

Polarity of Organic Supramolecular Materials: A Tunable Crystal Property

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Basic principles are reviewed which provide new access to the synthesis of acentric molecular crystals along with an application to the design of intermolecular interactions and the crystallization of polar host–guest materials. Because of the process of crystal growth, the primary confinement for the alignment of dipolar molecules is given by a surface–nutrient interface and not by the bulk state as usually assumed for the prediction of crystal structures by computational methods. Subject to defined restrictions, spontaneous polarity formation in slowly growing crystals can be regarded as a simple isomerization reaction, $\downarrow \rightleftharpoons \uparrow$ (\downarrow , \uparrow , orientations of the dipole moments in crystals). Following results of Monte Carlo simulations, performed for a surface layer (adlayer) on a nonrelaxing substrate layer, we conclude the following: (i) Although binding motifs (synthons) are important to induce 1D or 2D order into chains, ribbons, and planes, lateral interactions between such structural elements enter polarity formation by a much higher weight factor. (ii) Particular lateral interactions favoring $\downarrow \cdots \downarrow$ are not necessary to obtain polarity in some molecular crystals. Channel-type inclusion materials represent a solution to (ii). Experimental confirmation is provided by, e.g., a large number of polar inclusion compounds of perhydrotriphenylene (PHTP). It is shown that in general a combination of van der Waals interactions for a 2D confinement (alignment of molecular frames) and one of the most nonbonding recognition motifs (\downarrow vs \uparrow orientation) can optimize polarity formation in host–guest lattices. In essence, we review that in some molecular crystals polarity is a tunable property, and that a supramolecular synthesis can produce a material and a property by parallel reactions. © 2000 Academic Press

Key Words: polarity formation; Markov chain; supramolecular; Ising model; inclusion compound; isomerization reaction; Monte Carlo method.

1. INTRODUCTION

Materials (single crystals, ceramics, polymers, and mesophases) providing an *acentric* point symmetry of are of interest to studies of solid-state properties (pyroelectricity, piezoelectricity, optical nonlinearity, and others), and are of use in some real-world applications (frequency conversion and amplitude modulation, mechanical actuators and sensors, etc.) (1, 2). Modern solid-state chemistry may therefore focus on strategies to obtain an acentric order of highly polarizable constituents in condensed phases.

In this review we summarize basic principles providing access to the synthesis of acentric *molecular* materials along with an application of these findings to the design of intermolecular interactions (synthons (3)) and the crystallization of host–guest lattices. For complementary reviews, see Refs. (4–9).

If attempting to produce polar properties by aggregation of molecular bricks, we assume effects of polarity which originate from polar properties of molecules. For the purpose of representation we will use the dipole moment ($\mu_{e1} \equiv A \rightarrow D$: \downarrow or \uparrow with respect to the polar axis of a crystal) as a descriptor for the occurrence of polarity in molecular materials built up by, e.g., *A*– π –*D* type molecules (for a definition, see Fig. 1). Put forward this way, we will discuss a mechanism of property formation yielding a nonvanishing dipolar sum within macroscopic parts of a crystal. There are two extreme cases of dipolar ordering: dipoles confined into (i) a *parallel* or (ii) an *antiparallel* state. “Crystal engineering” of organic compounds (10) has shown that certain dipolar compounds may well form polar chains, ribbons, or planes in many crystal structures, but polar structural elements are often arranged in such a way as to form a centric crystal structure. Representative examples are given by 4-iodo-4'-nitrobiphenyl (where *D* = I, *A* = –NO₂, and

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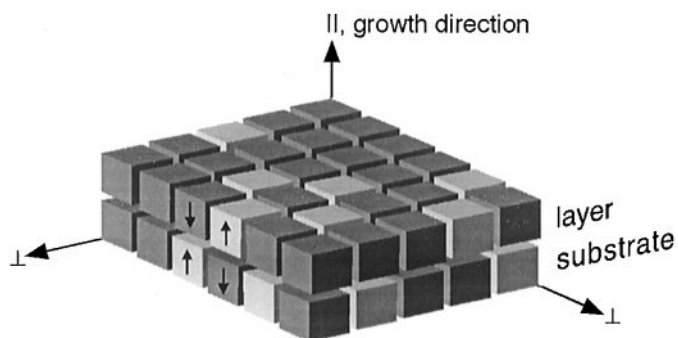


FIG. 3. Definition of a substrate layer onto which an adlayer is placed for thermal relaxation. Dark gray (\downarrow) and light gray (\uparrow) cubes represent the polarity of dipoles. Interactions in the \perp and \parallel directions are taken into account. For Monte Carlo simulations we assume $z_{\perp} = 4$ and $T = 300$ K.

