J. F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194–199.
- [27] Kuivalainen, C. D.; Furman, B.; Graham, T.; Hegde, S.; Purushothaman, S. *Synthetic Metals* **1998**, *92*, 47–52.
- [28] Heilmeyer, G. H.; Zannoni, L. A. *J. Phys. Chem. Solids* **1964**, *25*, 603–611.
- [29] Kudo, K.; Yamashina, M.; Moriizumi, T. *Jpn. J. Appl. Phys* **1984**, *23*, 130–130.
- [30] Tsumura, A.; Koezuka, H.; Ando, T. *Appl. Phys. Lett.* **1986**, *49*, 1210–1212.
- [31] Clarisse, C.; Riou, M. T.; Gauneau, M.; Le Contellec, M. *Elect. Lett.* **1988**, *24*, 674–675.
- [32] Assadi, A.; Svensson, C.; Willander, M.; Inganäs, O. *Appl. Phys. Lett.* **1988**, *53*, 195–197.
- [33] Paloheimo, J.; Punkka, E.; Stubb, H.; Kuivalainen, P. In *Lower Dimensional Systems and Molecular Devices, Proceedings of NATO ASI*, Spetses, Greece, Mertzger, R. M. Ed., Plenum, New York, NY, USA, 1989.
- [34] Horowitz, G.; Fichou, D.; Peng, X.; Xu, Z., Garnier, F. *Solid State Commun.* **1989**, *72*, 381–384.
- [35] Horowitz, G.; Peng, X.; Fichou, D.; Garnier, F. *Synth. Met.* **1992**, *51*, 419–424.
- [36] Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Dellofre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716–8721.
- [37] Fuchigami, H.; Tsumura, A.; Koezuka, H. *Appl. Phys. Lett.* **1993**, *63*, 1372–1374.

- [38] Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684–1686.
- [39] Dimitrakopoulos, C. D.; Brown, A. R.; Pomp, A. *J. Appl. Phys.* **1996**, *80*, 2501–2508.
- [40] Bao, Z.; Lovinger, A. J.; Dodabalapur, A. *Appl. Phys. Lett.* **1996**, *69*, 3066–3068.
- [41] Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108–4110.
- [42] Lin, Y. Y.; Gundlach, D. J.; Jackson, T. N. In *54th Annual Device Research Conference Digest*; IEEE: Santa Barbara, CA, USA, 1996; p. 80.
- [43] Lin, Y. Y.; Gundlach, D. J.; Nelson, S.; Jackson, T. N. *IEEE Electron Device Lett.* **1997**, *18*, 606–608.
- [44] Sirringhaus, H.; Friend, R. H.; Li, X. C.; Moratti, S. C.; Holmes, A. B.; Feeder, N. *Appl. Phys. Lett.* **1997**, *71*, 3871–3873.
- [45] Dimitrakopoulos, C. D.; Afzali-Ardakani, A.; Furman, B.; Kymissis, J.; Purushothaman, S. *Synthetic Metals* **1997**, *89*, 193–197.
- [46] Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741–1744.
- [47] Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. *Chem. Mater.* **1998**, *10*, 457–459.
- [48] Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664–672.
- [49] Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478–481.
- [50] Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812–8813.
- [51] Afzali, A.; Dimitrakopoulos, C. D.; Graham, T. O. *Adv. Mater.* **2003**, *15*, 2066–2069.
- [52] Kelley, T. W.; Boardman, L. D.; Dunbar, T. D.; Muyres, D. V.; Pellerite, M. J.; Smith, T. P. *J. Phys. Chem. B.* **2003**, *107*, 5877–5881.
- [53] de Boer, R. W. I.; Gershenson, M. E.; Morpurgo, A. F.; Podzorov, V. *Phys. Status Solidi (A)* **2004**, *201*, 1302–1331.
- [54] Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. *Science* **2004**, *303*, 1644–1646.
