Transactions of the Materials Research Society of Japan 29 [1] 197-202 (2004)

Conjugated Material Self-assembly: Towards Supramolecular Electronics

Ph. Leclère[1,2*], M. Surin[1], M. Cavallini[3], P. Jonkheijm[2], O. Henze[4],
A.P.H.J. Schenning[2], F. Biscarini[3], A.C. Grimsdale[5], W.J. Feast[4], E.W. Meijer[2],
K. Müllen[5], J.L. Brédas[1,6], and. R. Lazzaroni[1]

[1] Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut / *Materia* Nova,
Place du Parc, 20, B - 7000 Mons (Belgium).
Fax: + 32 65 37 38 61, e-mail: Philippe@averell.umh.ac.be

[2] Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology,
PO Box 513, NL - 5600 MB Eindhoven (The Netherlands).

[3] Consiglio Nazionale delle Richerche (CNR) – Istituto per lo Studio dei Materiali Nanostrutturati (ISMN),
Via P. Gobetti 101, I - 40129 Bologna (Italy).

[4] IRC in Polymer Science and Technology, Durham University, South Road,
UK - Durham DH1 3LE, (United Kingdom).

[5] Max-Planck Institut für Polymerforschung (MPI-P), Ackermannweg 10, D - 55128 Mainz (Germany).

[6] School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400 (USA).

The properties of organic electronic materials in the solid-state are determined not only by those of individual molecules but also by those of ensembles of molecules. The ability to control the architectures of these ensembles is thus essential for optimizing the properties of conjugated materials for use in electronic devices (light emitting diodes, field effect transistors, solar cells, ...) and is primordial for potential technological applications in nanoelectronics.

Here, we report on the observation by atomic force microscopy (AFM) of 1D and 2D nanoscale architectures obtained in the solid-state from solutions of molecularly-dissolved conjugated block copolymers or oligomers, and demonstrate that the conjugated molecules can organize onto a surface over lengthscales from nanometers to several microns, forming semiconducting fibrils or bi-dimensional organizations (monolayers) by π-stacking processes (by changing the sample preparation conditions). Finally, these objects can be used for applications in optoelectronics at the nanoscale for instance through alignment between electrodes separated by few hundreds nanometers.

Key words: supramolecular electronics, scanning probe microscopy, conjugated material.

1. INTRODUCTION

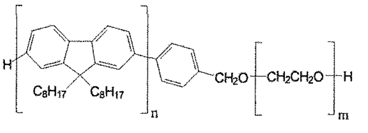
Since the first report of metallic conductivities in doped poly(acetylene) in the 70's, conjugated materials are investigated for a manifold of electronic semiconductor applications [1]. Emissive conjugated polymers have attracted significant attention due to their electronic, optical, and energy-transfer properties. Exact control over both function and ordering of the π-conjugated molecules will beneficially impinge on their performance. It is widely accepted that well-defined oligomers will play a crucial role in the future advancement of π-conjugated materials, since their precise chemical structure and conjugation length give rise to defined functional properties and facilitate enhanced control over their supramolecular architecture [2]. For instance, a clear correlation between the molecular structures, the mesoscopic structures, as shown by the film morphologies, and the luminescence properties, has been established. Moreover, well-defined nanosized aggregates could be very useful for the understanding of the effects of interchain interactions on the emissive properties of conjugated polymers [3-5]. The preparation of nanostructures made from conjugated polymers, such as nanotubes and nanowires, is of considerable interest in the design of novel functional materials and nanoelectronic devices, such as nanosized transistors [6], and sensors [7]. Self-assembly of synthetic materials has been recently proposed as a means of fabrication of nano-devices. In this domain, the ordering of block copolymers and oligomers leads to the formation of well-defined nanostructures.

A current objective is the realization of supramolecular electronics, involving the assembly of different π-conjugated functionalities into highly ordered extended structures (i.e., nanowires). Here, we discuss our investigations by AFM on three families of conjugated molecules based on: (i) oligo(fluorene)s; (ii) oligo(thiophene)s and (iii) oligo(paraphenylene vinylene)s.