2. THEORY OF POLARITY FORMATION IN MOLECULAR CRYSTALS

Following the reductionism introduced above, we reduce the phenomenon of polarity formation to a general packing of molecules (acentric or centric) (14) subjected to one degree of orientational freedom with respect to their dipole moment (17). As a result of a growth process, dipoles within an adlayer are assumed to be free to accommodate a state of perfect 0° ($\downarrow\downarrow$) or 180° ($\uparrow\uparrow$) orientational order or some disorder for given interactions \parallel , \perp at temperature T . As defined, such a system shows a formal analogy to *magnetic solids*, where a spin may interact in the \perp and \parallel directions with neighboring spins. In the case of a unipolar substrate, we could describe the ordering within the adlayer by a 2-D

Ising model taking into account lateral coupling and a magnetic field in the \parallel direction (19).

A straightforward solution to numerical values of x_{net} for adlayers was obtained by Monte Carlo simulations (20). According to Fig. 3, the calculations started from a substrate layer of a given and constant state of polarity on which an adlayer was subjected to thermal relaxation. The chemical inputs to these calculations are the growth temperature and the \parallel and \perp interactions, namely $E_{AD} \equiv -A \cdots D-$, $E_{DD} \equiv -D \cdots D-$, $E_{AA} \equiv -A \cdots A-$, and $E_{\text{ap}} \equiv \downarrow \cdots \uparrow$, $E_p \equiv \downarrow \cdots \downarrow$, including a coordination number z_{\perp} , indicating the number of nearest neighbors taken into account within the adlayer only.

Figure 4 shows the evolution of polarity x_{net} as a function of the index q of subsequently attached layers: Upon a seeding layer featuring no polarity, an increase of x_{net} to a constant value is obtained (20, 21). A constant value x_{net} above a certain number of attachment steps means that by adding further layers, the global minimum of the free energy of the adlayer cannot be lowered any more. Therefore, we consider this the thermodynamic limit for the polarity of a crystal volume produced by a *growth process*. It is important to notice here that x_{net} (growth) may well differ from x_{net} (bulk equilibrium) (22). Another basic feature of the evolution of polarity up to a constant value of x_{net} is that in representative cases (20) *the final result at large q does not depend on the state of the polarity of the seeding substrate* (Fig. 5).

In the introduction we emphasized the importance of the lateral interaction. In Fig. 6, we show plots for x_{net} ($q \rightarrow \infty$) calculated by using typical values for $\Delta E_A(\parallel) \equiv E_{AA} - E_{AD}$ (here, $\Delta E_D(\parallel) = E_{DD} - E_{AD} \equiv 0$; see comments on particular $A-\pi-D-R$ molecules in Section 3) and a reasonable range

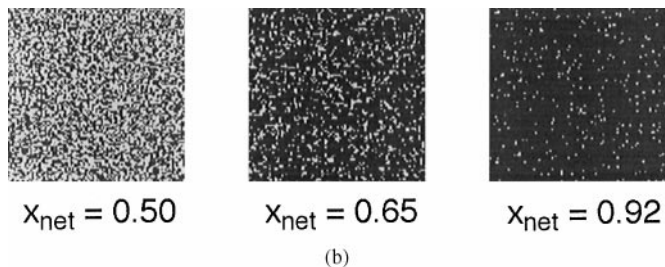
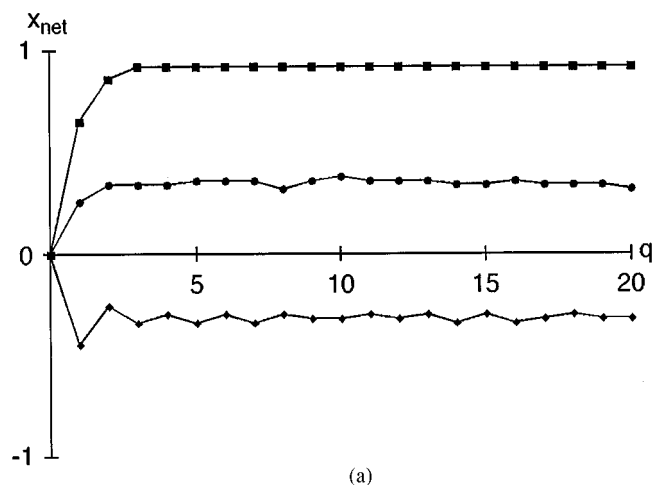