- [55] Stingelin-Stutzmann, N.; Smits, E.; Wondergem, H.; Tanase, C.; Blom, P.; Smith, P.; de Leeuw, D. *Nat Mater.* **2005**, *4*, 601–606.
- [56] Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C. C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986–4987.
- [57] Ando, S.; Murakami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14996–14997.
- [58] Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604–12605.
- [59] Park, S. K.; Jackson, T. N.; Anthony, J. E.; Mourey, D. A. *Appl. Phys. Lett.* **2007**, *91*, 063514–063514-3.
- [60] Jurchescu, O. D.; Popinciuc, M.; van Wees, B. J.; Palstra, T. T. M. *Adv. Mater.* **2007**, *19*, 688–692.
- [61] Yamagishi, M.; Takeya, J.; Tominari, Y.; Nakazawa, Y.; Kuroda, T.; Ikehata, S.; Uno, M.; Nishikawa, T.; Kawase, T. *Appl. Phys. Lett.* **2007**, *90*, 182117–182117-3.
- [62] Takahashi, Y.; Hasegawa, T.; Horiuchi, S.; Kumai, R.; Tokura, Y.; Saito, G. *Chem. Mater.* **2007**, *19*, 6382–6384.
- [63] Li, L.; Tang, Q.; Li, H.; Yang, X.; Hu, W.; Song, Y.; Shuai, Z.; Xu, W.; Liu, Y.; Zhu, D. *Adv. Mater.* **2007**, *19*, 2613–2617.
- [64] Haas, S.; Takahashi, Y.; Takimiya, K.; Hasegawa, T. *Appl. Phys. Lett.* **2009**, *95*, 022111–022111-3.
- [65] Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T. *Nature* **2011**, *475*, 364–367.
- [66] Giri, G.; Verploegen, E.; Mannsfeld, S. C. B.; Atahan-Evrenk, S.; Kim, D. H.; Lee, S. Y.; Becerril, H. A.; Aspuru-Guzik, A.; Toney, M. F.; Bao, Z. *Nature* **2011**, *480*, 504–U124.

- [67] Kang, M. J.; Doi, I.; Mori, H.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H. *Adv. Mater.* **2011**, *23*, 1222–1225.
- [68] Nakayama, K.; Hirose, Y.; Soeda, J.; Yoshizumi, M.; Uemura, T.; Uno, M.; Li, W.; Kang, M. J.; Yamagishi, M.; Okada, Y.; et al. *Adv. Mater.* **2011**, *23*, 1626–1629.
- [69] Sokolov, A. N.; Atahan-Evrenk, S.; Mondal, R.; Akkerman, H. B.; Sánchez-Carrera, R. S.; Granados-Focil, S.; Schrier, J.; Mannsfeld, S. C. B.; Zoombelt, A. P.; Bao, Z.; et al. *Nature Communications* **2011**, *2*, 437–444.
- [70] Watanabe, M.; Chang, Y. J.; Liu, S. W.; Chao, T. H.; Goto, K.; Islam, M. M.; Yuan, C. H.; Tao, Y. T.; Shinmyozu, T.; Chow, T. J. *Nat. Chem.* **2012**, *4*, 574–578.
- [71] Amin, A. Y.; Khassanov, A.; Reuter, K.; Meyer-Friedrichsen, T.; Halik, M. *J. Am. Chem. Soc.* **2012**, *134*, 16548–16550.
- [72] Li, J.; Zhao, Y.; Tan, H. S.; Guo, Y.; Di, C. A.; Yu, G.; Liu, Y.; Lin, M.; Lim, S. H.; Zhou, Y.; et al. *Sci. Rep.* **2012**, *2*, 754–762.
- [73] Diao, Y.; Tee, B. C. K.; Giri, G.; Xu, J.; Kim, D. H.; Becerril, H. A.; Stoltenberg, R. M.; Lee, T. H.; Xue, G.; Mannsfeld, S. C. B.; et al. *Nature Materials* **2013**, *12*, 665–671.