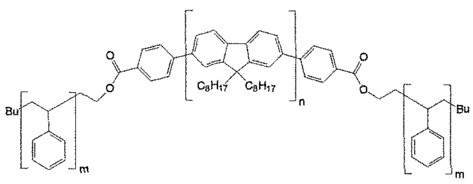
2. RESULTS AND DISCUSSION

2.1 Oligo(fluorene)s-based molecules

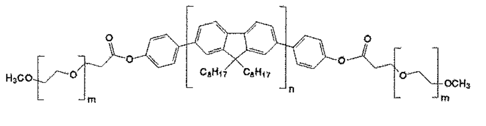
Fluorene oligomers and polymers have emerged as a promising new class of stable organic semiconducting material because of their interesting optoelectronic properties [8]. Since the microscopic morphology of films drastically affects these properties, it is of prime importance to create well-ordered nanostructures. Recently, we have investigated a series of fluorene-based block copolymers [8-10]. Figure 1 shows the chemical structures of the conjugated systems considered in the present study. The role of the alkyl side groups is to ensure a good solubility in common organic solvents.



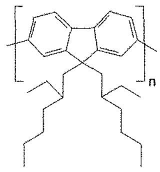
1a : n = m = 8; **1b** : n= 29, m = 116



1c : n = 23; m = 83.



1d : n = 20; m = 45.



1e

Fig.1. Chemical structure of fluorene-based diblock and triblock copolymers.

Figure 2 illustrates the typical results obtained on different oligofluorene-based systems. The AFM images of thin deposits of these compounds show a typical morphology: fibrils as long bright objects lying flat on the mica substrate.

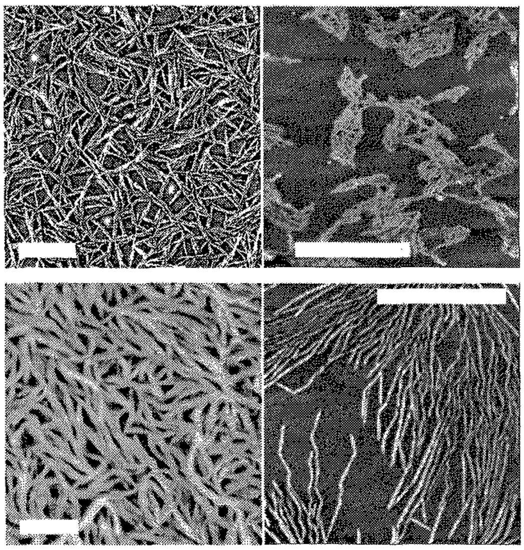
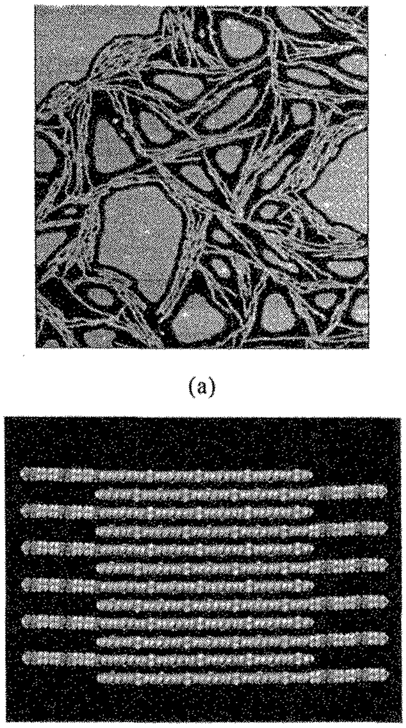


Fig. 2. AFM image of a thin deposit on mica of (a) **1a** from THF; (b) **1b** from THF; (c) **1c** from THF; (d) **1d** from toluene. The scale bar represents 500 nm.