FIG. 4. (a) Monte Carlo simulations of the polarity evolution of subsequently attached adlayers (see Fig. 3 for definition). A random state substrate ($x_{\text{net}} = 0$) was assumed. $T = 300$ K, number of trials per pixel = 4×10^6 , layer size = 100×100 . Interaction energies: $\Delta E_{\perp} = -1$ and $\Delta E_A(\parallel) = 5, 1, -2$ (kJ mol^{-1}) ($\Delta E_D(\parallel) \equiv 0$), corresponding to diminishing values for x_{net} at $q = 20$. (b) View onto a growing face: selected states of polarity evolution as obtained for (a). Dark gray pixels, \downarrow ; light gray pixels, \uparrow . Interaction energies: $\Delta E_{\perp} = -1$ and $\Delta E_A(\parallel) = 5$ (kJ mol^{-1}) ($\Delta E_D(\parallel) \equiv 0$).

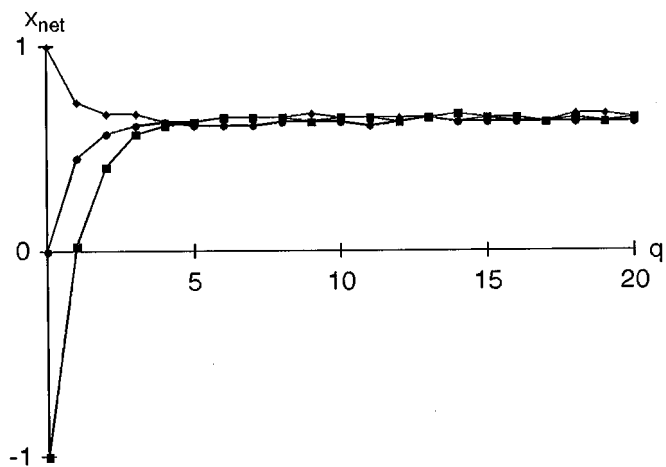


FIG. 5. Monte Carlo simulations showing that for some interaction energies (20), there is no influence of the substrate state on x_{net} at sufficiently large q . Interaction energies: $\Delta E_{\perp} = -1$ and $\Delta E_A(\parallel) = 2$ (kJ mol^{-1}) ($\Delta E_D(\parallel) \equiv 0$).

for $\Delta E_{\perp} \equiv E_p - E_{\text{ap}}$ ($z_{\perp} = 4$). This graph is the key to an understanding of polarity formation in crystals grown from dipolar components: there are two extreme cases, as mentioned earlier. In magnetism they would correspond to the ferromagnetic or antiferromagnetic state. In between, there are states of variable polarity, where either the $[\downarrow\downarrow\downarrow\downarrow \dots]$ or the $[\uparrow\downarrow\uparrow \dots]$ state is to some extent disordered. Nearly independent of reasonable $\Delta E_A(\parallel) > 0$ values at $\Delta E_D(\parallel) \equiv 0$, we can give quite general limits for ΔE_{\perp} in order to achieve one of the ordered states: $\Delta E_{\perp} [\downarrow\downarrow\downarrow\downarrow \dots] \leq -3$, $\Delta E_{\perp} [\uparrow\downarrow\uparrow \dots] \geq 4 \text{ kJ mol}^{-1}$ ($z_{\perp} = 4$, $T = 300 \text{ K}$).

