Model for In-Plane Directional Ordering of Organic Thin Films by Oblique Incidence Organic Molecular Beam Deposition**

By *Chengzhi Cai,* Bert Müller, Jens Weckesser, Johannes V. Barth, Ye Tao, Martin M. Bösch, Armin Kündig, Christian Bosshard,* Ivan Biaggio,* and *Peter Günter*

Organic π-conjugated molecules have attracted increasing interest as novel electronic, optical, and electro-optical materials.[1–3] For many potential applications it is necessary to process these materials into thin films. Several approaches have been developed, including Langmuir–Blodgett transfer,[4] self-assembly in solution,[5] chemical vapor deposition, and organic molecular beam deposition (OMBD).[6] Among them, OMBD has its unique advantages. It is one of the physical vapor deposition (PVD)[7–9] techniques, which have been widely used for growing inorganic thin films, especially in the microelectronic and optical industries.[9] With minor modification, the equipment for PVD can be used for OMBD, and both organic and inorganic layers can be grown in the same ultra-high vacuum system for the fabrication of hetero-layer devices, such as organic light emitting devices,[3] integrating organic and inorganic materials in one chip. It is well known that the desired electronic and optical properties of thin films are usually strongly affected by the materials and the ordering and microstructure of the films, which are in turn dependent on the materials and the deposition conditions.[9] However, these relationships for amorphous or polycrystalline organic thin films are still poorly understood, although attention has been paid to the single crystalline films, the growth of which is still not practical.[6] In the preceding paper[10a] we proposed a new type of nonlinear optical material: dipolar supramolecular assemblies, such as 4-[trans-(pyridin-4-ylvinyl)] benzoic acid (**1**, Fig. 1) and 4-(pyridin-4-ylethynyl) benzoic acid (**2**). We have demonstrated that **1** and **2** can be preferentially aligned within both the substrate plane and the deposition plane by oblique incidence OMBD.[10] To our knowledge, this was the first report of using oblique deposition to align organic molecules. Both from a scientific point of view and for potential applications, it is important to understand the reasons for the alignment. In this paper, a growth mechanism is proposed to explain the experimental results presented in this and the previous papers.[10] It suggests that hydrogen bonding is a key factor for the observed preferential alignment of the molecules.

Many obliquely deposited inorganic thin films are known to be anisotropic within the substrate plane, due to the formation of columnar microstructures inclined toward the vapor source during the deposition.[7–9,11–14] There are two significant differences between the obliquely deposited inorganic films and the films of **1** or **2**. First, although linear optical anisotropy was observed,[12] to the best of our knowledge, the second-order nonlinear optical effect connected with a non-centrosymmetric order has not been reported in such inorganic films. On the other hand, the films of **1** or **2** on amorphous glass substrates displayed not only in-plane linear optical anisotropy, but also second-order nonlinear optical effects.[10] Second, for the inorganic films, the angle between the long axis of the columnar structures and the substrate normal is less than that between the incoming molecular beam and the substrate normal (deposition angle).[7–9,11–14] It was often necessary to choose deposition angles larger than 60° to obtain anisotropic films.[13] For our organic thin films, the deposition angle was only about 26°! Nevertheless, the incident angle-dependent second harmonic generation experiments proved that the molecules were preferentially aligned parallel to the substrate surface.[10] Therefore, another mechanism has to be developed in order to understand the results of the preceding papers. These differences are probably due to the different types of materials. The inorganic films are grown by formation of ionic or covalent bonds between atoms having mostly a spheroidal shape with a diameter of 2–4 Å; the growth mechanism has been intensively studied.[7–9,11–14] On the other hand, our films are grown out of asymmetric rigid rod molecules (**1** or **2**) with a length of 12–14 Å. The following discussion suggests that hydrogen bonding is a key factor for the growth and ordering of the films.

