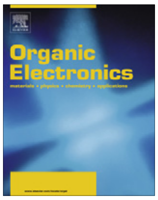
Organic Electronics 13 (2012) 419–424

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Selective orientation of discotic films by interface nucleation

Ishviene Cour [a], Zhenwen Pan [a], Lyndelle T. Lebruin [b], Martin A. Case [b], Madalina Furis [a], Randall L. Headrick [a,*]

[a] *Department of Physics, Materials Science Program, University of Vermont, Burlington, VT 05405, United States*
[b] *Department of Chemistry, University of Vermont, Burlington, VT 05405, United States*

ARTICLE INFO

Article history:
Received 15 August 2011
Received in revised form 23 October 2011
Accepted 24 October 2011
Available online 26 November 2011

Keywords:
Discotic liquid crystals
Nucleation
Supercooling
X-ray diffraction
Space charge limited current
Homeotropic

ABSTRACT

Thin films deposited from solution by the hollow capillary writing technique exhibit macroscopic uniaxial grains with an in-plane arrangement of discotic stacks. We report a method to change the orientation of thin films from in-plane to homeotropic (discotic columns perpendicular to the substrate). It is observed that annealing of open supported films at a temperature 25 °C below the equilibrium LC/isotropic phase boundary induces homeotropic alignment, while rapid cooling leads to predominantly in-plane alignment. A model based on heterogeneous nucleation at the film/substrate interface accounts for the experimental observations.

1. Introduction

The self assembling properties of liquid crystals (LC) in combination with their anisotropic carrier transport, makes them attractive candidates for technologies such as field effect transistors, photovoltaic devices and light emitting diodes. Various liquid crystalline states such as discotic (1D columns), smectic (2D layers) and nematic (oriented in parallel with no positional order) have been studied with the goal of promoting the anisotropic carrier transport [1]. Several classes of discotic mesophase materials such as phthalocyanines [2], triphenylenes [3], hexabenzocorones [4], have emerged as promising soluble organic semiconductors that have gained increased attention due to their stability and anisotropic properties. Promising photovoltaic devices have been obtained by making use of discotic columnar structures [5,6].

Discotic liquid crystals (DLCs) can be deposited uniformly on a single surface or between two surfaces with the disc like molecules forming one dimensional columns. DLCs typically exhibit higher carrier mobility along the columns compared to perpendicular, possibly approaching single-crystal values in some cases. The two predominant alignments of DLCs are planar and homeotropic: in the former the column orientation is parallel to the substrate and in the latter columns lie perpendicular to the substrate. In the literature, many discotic materials that can be aligned homeotropically were studied mostly with the discotic layer sandwiched between two substrates [7–9]. Organic photovoltaic devices are made by sequential deposition of the organic films that serve as donor and acceptor layers. In order to optimally use discotics as the donor layer, it would be desirable to orient the film as an open layer with molecular columns oriented vertically with respect to the substrate. Several factors contribute to the alignment process such as interface free energy, kinetics of the phase change during cooling from the isotropic phase, role of substituents, etc. In this article, we explicitly address how nucleation influences the alignment behavior, and

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* Corresponding author.
E-mail address: rheadrick@uvm.edu (R.L. Headrick).

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doi:10.1016/j.orgel.2011.10.021

how kinetics limit the growth of nuclei along the columnar direction.

2. Experimental

The DLC used in the present study is 2, 3, 9, 10, 16, 17, 23, 24-Octakis (Octyloxy)-29H, 31H-Phthalocyanine abbreviated as $H_2Pc–OC_8$ and was purchased from Sigma–Aldrich. The material was purified twice by column chromatography with chloroform used as the solvent. All the samples were written on indium tin oxide (ITO) coated glass substrates from 0.5% to 1% weight/volume chloroform solution at a speed of 0.02–0.04 mm/s by a direct write method [10]. The alignment behavior was studied on films supported by a single substrate with the other side free. An optical microscope equipped with rotatable linear polarizers (Olympus DP71) was used for polarized optical microscopy (POM) along with a hot stage (Linkam THMSE 600) to observe the orientation of the films. Planar orientation of the columns is established by birefringence seen between the crossed polarizers. Inversely, lack of birefringence is a characteristic of homeotropic alignment, where the optical axis of the liquid crystal is perpendicular to the substrate. Specular X-ray measurements were performed with a Rigaku Ultima III Cu Kα source (λ = 0.154 nm) in the reflection geometry to confirm the crystallographic alignment of the films. Space charge limited current measurements were performed on ITO/DLC/Gold samples with Cascade Microtech Probe station and Keithley 2636 source meter. Gold was evaporated on DLC films as 1 mm size diameter circular electrode at a pressure of 3×10^{-6} Torr. The film thickness was determined by atomic force microscopy (AFM) of a scratched line on the film.