Particularly at $\Delta E_{\perp} = 0$, x_{net} is not vanishing. For a strongly positive (nonbonding²) \parallel interaction, x_{net} can be close to 1. This means: that a negative ΔE_{\perp} is not a necessary condition to have spontaneous polarity formation resulting from a crystal growth process. Knowing this, we can think of real systems where to a good approximation ΔE_{\perp} is zero. An obvious solution to the problem is given by use of a supramolecular compound (Section 3), where a centric host lattice is housing dipolar guest molecules in, e.g., parallel channels separated well enough laterally to preclude antiparallel alignment (Fig. 7) (9, 16). By other approaches one may introduce steric substituents to the π -frame of $A-\pi-D$ molecules with the aim of reducing the tendency for antiparallel packing (6).

Before discussing polarity formation of inclusion compounds in more detail (15), we briefly summarize a second, analytical approach to obtain values for x_{net} . In magnetism

²By nonbonding we mean that the intermolecular potential energy curve does not show a minimum at the typical van der Waals distance between, e.g., collinearly arranged functional groups such as $D-\pi-A \cdots A-\pi-D$ ($A: -\text{NO}_2, -\text{CN}, \text{etc.}$).

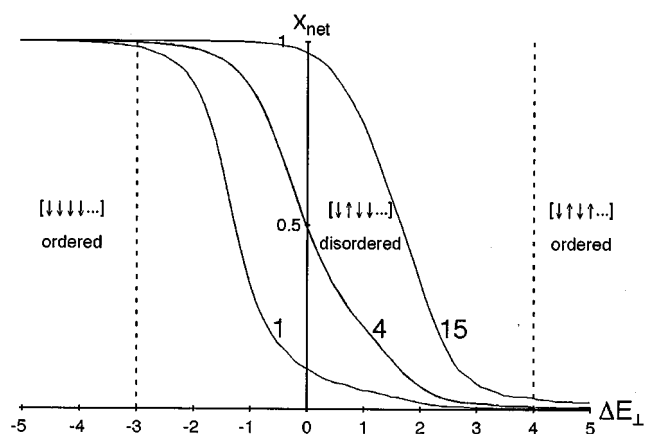


FIG. 6. Monte Carlo simulations featuring the influence of the lateral interaction (ΔE_{\perp}) on x_{net} for a series of energies typical of a non-bonding molecular recognition ($\Delta E_A(\parallel) > RT$, $\Delta E_D(\parallel) \equiv 0$ (kJ mol^{-1})). Curves represent fits to simulation results for 10^7 trials per point within a field of 60×60 dipoles ($T = 300 \text{ K}$, $z_{\perp} = 4$). Abscissa: ΔE_{\perp} in kJ/mol .

(19), as well as surface melting (23) and solid solution formation (24), *mean-field* models are commonly applied. When Kitaigorodsky was discussing orientational disorder of dipolar molecules in the early 1960s (25), he made use of the idea that orientational disorder of single-component molecular crystals can be described by the thermodynamics of

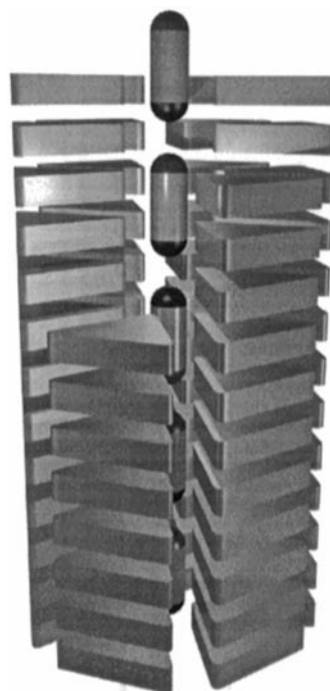


FIG. 7. Typical packing architecture of a channel-type inclusion lattice. Triangular bricks (PHTP) form a channel wherein dipolar species are aligned.

ideal solid solution formation. If applied to the present case, calculation of the global minimum of $F_{\text{mean-field}}$ yielded an exact implicit and an approximative explicit equation for x_{net} . Without providing here the details of the calculation, we give the approximate solution, which is fairly accurate for $\Delta E_{\perp} < 0$ ($\Delta E_f \equiv E_{AA} - E_{DD} > 2RT$), holding to some extent also for $\Delta E_{\perp} > 0$ (20):

$$\frac{x(\downarrow)}{x(\uparrow)} \approx e^{(\Delta E_f - \gamma z_{\perp} \Delta E_{\perp})/RT} \quad [2]$$

and

$$x_{\text{net}}(\text{mean-field}) \approx 1 - 2e^{-(\Delta E_f - \gamma z_{\perp} \Delta E_{\perp})/RT}, \quad [3]$$

where Eq. [3] is most accurate for x_{net} near 1 (the scaling factor γ is in the range of about 1 to 2, depending on the model used for the calculation).