Thin film growth occurs when molecules arriving at the surface bond with those in the surface layer. Whether this process is possible or not is determined by its free energy change $\Delta G = \Delta H - T\Delta S$ at a certain temperature T. For molecules of **1** and **2**, the intermolecular bonding involves cooperatively the weak van der Waals and π–π-stacking interactions (estimated enthalpy $\Delta H < 1$ kcal mol^{-1}), and is dominated by the strong hydrogen bonding. Since the hydrogen bonding is due to the interaction of the carboxylic H atom with the non-bonding electron pairs of the O and N atoms (Fig. 1), several bonding possibilities exist. However, the strongest hydrogen bonds are between the carboxylic and pyridyl groups (head-to-tail, Fig. 1), and between the carboxylic groups (tail-to-tail). In fact, molecules of **1** or **2** in the solid states are mostly bonded via head-to-tail hydrogen bonds as shown by the ^{15}N NMR studies.[10] We used in situ ellipsometry to monitor growth and desorption of a film of **1** on a silicon substrate. The desorption started at a substrate temperature around 128° C

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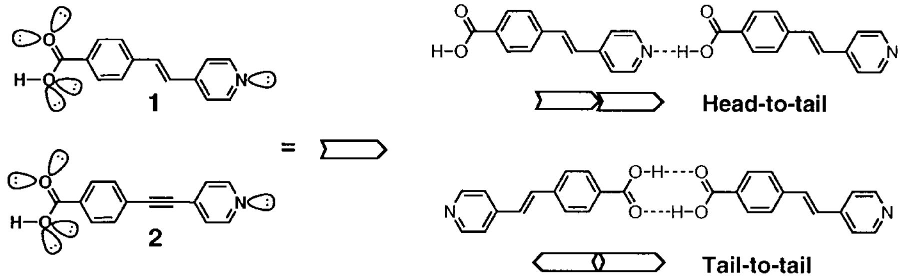

Fig. 1. Molecular structures and non-bonding electron pairs of **1** and **2**, and the two strongest hydrogen-bonded dimers of **1**.

(Fig. 2). This is probably the dissociation temperature for the head-to-tail hydrogen bond. On the other hand, tail-to-tail hydrogen bonding is also possible. The typical enthalpy (ΔH) for dimerization of carboxylic acids, forming two O–H···O hydrogen bonds, is about –15 kcal mol^{-1}, while the entropy is $\Delta S \approx -36$ cal mol^{-1}.[15] This leads to $\Delta G \approx -4$ kcal mol^{-1} K^{-1} at 27° C, and to a dissociation temperature (when $\Delta G = 0$) of about 144° C, which is significantly higher than the desorption temperature of the film (128° C). It suggests that the tail-to-tail hydrogen bond is even stronger than the head-to-tail one, although many more of the latter are formed during the growth as will be explained in Figure 4.

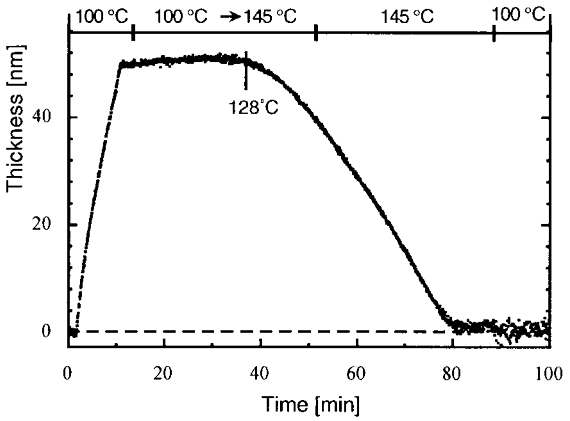

Fig. 2. In-situ monitoring of the growth and desorption of a film of **1** on a silicon substrate. The growth at 100° C lasted for 9 min, reaching a film thickness of 50 nm. The shutter of the vapor source was then closed, and the substrate temperature was increased to 145° C at a rate of about 1.2 K min^{-1}. Desorption was observed starting at about 128° C. The desorption rate at 145° C was 1.33 nm min^{-1}. The substrate was an oxidized silicon wafer silylated with trichloro(4-chloromethylphenyl)silane.

The above discussion implies that the main driving force for the thin film growth of **1** and **2** is hydrogen bonding, and that it is possible for the arriving molecules to bond to the surface molecules at room temperature through the formation of head-to-tail or tail-to-tail hydrogen bonds. However, whether the bonding is feasible or not is dependent on the kinetics. In particular, we believe that the orientation of the surface molecules determines the rate of hydrogen bond formation, and hence the growth rate, because hydrogen bonding has a directional requirement. Following the simplest electrostatic model,[16] hydrogen bonding can be viewed as the interaction between two electric dipole moments. The H atom is the electrophile that seeks the direction of maximum electron density in the hydrogen bond acceptor.[16] In our case, this direction is along the axes of the non-bonding electron pairs at the O and N atoms (Fig. 1).