3. Results

3.1. Annealing procedure for orientation control

We observe the well known phase transitions from the crystalline to liquid crystalline state and from liquid crystalline to isotropic at 124 °C and 395 °C, respectively. Both of these transitions are about 30 °C higher than the typical values reported in the literature i.e. at 94 °C and 368 °C [11]. However, for the as received material the transitions were close to the literature values. The transition temperatures are shifted higher during heating of highly purified materials, which may be attributed to superheating. On reaching the isotropic phase a uniform isotropic layer is formed with no optical polarization contrast. During cooling from this melt pronounced supercooling is observed.

Fig. 1 summarizes the POM results on cooling the DLC films. Two different conditions are represented: Procedure A is continuous cooling at 20 °C/min to room temperature. A large supercooling is observed, where polarization contrast becomes visible at 350 °C, corresponding to a supercooling of $\Delta T_A \approx 45$ °C. Procedure B is cooling the film at 20 °C/min to 370 °C, annealing at 370 °C for 20 min followed by 20 °C/min to room temperature. Cooling via procedure B is observed to induce homeotropic alignment of columnar liquid crystals, while procedure A produces mainly in – plane alignment. The equilibrium transition temperature must be between the transition temperature observed on heating (395 °C) and that observed on cooling. In condition B nucleation at 370 °C is inferred, and therefore 25 °C is considered to be the upper limit of ΔT_B. Thus, we find that $\Delta T_A > \Delta T_B \leqslant 25$ °C. A model based on these observations will be described in the discussion section.

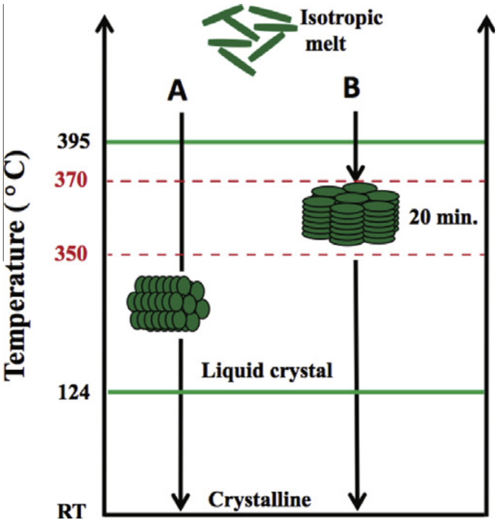

Fig. 1. Process diagram showing two different procedures for cooling $H_2Pc–OC_8$ films from the isotropic melt. Solid green lines are the phase boundaries during heating for the Crystalline/LC Transition and LC/Isotropic transition, and the dotted red lines at 370 °C and 350 °C correspond to the maximum supercooling temperatures for homeotropic and in-plane alignment, respectively. The cooling rate is 20 °C/min for both procedures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Study of crystalline to liquid crystalline phase transition

The as-written films have macroscopic oriented grains with (100) surface orientation and [001] along the writing direction (Fig. 2c). We found the spacing d_{100} = 23.7 Å from the X-ray measurements which is consistent with the orthorhombic lattice parameters found in the literature [12] (a = 25 Å, b = 42 Å and c = 4.3 Å) with a preferred tilt of molecules around the a-axis, and assuming 2 molecules per unit cell. Transformation of the solid material to the liquid crystalline state with increasing temperature is accompanied by melting of the alkoxy side chains. Under the polarized optical microscope a noticeable color change of the crystalline film from green to bluish was observed for this transition Fig. 2a and b. In the X-ray measurements Fig. 2c, we observe the orthorhombic peaks disappear at 124 °C and the hexagonal lattice peaks corresponding to (100) and weak (110) planes appear. The hexagonal columnar ordered (D_{ho}) mesophase with d_{100} = 25.8 Å and intercolumnar distance a_h = 29.8 Å was observed. This change is reversible and the crystalline state is recovered at around 70 °C on cooling the film from the LC phase.