Equation [2] allows for a quantitative description of equilibria we have addressed in Section 1. This means that in the realistic case as outlined above, *polarity formation in molecular crystals can be regarded in terms of a simple isomerization reaction* $\uparrow \rightleftharpoons \downarrow$. From the exponent we recognize the strong influence of the lateral interaction on polarity formation, because of the factor γz_{\perp} , where z_{\perp} at real crystal surfaces is certainly ≥ 2 . According to a general principle of polarity formation in molecular crystals, elaborated in Ref. (7), $\Delta E_{\varphi} \equiv \Delta E_f - \gamma z_{\perp} \Delta E_{\perp}$ represents an approximate expression for the energy difference being fundamental (φ) to polarity formation described by a mean-field model.

With respect to a design of interaction energies, it becomes clear that it is more feasible to seek for (i) $\Delta E_{\perp} \approx 0$, or (ii) negative values, than for solutions where the synthon interaction is dominating lateral interactions, $\Delta E_f > \gamma z_{\perp} \Delta E_{\perp}$ ($\Delta E_{\perp} > 0$).

For the first time we have here an expression (Eq. [3]) for polarity formation, reflecting the influence of both (i) synthons (\parallel), and (ii) other more collective interactions (\perp): $\rightarrow \dots \leftarrow$ vs $\leftarrow \dots \rightarrow$ and $\downarrow \dots \downarrow$ vs $\downarrow \dots \uparrow$. *Although synthons are import in order to induce 1D or 2D polar order into chains, ribbons, and planes, lateral interactions between such structural elements enter polarity formation by a much higher weight factor.*

3. CHANNEL-TYPE INCLUSION COMPOUNDS: A SOLUTION TO $\Delta E_{\perp} \approx 0$

Channel-type inclusion compounds are materials obtained by a co-crystallization of a host and a guest compound. Known examples of host materials are urea, thiourea (26), spirocyclotriposphazenes (27), perhydrotriphenylene (PHTP) (28), dumb-bell-shaped molecules (29), and others (4). Synthetic approaches producing co-crystals are indicated in Fig. 8. In many cases, crystallization from solvents being not co-included was the method of choice. In the case of perhydrotriphenylene, about 45 different $A-\pi-D$ molecules could be included. More than 90% of these inclusion lattices showed a second harmonic effect (SHG), if illuminated by a pulsed IR laser beam (17).

Guest molecules in different channels of PHTP are kept at distances about 14 Å and larger (30). This precludes most of the polarization-induced lateral (\perp) interactions, whereas close packing along channel allows for strong collinear (\parallel) synthons. A further advantage is that here θ is about zero degree, i.e. dipoles can in principle undergo fully parallel alignment (Eq. [1a]). From the theoretical point of view, channel-type lattices provide a frame, where $\Delta E_A(\parallel)$ and $\Delta E_D(\parallel)$ type interactions are active during the process of attachment, whereas ΔE_{\perp} can be neglected to a good approximation. Spontaneous polarity formation has therefore been explained by the thermodynamic model we have summarized in Section 2. However, here an equivalent description by a homogeneous *Markov* chain theory is possible (31–33). According to Fig. 9, the orientational ordering during the attachment of dipolar guests along the channels is governed by four probabilities (two of them being independent parameters), which are the elements of a transition matrix driving the system from the q to the $(q + 1)$ layer:

$$\begin{bmatrix} x(\downarrow, q) \\ x(\uparrow, q) \end{bmatrix} = \begin{bmatrix} p(A \cdots D) & p(D \cdots D) \\ p(A \cdots A) & p(D \cdots A) \end{bmatrix}^q \cdot \begin{bmatrix} x(\downarrow, q=0) \\ x(\uparrow, q=0) \end{bmatrix}. \quad [4]$$