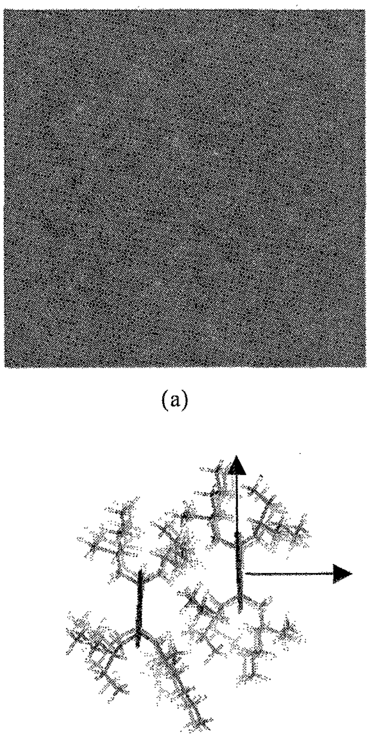
The AFM technique thus provides an extremely detailed description of the microscopic morphology of the material under study, but usually it does not allow to distinguish individual molecules or polymer chains. Therefore, in order to understand how those are formed from molecularly dissolved solutions and how the molecules are packed within the supramolecular organizations leading to the observed morphologies, models of the chain assembly can be proposed, using a theoretical approach based on Molecular Mechanics (MM) and Molecular Dynamics (MD) calculations. We present here the case of a diblock copolymer made of eight 9,9'-dioctylfluorene units and eight ethylene oxide units (F_8-b-EO_8, Figure 3a). The width of these structures appears to be constant, about 11 nm. The measured height is also constant and is around 2.0 nm. These values suggest that the fibrils resemble more to ribbons than cylinders. Based on what we observed for similar conjugated systems, we propose that the fibrils are built by π-stacking of the conjugated segments [11, 12]. Among the different possible configurations, the most stable is the "head-to-tail" configuration, where the fluorene chains have the possibility to pack and form the core of the ribbon, and the PEO segment of one chain is on the opposite side of the nanoribbon compared to the PEO segment on the adjacent molecule. This configuration globally provides enough space for the PEO segments to be fully extended, and could explain the larger width of nanoribbons compared to the estimation of the length of the molecule (11 ± 1 nm *vs* 9.7 nm) as shown on Figure 3b.


(a)

(b)

Fig. 3. (a) AFM picture (1.5 x 1.5 μm^2) of a thin deposit of **1a** on a mica substrate; (b) Molecular modelling of the proposed supramolecular organization within the nanoribbons.

Molecular modeling calculations of oligomer aggregates have shown the tendency of the molecules to form regular stacks where the conjugated parts of the molecules are planar and parallel to each other, with a typical distance between the molecules of 4.5-5.0 Å (Figure 3b), and with the octyl substituents pointing nearly perpendicular with respect to the stacking direction (not shown here for sake of clarity). These observations are in agreement with the results obtained by Samorì on conjugated oligomers [13]. When the linear lateral alkyl chain is replaced by a branched one (namely an ethyl hexyl instead of an octyl chain [14]) or by a more sterically important chain (like a triphenylamine-based moieties, [15]), the fibrillar morphology is drastically affected. Figure 4a illustrates the AFM results for an ethylhexyl substituted oligofluorene. From MM/MD calculations, it appears that the equilibrium distance is about 7.5-8.0 Å instead of 4.5-5.0 Å, meaning that the π−π stacking is not favorable and thus leading to the formation of an unstructurated morphology (Figure 4b).


(a)

(b)

Fig. 4. (a) AFM picture (3.0 x 3.0 μm^2) of a thin deposit of **1c** on a mica substrate;
(b) Molecular modeling of the proposed supramolecular organization.

2.2 Chiral oligomers

Extending our approach to create semiconducting nanowires for supramolecular electronics, we consider also chiral oligomers based on oligo(thiophene)s and oligo(*para*phenylene vinylene)s. Previously we have reported the formation of chiral aggregates in *n*-butanol of the chiral 2,2’:5’,2’’:5’’,2’’’:5’’’,2’’’’:5’’’’,2’’’’’-sexithiophene-5,5’’’’’-dicarboxylic acid-(2S)-2-methyl- 3,6,9,12,15 pentaoxahexadecyl ester **1a** [16, 17]. The π-conjugated oligomers studied differ in conjugation segment (thiophene versus *para*(phenylene vinylene); **2** *vs* **4**) (Figure 5), location of stereocenter (at the periphery on the ethyleneoxide segments or in the core on the conjugated segment), solubilizing units (hydrophilic oligo(ethylene oxide) versus hydrophobic alkoxy segments) and symmetry of the stereocenter (S,S’- and R,R’-enantiomer, **2a** and **2b,** respectively). The synthesis of the molecules has been reported elsewhere except for **2b** [16-19]. This mirror image is synthesized following the procedure of **2a**, however using the corresponding (2*R*)-2-methyl-3,6,9,12,15-pentaoxahexadecyl alcohol as starting material.