The absorption spectra for the as deposited film is shown in Fig. 2d. Two absorption maxima are observed

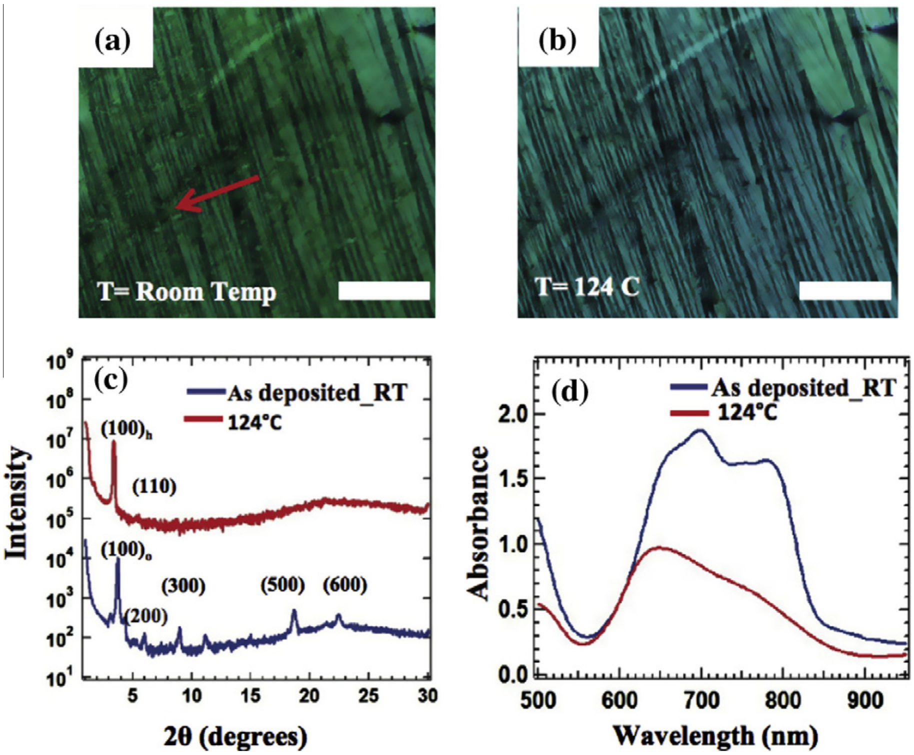

Fig. 2. Polarized optical microscopic (POM) images: (a) Thin crystalline film deposited by the hollow capillary writing method on an ITO coated glass substrate. The alternating domains are aligned perpendicular to the writing direction (red arrow). (b) A noticeable color change (Bluish Green) is observed on heating the as-deposited film up to 124 °C, indicating the transition from the orthorhombic (crystalline) phase to the hexagonal (LC) phase. The scale bars are 1 mm. (c and d) X-ray and UV–Vis absorption measurements for as deposited films at room temperature and in the liquid crystalline phase above 124 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

at 650 nm and 760 nm. With increasing temperature the spectral profile remains the same up to the liquid crystalline phase boundary: above this temperature, the short wavelength peak becomes predominant [13]. These changes are consistent with the structural change from orthorhombic herringbone to hexagonal columnar phase.

Photoluminescence was also observed for the as deposited crystalline films which disappeared on heating through 124 °C and reappeared on cooling from the LC phase at around 70 °C, which is in agreement with the optical microscopy results described above (see Supplementary information).

3.3. Polarized optical microscopy and X-ray measurements of annealed films

Fig. 3a and b shows polarized and bright field micrographs for in-plane and homeotropic alignments, respectively, selectively achieved with cooling conditions A and B. We have compared the specular X-ray diffraction spectra for thin films annealed via condition B with as-written films, Fig. 3c. On the annealed films with homeotropic molecular alignment, we observe $d_{001} = 4.13$ Å which is close to the expected value for the orthorhombic structure. The unlabelled peaks are higher order reflections from grains with a small misalignment.