Above a certain number of attachment steps q , x_{net} becomes constant. x_{net} (defined for the case where preferably A groups are at the surface) depends on two characteristic

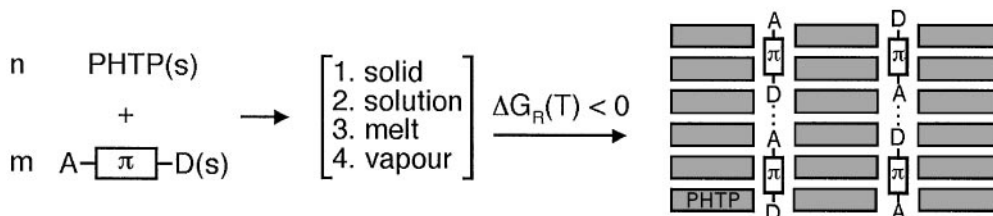


FIG. 8. General scheme summarizing the syntheses of a host-guest compound. Crystallization may be performed (1) by a solid-state reaction, (2) using a solvent, (3) from the melt, or (4) from the vapor phase.

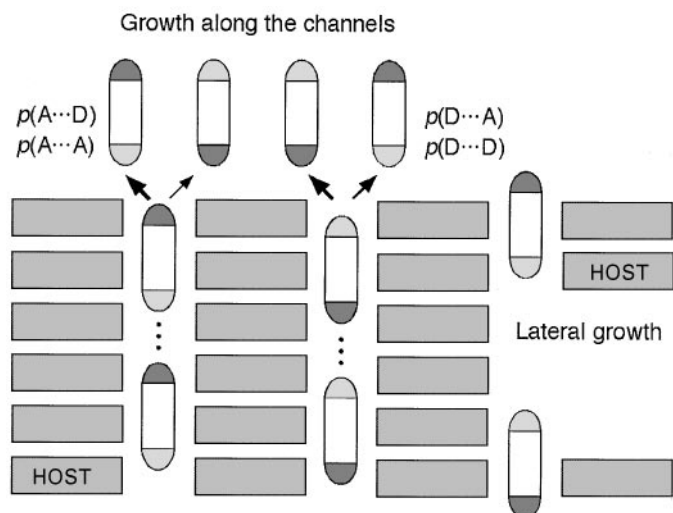


FIG. 9. Process of attachment of dipoles (i) to existing well-separated ($\Delta E_{\perp} \approx 0$) channels, and (ii) in the case of new channels. Growth in only one of the channel directions is indicated for (i). Pictorial definition of attachment probabilities.

energy differences [34], $\Delta E_f \equiv E_{AA} - E_{DD}$ and $\Delta E_A \equiv E_{AA} - E_{AD}$,

$$x_{\text{net}}(q \rightarrow \infty) = \frac{p(D \cdots D) - p(A \cdots A)}{p(D \cdots D) + p(A \cdots A)} = \frac{1 - e^{-\Delta E_f/RT}}{1 + e^{-\Delta E_f/RT} + 2e^{-\Delta E_A/RT}}. \quad [5]$$

For real examples of molecules, ΔE_A is of the order of 10–30 kJ mol⁻¹. This allows us to simplify corresponding equations for $x(\downarrow)$ and $x(\uparrow)$ into

$$\frac{x(\downarrow)}{x(\uparrow)} \approx e^{(E_{AA} - E_{DD})/RT}. \quad [6]$$

For $\Delta E_f > 2RT$ we can simplify Eq. [5] into

$$x_{\text{net}} \approx 1 - 2e^{-(E_{AA} - E_{DD})/RT}, \quad [7]$$

where Eq. [7] is most accurate for x_{net} near to 1 (33).

Equation [6] reflects again the nature of an isomerization reaction, leading to polarity. The driving force for the *non-cooperative* alignment of dipoles is simply ΔE_f , the fundamental (f) energy difference in polarity formation for $\Delta E_{\perp} = 0$.