- [74] Kurihara, N.; Yao, A.; Sunagawa, M.; Ikeda, Y.; Terai, K.; Kondo, H.; Saito, M.; Ikeda, H.; Nakamura, H. *Japanese Journal of Applied Physics* **2013**, *52*, 05DC11-1–05DC11-4.
- [75] Kim, G.; Kang, S. J.; Dutta, G. K.; Han, Y. K.; Shin, T. J.; Noh, Y. Y.; Yang, C. *J. Am. Chem. Soc.* **2014**, *136*, 9477–9483.
- [76] Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741–1744.
- [77] Kosbar, L.; Dimitrakopoulos, C. D.; Mascaro, D. J. In *MRS Proceedings, Symposium C: Electronic, Optical and Optoelectronic Polymers and Oligomers*, Jabbour, G. E.; Meijer, B.; Sariciftci, N. S.; Swager T. M. Eds. MRS Online Proceedings Library, volume 665, 2001, pp. C10.61–C10.6.6.
- [78] Yang, S. Y.; Shin, K.; Park, C. E. *Adv. Funct. Mater.* **2005**, *15*, 1806–1814.
- [79] Marcus, R. A. *Annual Review of Physical Chemistry* **1964**, *15*, 155–196.
- [80] Marcus, R. A. *Rev. Mod. Phys.* **1993**, *65*, 599–610.
- [81] Coropceanu, V.; Cornil, J.; da Silva, D. A.; Olivier, Y.; Silbey, R.; Bredas, J. L. *Chem. Rev.* **2007**, *107*, 926–952.
- [82] Brédas, J. L.; Calbert, J. P.; da Silva Filho, D. A.; Cornil, J. *PNAS* **2002**, *99*, 5804–5809.
- [83] Brédas, J. L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971–5004.
- [84] Wang, L.; Nan, G.; Yang, X.; Peng, Q.; Li, Q.; Shuai, Z. *Chem. Soc. Rev.* **2010**, *39*, 423–434.
- [85] Olivier, Y.; Niedzialek, D.; Lemaire, V.; Pisula, W.; Müllen, K.; Koldemir, U.; Reynolds, J. R.; Lazzaroni, R.; Cornil, J.; Beljonne, D. *Adv. Mater.* **2014**, *26*, 2119–2136.
- [86] Tang, M. L.; Mannsfeld, S. C. B.; Sun, Y. S.; Becerril, H. A.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 882–883.
- [87] Niimi, K.; Shinamura, S.; Osaka, I.; Miyazaki, E.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 8732–8739.
- [88] Dong, H.; Fu, X.; Liu, J.; Wang, Z.; Hu, W. *Adv. Mater.* **2013**, *25*, 6158–6183.
- [89] Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S., *J. Am. Chem. Soc.* **2004**, *126*, 8138–8140.
- [90] Anthony, J. E.; Eaton, D. L.; Parkin, S. R., *Org. Lett.* **2001**, *4*, 15–18.
- [91] Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R., *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483.
- [92] de Boer, R. W. I.; Klapwijk, T. M.; Morpurgo, A. F. *Appl. Phys. Lett.* **2003**, *83*, 4345–4347.
- [93] Reese, C.; Chung, W.-J.; Ling, M.-m.; Roberts, M.; Bao, Z. *Appl. Phys. Lett.* **2006**, *89*, 202108.
- [94] Mei, J.; Diao, Y.; Appleton A. L.; Fang, L.; Bao, Z. *J. Am. Chem. Soc.* **2013**, *135*, 6724–6746.
- [95] Greene, R. L.; Mayerle, R.; Schumaker, R.; Castro, C.; Chaikint, P. M.; Etemad, S.; Laplaca, S. J. *Solid State Commun.* **1976**, *20*, 943–946.
- [96] Dimitrakopoulos, C. D.; Purushothaman, S.; Kymissis, J.; Callegari, A.; Shaw, J. M. *Science* **1999**, *283*, 822–824.