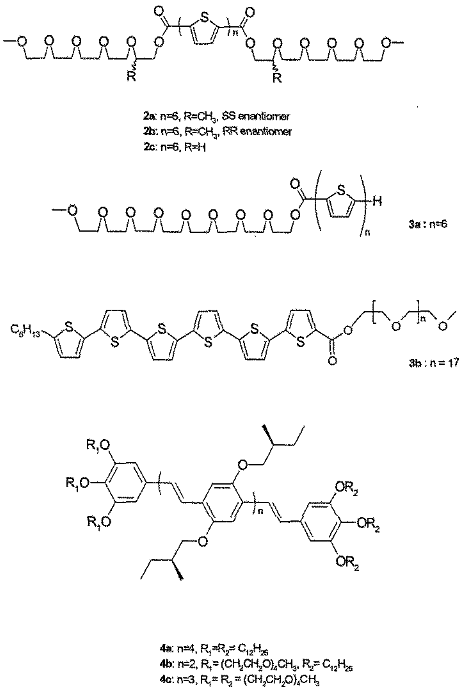
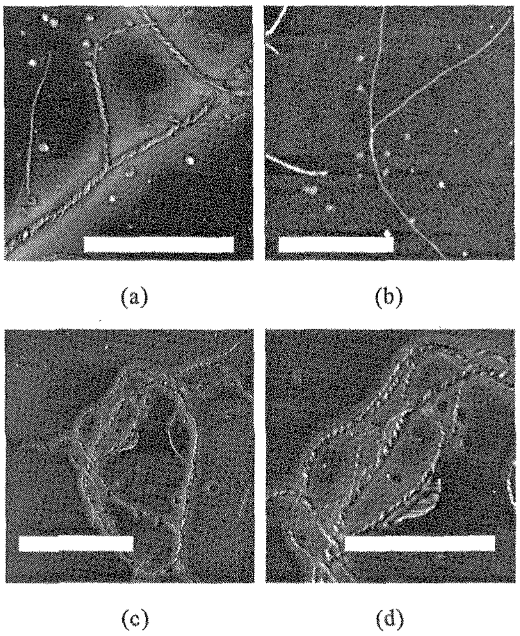


Fig. 5. Chemical structures of the studied chiral oligomers.

On a silicon wafer the aggregation of molecule **2a** leads to left-handed helical fiber-like structures (Figure 6a); moreover, we found that the achiral analogue **2c** forms non-chiral fibrils on the silicon surface (Figure 6b). From our systematic studies of the influence of the polar/hydrophilic character of the silicon wafer on the self-assembly behavior of **2a**, we conclude that the polarity of the silicon plays an important role in the expression of chirality in the fiber as a result of the interaction of the molecules with the surface.

When a tetrahydrofuran (THF) solution of **4a**, **4b**, or **4c** is slowly evaporated on a oxidized silicon wafer, left-handed fibrils are also observed (Figures 6c and d). The fact that always left-handed helices are observed is consistent with the circular dichroism (CD) studies of the molecules in poor solvents [17, 18]. In all cases, negative exciton-coupled CD spectra are observed corresponding to left-handed arrangements in the aggregates, when they are formed under thermodynamic control. However, by varying the conditions, kinetically controlled, CD mirror image spectra can be formed in solution [20]. This phenomenon in turn is in agreement with the results obtained for chiral phospholipids [21]. In that case, both left- and right-handed helices can be obtained from the same chiral molecule, implying that helix formation is not always directed by the molecular chirality. Similar results have been found before for thin films of other chiral poly(thiophene)s [22, 23].


(a) (b)

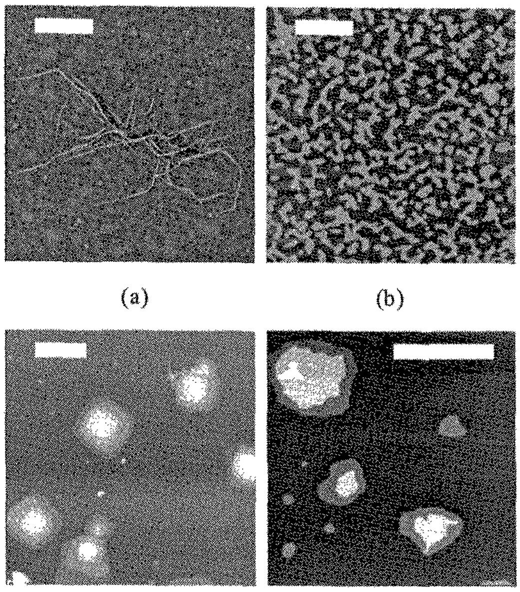
(c) (d)

Fig. 6. AFM images of conjugated chiral oligomers deposited on Si/SiO$_x$: (a) **2a** from toluene; (b) **2c** from toluene; (c) and (d) **4c** from THF. The scale bar represents 1.0 µm.