So far, we have not specified the particular role of synths involved in the process of polarity formation. Obviously, a strongly binding $-A \cdots D-$ interaction will give rise to polar chain formation in single channels. Because there

might be only weak electronic coupling between guests in different channels, no macroscopic polarity would arise if $\Delta E_f = 0$. An algebraic analysis has shown (33) that (i) a maximum x_{net} value, and (ii) a lowest density η of orientational defects along polar chains is obtained at (iii) a low number of steps q , if the three basic interactions obey the relation

$$E_{DD} \approx E_{AD} \ll E_{AA}. \quad [8]$$

A chemically interesting case results for $E_{DD} = E_{AD} \approx 0$, and $E_{AA} > RT$. There exists a large number of NLO active molecules which to a good approximation may be introduced this way: $A-\pi-D-R$ (R = less polarizable group, e.g., $-\text{CH}_3$, $-\text{CF}_3$; for real examples, see (6)). We have already made use of this class of molecules in Section 2 (Fig. 6, Eqs. [2, 3]). In Fig. 10 we see a key feature: *For $A-\pi-D-R$ molecules attached to separated channels maximum polarity is obtained for nonbonding E_{AA} interactions, whereas bonding interactions would only produce a x_{net} of $-1/3$ (a negative sign means that instead of A groups, we will preferably have D groups at the growing surface).*

So far, we have considered growth only along *one* direction of the channels or more generally, in one direction of a seed crystal. If not hindered by the applied growth technique, we will obtain *bipolar* crystals (32). Within two macrodomains, constant but opposing polarity is evolving. Because crystals grow also in lateral directions, there is another growth feature to discuss (Fig. 9): attachment of a single dipole to new channels is associated with a 50% probability for \downarrow or \uparrow . Additionally, there should be no preference for the position along the channel direction

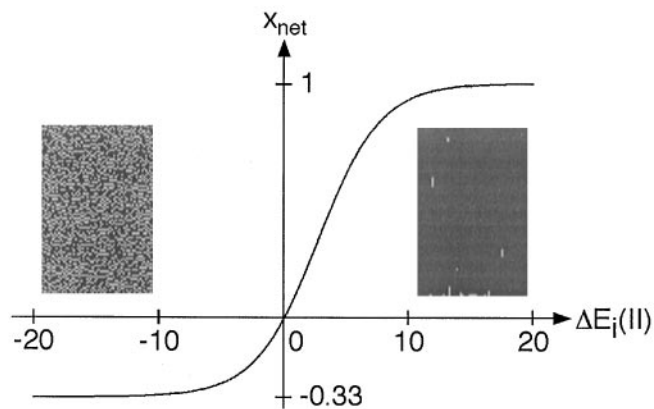


FIG. 10. Polarity for $X-\pi-Y-R$ type molecules, where $X = A$ or D , $Y = D$ or A , correspondingly (R , less-polarizable group, e.g., $-\text{CH}_3$, $-\text{CF}_3$). The best results are predicted for nonbonding molecular recognition motifs. The inset represents stochastic simulations. Dark gray pixels, \downarrow ; light gray pixels, \uparrow . Interaction energies: $\Delta E_i(\parallel) = -20, 20$ (kJ mol⁻¹) ($i = A$ or D) for bonding, nonbonding interactions, respectively. For $\Delta E_i > 0$, X groups preferably cover the growing face; for $\Delta E_i < 0$, R groups are preferably on top.