One of the major differences between thin film growth in solution and by OMBD is that the molecules in solution approach the surface via diffusion in all directions, while under our OMBD conditions[10a] the molecules are translated to the surface in the same direction, although they rotate randomly. When a molecule approaches the film surface, it starts to interact with the surface molecules.[7] We believe that the arriving molecule and, if possible, the surface molecules should orient themselves to obtain the maximum van der Waals attracting force. This force is dipolar in nature, favoring the interaction between polar groups—in our case the pyridyl and especially the carboxylic groups. Therefore, the arriving molecules should preferentially be oriented with the carboxylic group facing the film surface, if the surface molecules are allowed, that is, if they have a low energy barrier, to tilt towards the molecular beam direction. Moreover, we reason that such orientations of the surface molecules and the arriving molecules should lead to the highest growth rate, because they should be the most favorable orientations for the formation of the head-to-tail or tail-to-tail hydrogen bond. If the surface molecules cannot adapt to this orientation because of a high energy barrier, the arriving molecules have more difficulty with forming the hydrogen bond with the surface molecules, and hence are easier to desorb, resulting in slow or even no growth. Growth studies of **1** on Pd(110) surface support this assumption.

In-situ scanning tunneling microscopy (STM) was used to study the growth of **1** on Pd(110) (Fig. 3); the details will be published elsewhere. A high resolution STM image of a sub-monolayer of **1** on Pd(110) is depicted in Figure 3A. It shows that the individual molecules are lying flat on the surface. Bonding of these conjugated molecules to the Pd surface was found to be very strong with an estimated bonding energy as high as 2.8 eV (63 kcal mol^{-1}).[10e] The molecules could not rotate due to high energy barriers, and were forced to lie flat on the surface. Most importantly, growth at 27° C stopped after the monolayer (Fig. 3B) was formed. This observation suggests that the molecules lying flat cannot form hydrogen bonds with the arriving molecules because their fixed molecular orientation is not favored for hydrogen bonding.

It is well known that, in contrast to the Pd(110) surface, the hydroxy groups on a glass surface can hydrogen-bond carboxylic acid or pyridine derivatives.[17] For **1** and **2**, this leads to the orientation **a** (head-up, Fig. 4) or **b** (head-down); the molecules are unlikely to bond to the hydroxy surface with both ends due to steric hindrance. It is not clear whether **a** or **b** is preferred by the substrate surface. However, in both cases, the molecules can easily tilt towards the molecular beam direction, allowing efficient hydrogen bonding of the incoming molecules. This is in accord with our observation that, even at substrate temperatures up to 100° C, multi-layer films of **1** and **2** can be grown easily on a number of surfaces consisting of hydroxyl groups, such as amorphous glass, quartz, oxidized silicon, acidic functionalized silicon, etc. In the following, we will discuss molecular orientation during the growth of multi-layer films.

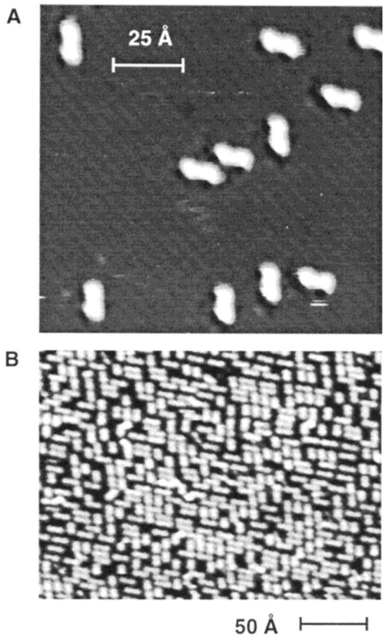

Fig. 3. STM images of molecules of **1** on Pd(110) with a submonolayer coverage (A) and a monolayer coverage (B). Molecules of **1** could not adsorb onto (B) at 27° C.