In order to gain understanding on the influence of the substrate hydrophilicity on the molecular assembly, we prepared the same type of deposits on (i) an apolar surface, *i.e.*, graphite (HOPG) and on (ii) a strongly polar surface, *i.e.*, muscovite mica. These two substrates are particularly suitable for AFM studies, since they are atomically-flat.

When the **2**- and **3**-type molecules are deposited on graphite, the molecules tend to organize as fibrils, and they prefer to align along a three-fold symmetry (most probably the symmetry of the basal graphite) as illustrated in Figure 7a. No chirality can be observed and the width of the fibers ranges from 7 nm (approximately the length of a single molecule) to few integer multiples of 7 nm, most frequently 21 and 35 nm.

When deposited on a mica substrate, they do not organize as fibrils but as monolayers as indicated on Figures 7b-d. From our AFM data, we estimated the thickness of these layers for the molecules; combining those data to molecular modeling calculations, we conclude that the molecules are packing with the conjugated segment almost perpendicular to the substrate, since the length of the fully extended oligo(thiophene) is consistent with the measured thickness. Once again, this indicates that the substrate has a strong influence on the packing of these compounds.


(a) (b)

(c) (d)

Fig. 7. AFM images of: (a) 2a on graphite; (b) **2a** on mica; (c) **3a** on Si/SiO$_x$; and (d) **3b** on graphite. The scale bar represents 1.0 μm.

3. CONCLUSIONS

The supramolecular organization of block copolymers containing one π-conjugated block and one non conjugated block was studied in the solid-state with a joint experimental and theoretical approach, combining Atomic Force Microscopy (AFM) measurements on thin polymer deposits, which reveal typical microscopic morphologies, and molecular modeling, which allows to derive models for chain packing most likely to explain the AFM observations. The conditions of preparation, such as the solvent evaporation kinetics and the characteristics of the substrate, strongly influence the assembly of the molecules, as a result of the high sensitivity of the supramolecular organization governed by weak forces like π-interactions. This AFM study indicates that the nature of the surface is one key parameter governing the formation of the supramolecular assemblies of conjugated oligomers and polymers. When the interactions between the molecules and the substrate are weak, the most usual obtained architecture is the fibrillar morphology with the molecules packing closely. The presence of bulky side groups or chiral centers (located either along the non-conjugated segment or on a substituent of the conjugated segment) is also drastically affecting the morphology of thin deposits. Tuning the polar character of the surface, we can observe fibrils or monolayers depending on the ratio between the molecule/molecule and molecule substrate interactions.

Moreover, we have found a general method to self-assemble chiral π-conjugated oligomers on silicon into highly ordered (left-handed) helical structures. Having these architectures available, this opens the way to align these stacks so as to connect their ends to electrodes and study the electro-optical properties of these nanosized wires and monolayers. Preliminary results indicate a promising behavior of the molecules for organic field effect transistors [24, 25].

4. ACKNOWLEDGEMENTS

The collaboration between Mons, Eindhoven, Bologna and Durham has been conducted within the European Commission RTN "*Large Area Molecular electronics Involving a Novel Approach to Training and Education* (LAMINATE)" program. The collaboration between Mons and Mainz has been conducted within the framework of the Belgian Federal Government Interuniversity Attraction Poles Program (PAI V/3) and the European Science Foundation "*Structuring, Manipulation, Analysis and Reactive Transformation of Nanostructures* (SMARTON)" program. Research in Mons is supported by the European Commission and the Government of the Région Wallonne (Phasing Out - Hainaut), the Belgian Federal Government Office of Science Policy (SSTC) and, the Belgian National Fund for Scientific Research FNRS/FRFC. R.L. is "Directeur de Recherches du F.N.R.S." (Belgium). M.S. acknowledges the F.R.I.A. (Belgium) for a doctoral scholarship.

5. REFERENCES

[1]. R.H Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.C.C. Bradley, D.A. dos Santos, J.L. Brédas, M. Logdlund, W.R. Salaneck, *Nature* **397**, 121-128 (1999).