3.4. Space charge limited current measurements

In this study, the charge mobility was estimated according to the space charge limited (SCLC) theory which is used to characterize the charge transport in organic and polymer thin film devices described by the Mott–Gurney Law Eq. (1)

$$J_{\mathrm{SCLC}} = \frac{9\epsilon_{\circ}\epsilon_{r}\mu V^{2}}{8L^{3}} \tag{1}$$

where J is the current density, $\epsilon_{\circ}$ vacuum permitivity, ϵ_r dielectric constant, V is the applied voltage, L is the device thickness and μ is the charge carrier mobility. The films were written from 1% chloroform solution at a speed of 0.02 mm/s. These measurements were performed for as written films (before annealing) and switched films (after annealing to homeotropic alignment via procedure B). The film thickness determined from AFM was found to be 900 ± 100 nm. We did not observe any systematic changes in the film thickness due to heating. The J—V characteristics in Fig. 4 show two different slopes: (i) ohmic region, and (ii) trap free space charge limited current region ($J \propto V^2$) Eq. (1) [14].

The mobility is extracted from current in the square-law region for the switched film and was found to be $\mu = 9 \times 10^{-5}$ cm^2/V s, which is nearly 2 orders of magnitude greater than the mobility $\mu = 2 \times 10^{-6}$ cm^2/V s for

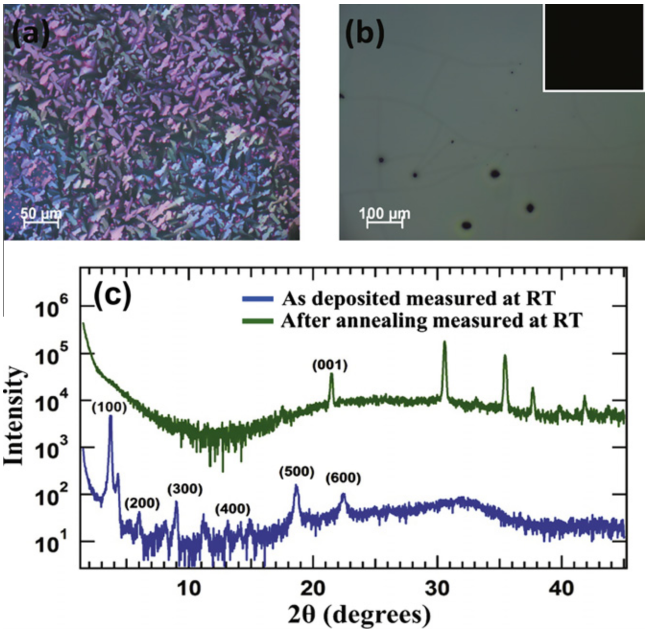

Fig. 3. Images obtained for $H_2Pc–OC_8$ films heated to the isotropic phase and then cooled by two different conditions. Above 395 °C the isotropic phase shows no contrast. (a) Image with crossed polarizers after cooling at 20 °C/min to room temperature. The film exhibits mainly in-plane alignment. (b) Annealing for 20 min at 370 °C during cooling from the isotropic phase allows the homeotropic alignment to preferentially nucleate and grow. The main image is bright field, showing a featureless surface, and the inset is with crossed polarizers showing no contrast. (c) Room temperature X-ray measurements performed on as deposited film (blue) and homeotropically aligned film (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

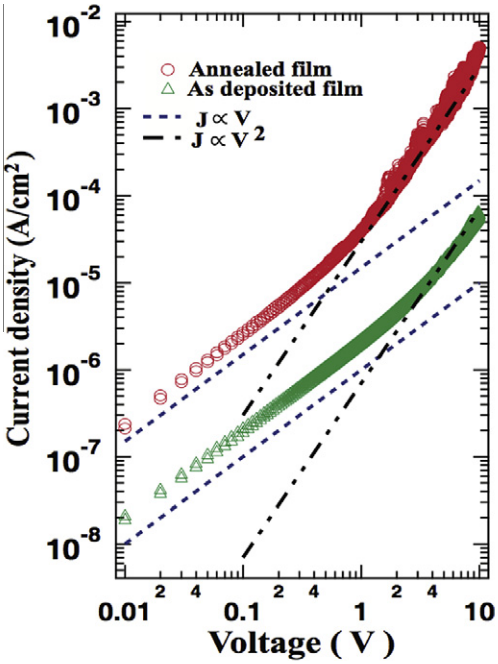

Fig. 4. Space charge limited current measurements. (a) On as written crystalline film. (b) Measurement performed at room temperature after switching the alignment to homeotropic by cooling condition B.