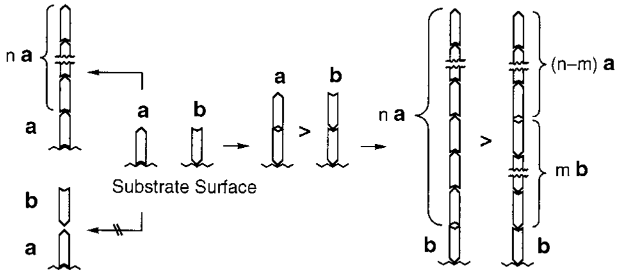

Fig. 4. Illustration of the self-correction of orientation **b** to **a** during growth. See text for details. Due to the weak head-to-head bonding, many more head-to-tail than tail-to-tail hydrogen bonds are formed during growth.

For the growth on surface molecules having orientation **a**, this orientation will be preserved in the surface layers through the head-to-tail hydrogen bonding of the continuously arriving molecules (Fig. 4), because bonding between the pyridyl groups (head-to-head) is negligible, and the preferred hydrogen bond angle of O–H···N is 180°.[15] On the other hand, if the surface molecules adapt to orientation **b**, they can form both head-to-tail and tail-to-tail hydrogen bonds with the arriving molecules (Fig. 4). As estimated before, the dissociation temperatures of both bonds are higher than 128° C. Hence, at 27° C, the bond which forms faster is determined by the bonding probability. We have pointed out that the arriving molecules should have a high probability of orienting their carboxylic group towards the film surface. In addition, the probability of the carboxylic H atom interacting with the O atoms of another molecule is higher than with the N atom. Therefore, a higher rate is expected for the formation of the tail-to-tail hydrogen bonds, leading to orientation **a**, than for the head-to-tail ones in which orientation **b** remains. Consequently, in the second layer, more molecules with orientation **a** than **b** are formed (Fig. 4). Accordingly, after m layers have grown, the number of molecules having orientation **b** in the last layer is reduced to less than $1/2^{m-1}$ of the one in the first layer. Therefore, during the growth, orientation **a** should rapidly overwrite **b** even if it is preferred by the substrate surface. Note that so far the discussion concerns only the outermost layers where the pyridyl groups should preferentially orient towards the molecular beam direction as illustrated with **1** in Figure 5.

During growth, the arriving molecules should have a higher probability of bonding to the nearest, less crowded, and directionally favored N atoms on the film surface. The tilted surface molecules then block their neighboring N atoms from being reached by the successive arriving molecules, resulting in the formation of voids (self-shadowing effect,[7–9] Fig. 5). If the inertia of the arriving molecules is ignored, the smallest void diameter should be larger than the molecular length. Both the voids and the molecules in the outmost layers are preferentially oriented towards the molecular beam direction (Fig. 5).[10b] While they are growing, the sum of the weak van der Waals and π–π-stacking interactions between the tilted chains is increasing, which attracts the molecules to fill the voids to give close packing. The most probable way to fill the voids, while keeping the chain parallel to the molecular beam direction, is that the molecules in the inner layers are inclined in the X_3 direction (Fig. 5) towards the substrate surface. During this process, the hydrogen bonds need to be reformed. In the inner layers, the molecules are close to each other, so that hydrogen bond breaking and reforming can happen simultaneously through the two-center hydrogen-bonded intermediates as illustrated in the gray box in Figure 5. In this way, the activation energy is lower than that for simply breaking the strong O–H···N hydrogen bonds. The molecules in the inner layers are then aligned parallel to the substrate plane with their long axis headed by the carboxylic group along the X_3 axis, as shown in the upper part of Figure 5. This molecular orientation is in agreement with the results of second harmonic generation experiments.[10a]

It should be noted that voids are also generated in the outer layers along the $\pm X_1$ axis (Fig. 5). However, the tilted molecular chains in the outer layers can migrate along this axis to fill the voids. The migration is driven by the van der