[2]. R.E.Martin, F. Diederich, *Angew. Chem. Int. Ed.*, **38**, 1350-1377 (1999).

[3]. J. Cornil, D. A. dos Santos, X. Crispin, R. Silbey, and J. L. Brédas, *J. Am. Chem. Soc.*, **120**, 1289-1299 (1998).

[4]. S.A. Jenekhe, X.L Chen, *Adv. Mater.*, **12**, , 1042-1046 (2000).

[5]. E.W. Meijer, A.P.H.J. Schenning, *Nature*, **419**, 353-354 (2002).

[6]. X. Duan, Y. Huang, Y. Cui, J. Wang, C.M. Lieber, *Nature*, **409**, 66-69 (2001).

[7]. J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, *Science*, **287**, 622-625 (2000).

[8]. D. Marsitzky, M. Klapper, K. Müllen, *Macromolecules*, **32**, 8685-8688 (1999).

[9]. S. Setayesh, D. Marsitzky, K. Müllen, *Macromolecules*, **33**, 2016-2020 (2000).

[10]. S. Setayesh, A.C. Grimsdale, T. Weil, V. Enkelman, K. Müllen, F. Meghdadi, E.J.W. List, G. Leising, *J. Am. Chem. Soc.*, **123**, 946-953 (2001).

[11]. Ph. Leclère, A. Calderone, D. Marsitzky, V. Francke, Y. Geerts, K. Müllen, J.L. Brédas, R. Lazzaroni, *Adv. Mater.*, **12**, 1042-1046 (2000).

[12]. Ph. Leclère, E. Hennebicq, A. Calderone, P. Brocorens, A.C. Grimsdale, K. Müllen, J.L. Brédas,and, R. Lazzaroni, *Progr. Polym. Sci.*, **28**, 55-81 (2003).

[13]. P. Samorì., V. Francke, T. Mangel, K. Müllen, J.P. Rabe, *Opt. Mat.*, **9**, 390-393 (1998).

[14]. A.C. Grimsdale, Ph. Leclère, R. Lazzaroni, J.D. Mackenzie, C. Murphy, S. Setayesh, C. Silva, R.H. Friend and, K. Müllen, *Adv. Funct. Mater.*, **12**, 729-733 (2002).

[15]. M. Surin, D. Marzistsky, A.C. Grimsdale, K. Müllen, R. Lazzaroni and, Ph. Leclère, *to be published.*

[16]. A.F.M. Kilbinger, A.P.H.J. Schenning, F. Goldoni, W.J. Feast, E.W. Meijer, *J. Am. Chem. Soc.*, **122**, 1820-1821 (2000).

[17]. A.P.H.J. Schenning, A.F.M. Kilbinger, F. Biscarini, M. Cavallini, H.J Cooper, P.J. Derrick, W.J Feast, R. Lazzaroni, Ph. Leclère, L.A McDonell, E.W. Meijer, S.C.J. Meskers, *J. Am. Chem. Soc.*, **124**, 1269-1275 (2002).

[18]. P. Jonkheijm, M. Fransen, A.P.H.J. Schenning, E.W. Meijer, *J. Chem. Soc. Perkin. Trans. 2*, **8**,1280-1286 (2001).

[19]. A.P.H.J. Schenning, A. El-ghayoury, E. Peeters, E.W. Meijer, *Synth. Met.*, **121**, 1253-1256 (2001).

[20]. O. Henze, P. Jonkheijm, A.P.H.J., Schenning, E.W. Meijer, W.J. Feast, *to be published.*

[21]. B.N. Thomas, C.M. Lindemann, and N.A. Clark, *Phys. Rev. E*, **59**, 3040-3047 (1999).

[22]. M.M. Bouman, E.W. Meijer, *Adv. Mater.*, **7**, 385-387 (1995).

[23]. G. Bidan, S. Guillerez, V. Sorokin, *Adv. Mater.*, **8**, 157-160 (1996).

[24]. H.G. Sandberg, O. Henze, H. Sirringhaus, A.F.M. Kilbinger, W.J. Feast, R.H. Friend, *Proc. SPIE*, **4466**, 35-43 (2001).

[25]. Surin M., Cavallini M., Leclère Ph., Biscarini F., and Lazzaroni R., *to be published.*

(Received October 9, 2003; Accepted November 17, 2003)