the as deposited film. For the as deposited film, the square law region is poorly visible which could be associated with the dispersive nature of the charge carriers as discussed by Rybak et al. [15] These results are consistent with the change in the film alignment since high charge carrier transport is expected to be along the discotic columns.

4. Discussion

A model based on standard heterogeneous nucleation theory reasonably describes the observation of two different supercooling temperatures for homeotropic and in-plane alignment. In adapting this model, we assume that nuclei can form at the interface between the isotropic liquid (L) and the substrate (Q) or at the liquid–vapor (LV) interface and that each orientation – homeotropic or in-plane – have different interface energies with the substrate, as illustrated in Fig. 5. A well-known method of inducing homeotropic alignment is the sandwich geometry which eliminates the interface with air, in favor of having two liquid–substrate (LQ) interfaces. Thus we assume that the (100) orientation preferentially forms at the LV interface, and the (001) homeotropic alignment tends to nucleate at the LQ interface. We denote the relevant surface energies as γ_{LV} and $\gamma_{SV}(100)$ for the in-plane alignment and γ_{LQ} and $\gamma_{SQ}(001)$ for the homeotropic alignment. We also assume that $\gamma_{LS}(100) \approx \gamma_{LS}(001)$ for simplicity.

The difference in interface energies has a profound effect on the nucleation rate for a given supercooling ΔT. The nucleation rate for a supercooled liquid or melt is given by $N = N_0 \exp(-\Delta G^*/KT)$, where ΔG^* is the nucle-

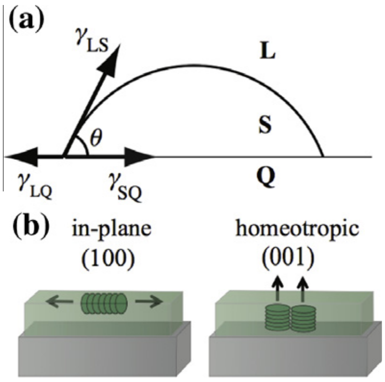

Fig. 5. (a) Schematic representation of classic heterogeneous nucleation on the substrate Q, where the equilibrium shape of the nucleating solid is spherical. (b) We assume the growth of the nuclei is kinetically limited and it grows faster along the columnar direction. With cooling condition B, the fast growing direction is perpendicular to the substrate. With condition A, the nucleation can occur in both the directions but the lateral growth is much faster.

ation barrier which is defined as the free energy of a critical nucleus relative to the liquid phase [16].

$$\Delta G^* = \frac{16\pi\gamma_{LS}^3}{3(\Delta S_v \Delta T)^2} S(\theta), \quad (2)$$

where $S(\theta)$ is a function that depends on the wetting angle θ given by Young's equation $\cos\theta = (\gamma_{SQ} - \gamma_{LQ})/\gamma_{LS}$. For simplicity, we only take into account the lowest order term i.e. $S(\theta) \approx 3\theta^4/16$. We assume γ_{LS} and ΔS_v to be constant for either alignment. At the temperatures where the nucleation rates become significant, the nucleation barriers for the two alignments are also considered to be the same $\Delta G_A^*(\Delta T_A) \approx \Delta G_B^*(\Delta T_B)$. Using the above assumptions, we find the relation of the respective wetting angles

$$\frac{\theta_A}{\theta_B} \propto \left(\frac{\Delta T_A}{\Delta T_B}\right)^{1/2} \geqslant 1.4 \quad (3)$$