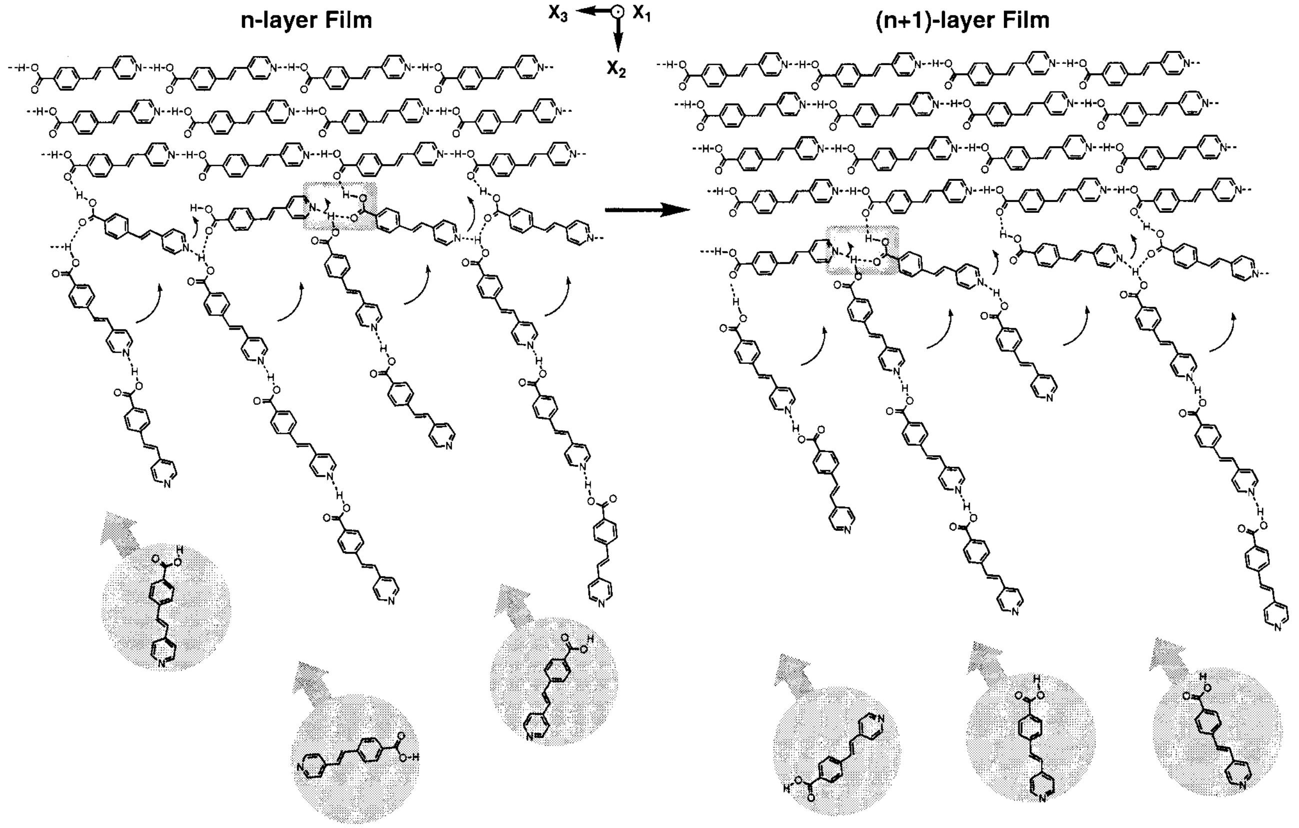

Fig. 5. Illustration of the growth mechanism and molecular orientations of a film of **1**. The arriving molecules are randomly rotating as shown in the bottom gray spheres. Their translating direction is indicated by arrows. When they are close to the surface molecules, they become attracted by van der Waals forces, and preferentially orient the polar carboxylic group towards the surface, while the surface molecules tilt towards them. Hydrogen bonds are then formed, together with voids due to the self-shadowing effect. To fill the voids, the molecules in the inner layers are inclined towards the substrate surface through the hydrogen bonds (gray box) reforming, resulting in the molecular orientation inside the film (upper part). X_3: the projection of the molecular beam direction on the substrate surface; X_2: surface normal; X_1: perpendicular to both X_3 and X_1.