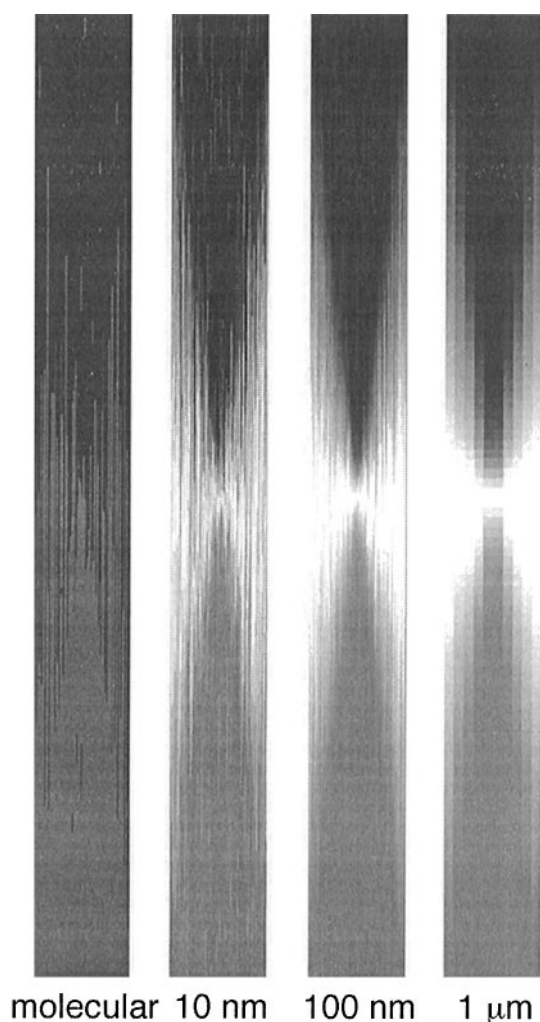


FIG. 11. 2D simulations obtained with $\Delta E_r = 12.4$, $\Delta E_A = 32.3$, $\Delta E_D = 19.9$ (kJ mol^{-1}). In simulations at molecular resolution (1 pixel corresponds to 1 nm^2 , left), 10^2 channels and 10^3 layers are shown. For the other images, 10^4 channels and 10^5 layers were taken into account. Shown is the effect of averaging (10×10 pixels), which allows us to make comparisons with experimental resolution: 10 to 100 nm is in the range of scanning near-field optical microscopy, $1 \mu\text{m}$ is just below the present resolution of scanning pyroelectric microscopy.

where a first attachment occurs. Therefore, the as-grown state of such crystals can be described by a *double-cone* structure (Fig. 11). For particular interaction energies we calculated (stochastic simulations) a possible distribution of the polarization as it may be observed at different scale lengths of experiments. Up to now, *scanning pyroelectric microscopy* (SPEM) was the only technique which was able to image the double-cone structure in real crystals (34, 35). New experiments attempt to reveal cones by scanning SHG microscopy (36). However, just recently we succeeded in demonstrating polarization reversal in as-grown thin crystals by *phase-sensitive* SHG microscopy (37).

Summarizing known results, channel-type supramolecular materials are evidently prime candidates for a system providing $\Delta E_{\perp} \approx 0$. Present synthesis efforts (29) are directed toward syntheses of new *host* molecules bringing in the lowest possible molar volume, because of the effect of dilution. By use of a two-component system, i.e., $(\text{HOST})_{1-x} (\text{GUEST})_x$, we reduce the density of polar constituents (15), which in turn is reducing effects of macroscopic polarity.

4. CONCLUSIONS

A stochastic approach to polarity formation in molecular crystals has led to synthetic strategies which are fairly different, compared to those attempted by others (18). Following the classical view, “Crystal engineers” are producing molecular compounds which upon nucleation should grow into an acentric crystal structure. This endeavor is associated with a probability for a failure of about 70–80%. In essence, design of intermolecular interactions ensuring polar packing of one-component crystals still remains an ambiguous task. Following the analysis given in Section 2, it becomes clear that paying attention only to synthons is not sufficient for polarity formation. The lateral interactions between chains, ribbons, or planes affect property formation much more than for synthons (see Eqs. [2, 3]). Previously, the only secure way to obtain an acentric material was the use of enantiomerically pure components.

Ideas summarized above bring in a new view: it turned out that polarity is a *tunable property*. To take full advantage of tunability, molecular bricks should preferably provide $\Delta E_{\perp} \approx 0$. With respect to both types of interactions \parallel and \perp , we arrive at a conclusion opposite to what “Crystal engineering” claims: *van der Waals interactions for a 2D confinement and one most nonbonding recognition motive* can optimize polarity formation in host–guest systems (6). Polarity resulting from individual molecular bricks is a complex physical property of molecular crystals which can systematically be tuned by chemical synthesis. Polarity formation during crystal growth is formally equivalent (about restrictions, see above) to an *isomerization reaction* $\uparrow \rightleftharpoons \downarrow$. As a consequence, the final result does not depend on the state of polarity of the seed crystal used for growth up to the macroscopic size.

In essence, the new thing about it is a *supramolecular synthesis can produce a material and a property by parallel reactions*.

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