From this relationship we predict the following inequality of interfacial energies,

$$\gamma_{SV}(100) - \gamma_{LV} > \gamma_{SQ}(001) - \gamma_{LQ}. \quad (4)$$

The initial nucleation occurs heterogeneously at the liquid–substrate interface in the homeotropic case and at the liquid–air interface in the homeogeneous case. This model predicts that the homeotropic (001) orientation will always nucleate first due to the lower interface energy at the substrate, i.e. standard theory fails to predict the dominance of the (100) orientation on fast cooling (cooling condition A). To resolve this discrepancy, we note that Eq. (4) is actually more general than Eq. (3) in the sense that Eq. (4) does not strictly rely on the assumption of spherical nuclei. Hence, we add a different assumption to our model: that the growth of the nuclei is strongly influenced by kinetics and that they grow faster along the columnar direction than perpendicular to it. The fast growth direction is indicated by arrows in Fig. 5(b). Hence, on cooling the film via condition B, annealing for a long time helps to achieve complete lateral growth. Whereas, with the fast cooling via condition A, the nucleation can occur for both alignments but the growth rate of orientation A is much faster laterally than that of orientation B and so the in-plane alignment dominates over the homeotropic alignment (see Supplementary information for in-plane alignment polarized optical micrographs).

In the literature, homeotropic alignment has previously been achieved by following a slow cooling rate of 1 °C/min or less from the isotropic phase. These studies typically utilize a sandwich geometry with the discotic layer between two substrates [7–9], but in several cases homeotropic alignment has been achieved with a single substrate [4,17,18]. Our results give insight into how these processes work, and suggest the following general points: (i) materials must be highly purified in order to induce heterogeneous nucleation at the substrate/film interface, otherwise randomly oriented grains can nucleate in the bulk of the film; (ii) homogeneous and homeotropic alignments typically have unequal interface free energies (i.e. with the substrate and/or free surface) that can be exploited through a judicious choice of the annealing temperature and/or cooling rates in order to promote one alignment at the expense of the other; (iii) growth of the nuclei can be faster in one direction, typically along the columnar axis, and hence the kinetics of grain growth also plays an important role in determining which orientation dominates.

We note that Wang et al. [18] studied a triphenylene derivative, and found that for slow cooling homeotropic alignment is observed, but proposed that if the cooling process is too fast or if a large supercooling exists, the structural development is very fast and nucleation occurs throughout the bulk. We suggest another interpretation of this effect: that faster cooling may induce nucleation at one or both of the interfaces, but with a homogeneous orientation that dominates due to the fast lateral growth of these grains in the plane of the surface. In contrast, slow cooling allows time for the energetically preferred homeotropic aligned grains to grow. Note that we find that supercooling is an essential part of the orientation selection mechanism.

Grelet and Bock [17] find that thicker triphenylene films tend to orient homeotropically on slow cooling, while in-plane alignment was observed for thinner films (≈100 nm). They suggest that if the homeotropic domains quickly grow up to the liquid crystal air interface, then a transition to planar anchoring takes place. Our model suggests that larger domains would be too large to spontaneously reorient, but this effect could be explained if the film thickness is not much greater than the size of the critical nucleus because the nucleation rate for embryos that are simultaneously in contact with two interfaces can be dominant over the nucleation rate at a single interface.

Pisula et al. [4] observe almost the opposite effect for a hexabenzocoronene derived material; thinner films on a single substrate were found to orient homeotropically during slow cooling, but thicker films exhibited random orientations. This effect may be evidence for nucleation in the bulk of the film due to residual impurities. From our observations, homogeneous nucleation (i.e. without the influence of impurities or interfaces) is not likely to play a role in the transition because of the much larger nucleation barrier.

5. Conclusions

We have fabricated crystalline phthalocyanine films at room temperature with in-plane molecular alignment by a solution direct write method. We can selectively control the orientation of discotic molecules on cooling from the isotropic phase on open thin films. These observations are explained by simple considerations of heterogeneous nucleation theory and anisotropic grain growth.

Acknowledgements

This research was carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the US Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. We thank Dmytro Nykypanchuk for his kind assistance in X-ray data collection and Jacob M. Wahlen-Strothman for helping with AFM measurements. This work was supported by National Science foundation (NSF) Career Award DMR-0348354, NSF EPS-0701410, NSF award DMR-0907599 and NSF DMR-0821268.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2011.10.021.

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