Waals and π–π-stacking interactions between the chains. It involves the breaking of the relatively weak O–H···O hydrogen bonds, that connect the outer tilted chains with the inner lying chains, and reforming them after the migration. On the other hand, the distance between the O atoms of two molecules is much shorter in the $\pm X_1$ direction than in the $\pm X_3$ direction. Hence, it can be assumed that the migration along the $\pm X_1$ axis is much faster than along the $\pm X_3$ axis. In addition, since the O–H···N bond is much stronger than the O–H···O bond, the migration process should be faster than the aforementioned process in which the molecules are inclined towards the substrate surface. Both processes should be favored at high substrate temperatures to overcome the activation energy. Higher temperatures also reduce the bonding capability of the van der Waals force, which is less directional. This is probably why the second harmonic intensity of films of **1** grown at –190° C was only about 10 % of those grown at 30° C, which was in turn about 80 % of those grown at 100° C, indicating that the alignment of **1** was improved at elevated temperatures.

The above proposed mechanism suggests the possibility of designing molecules so that they can not only self-assemble, but also self-correct the molecular orientations (Fig. 4) during growth.[18] In this way, ordered thin films can be grown repeatedly and continuously, using only one component, into any desired thickness without losing the ordering. In fact, the ordering of the films of **1** or **2** was independent of film thickness up to at least 400 nm, as indicated by the quadratic increase of the second harmonic intensity with film thickness.[10a,b] In addition, we have shown that the molecular directions of films of **1** grown on a bare glass and on a strong acidic surface are the same.[10c] Moreover, we obliquely deposited 100 nm of **1** on a glass substrate, and then rotated the sample by 180° around the surface normal before we continued to deposit another 100 nm. The second harmonic intensity of the film dropped by more than 90 % as compared to that of a 200 nm film deposited without substrate rotation. This is due to the fact that the second order nonlinear optical susceptibility tensor $\chi^{(2)}$ of the first layer (100 nm) is nearly canceled out by that of the second layer (100 nm). This suggests that, during the growth, the surface molecules can self-correct their orientation to the one most favorable for the growth, which we believe to be the one shown in Figure 5.

In conclusion, we propose that the preferential alignment of the dipolar molecules **1** and **2** in films grown by oblique

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OMBD is due to the combination of shape and bonding features of the molecules, together with kinetic factors such as directional hydrogen bonding, and the self-shadowing and self-correcting effects. Not all organic molecules having shapes similar to **1** and **2** can be used to obtain in-plane ordering by oblique OMBD. Long-range ordering was not observed in films of several other stilbene-type dipolar chromophores without sticky ends.[19] This suggests that the bonding feature of **1** and **2** is necessary to achieve the alignment. We believe that our preliminary results[10] and the mechanism proposed here for the growth and alignment will stimulate interests in using supramolecular assemblies based on hydrogen bonding[18,20] for OMBD growth of ordered thin films. Further experimental and theoretical studies, including computer simulation, are necessary to fully understand the origin of the in-plane ordering, and the role of the materials and deposition conditions on the ordering. Such understanding will rationalize material design and processing conditions for the fabrication of oriented organic thin films for advanced applications, such as nonlinear optics and electro-optics.

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Hierarchical Organization of Functional Perylene Chromophores to Mesoscopic Superstructures by Hydrogen Bonding and π–π Interactions**

By *Frank Würthner*,* *Christoph Thalacker*, and *Armin Sautter*

Nature is abundant with functional structures that are organized hierarchically through non-covalent interactions. Introducing functionality is also a main goal in supramolecular chemistry[1] to make use of molecular recognition events for sensor applications,[2] control of transport processes,[3] or electrical and optical devices.[4] Especially for the latter, spontaneous self-assembly could provide a powerful tool to achieve architectural control and functional specificity. The major challenge confronting such a bottom-up approach is how to position predefined functional building blocks in space to optimize complex processes such as energy or charge transport.

As electrical and optical functionalities rely on extended conjugated systems, a lot of work has been devoted to π stacking as the major driving force for one-dimensional columnar superstructures.[5] However, the concomitant electronic interactions are not always desired because of substantial and hardly predictable changes of the molecular properties of the chromophores. Moreover, progress toward long-range three-dimensional structures is difficult to realize for these systems because additional non-covalent forces, such as hydrogen bonding or metal–ligand coordination, often cause the formation of insoluble pigments.[6,7]

In this paper we report our initial results toward well-defined mesoscopic structures based on a multifunctional perylene chromophore of high photostability, high fluorescence quantum yield,[8] and distinct redox activity.[9] The process of superstructure formation is shown to involve multiple orthogonal intermolecular interactions, appropriate solubilizing substituents, and a solvent of low polarity (Scheme 1).

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