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Tunable Columnar Mesophases Utilizing C_2 Symmetric Aromatic Donor−Acceptor Complexes

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Abstract: Derivatives of relatively electron rich 1,5-dialkoxynaphthalene (Dan) donors and relatively electron deficient 1,4,5,8-naphthalenetetracarboxylic diimide (Ndi) acceptors have been exploited in the folding and self-assembly of a variety of complex molecular systems in solution. Here, we report the use of Dan and Ndi derivatives to direct assembly of extended columns with alternating face-centered stacked structure in the solid state. A variety of 1:1 Dan:Ndi mixtures produced mesophases that were found to be stable over temperature ranges extending up to 110 °C. Analysis of these mesophases indicates mixtures with soft/plastic crystal phases and a few mixtures with the thermodynamic properties of true liquid crystals, all composed of alternating donor−acceptor columns within. Importantly, a correspondence was found between the clearing and crystallization points of the mesophase mixtures and the melting/clearing points of the component Ndi and Dan units, respectively. This correspondence enables the predictable tuning of mesophase phase transition temperatures. The study of sterically hindered derivatives led to a set of mixtures in which a dramatic and sudden color change (deep red to yellow) was observed upon crystallization of the mesophase due to a phase separation of the component donor and acceptor units.

Introduction

Alternating stacks of electron-rich and electron-deficient aromatic moieties have proven to be a versatile tool for molecular self-assembly in solution.[1−4] Examples include the catenane and rotaxane assemblies that are designed around electron-rich and electron-deficient aromatics to produce complex preorganized structures.[2,3] We have previously reported that oligomers containing tethered electron-rich 1,5-dialkoxynaphthalene (Dan) and electron-deficient 1,4,5,8-naphthalenetetracarboxylic diimide (Ndi) exhibit intramolecular folding in water based upon an alternating column of aromatics stacked in a face-centered geometry.[4] This folding is largely driven by desolvation of the aromatic faces (the hydrophobic effect), directed by the complementary geometry and electrostatics of the Dan:Ndi complex.[5,6] Independent Dan and Ndi oligomers have also been shown to promote intermolecular hetero-duplex formation in water.[7] As a continuation of our studies of the folding and assembly of molecular systems based upon complementary Dan and Ndi stacking, we report here various mesophases created from the 1:1 mixtures of several Dan and Ndi derivatives.

The solid state assembly of aromatic donor−acceptor complexes has previously attracted much attention. For example, in 1960, a crystalline phase was reported in a 1:1 mixture of benzene and hexafluorobenzene in which the two molecules were found to be in long alternating stacks.[8] Work with liquid crystalline materials has shown that electron-rich mesogens can be modified by the introduction of electron-deficient moieties.[9] Equimolar mixtures have been key in developing novel films with linear charge-transfer (CT) channels, and improving the efficiency of organic photovoltaic devices.[10,11] Recently, 1:1

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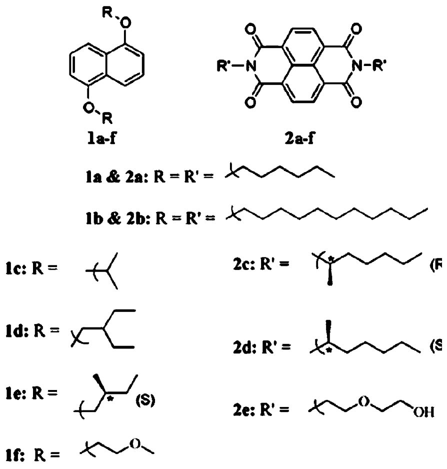
Chart 1. Dan and Ndi Derivatives Used in This Study.



mixtures of structurally complementary electron-rich and electron-deficient aromatics have been shown to greatly alter and/or create phase behavior unique from individual components.[12] The complementary electrostatics and comparable geometries of Dan and Ndi lend themselves to moving from folding and self-assembly in solution to mesophase assembly in bulk phase.

Advantages of using aromatic donor−acceptor interactions to create mesophases from two different molecules include: (1) having a driving force for the creation of columnar aromatic stacks with face-centered geometry, (2) opportunities for tuning phase transition temperatures and mesophase geometries by altering side chains on one component at a time, and (3) the ability to adjust the ratio of donors and acceptors to further affect and tune properties. For mesophase formation to occur, it is assumed that interactions between Dan and Ndi molecules are preferred over Ndi:Ndi and Dan:Dan self-association in the solid state, and that the Dan:Ndi stacks are face-centered columns. For comparison, crystal structures have revealed that indeed in the solid state, Dan:Ndi stacks are face-centered,[4] while Dan:Dan association is dominated by relatively weak edge-to-face interactions (vide infra) (a so-called herringbone structure), and Ndi alone packs in an offset face-to-face geometry (vide infra).

Herein, we report the synthesis and initial characterization of several novel and highly colored mesophases, including examples of soft/plastic crystals and liquid crystals, produced from mixtures of various Dan and Ndi derivatives. The temperatures associated with the mesophase phase transitions were found to depend in a predictable way on the melting points or in some cases the clearing points of the component Dan and Ndi units. In addition, one set of mixtures displayed a sudden and dramatic change in color when undergoing a sharp mesophase to crystalline phase transition.

Results.

Synthesis. The Dan derivatives were synthesized through deprotonation of dihydroxynaphthalene (Dhn) followed by reaction with various alkyl bromides. Ndi derivatives were synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (Nda) and the corresponding alkylamines. A range of alkyl substituents were chosen in order to investigate the role played by representative side chains on mesophase formation (Chart 1). In particular, the location and extent of branching was varied to evaluate steric constraints on face-centered stacking.

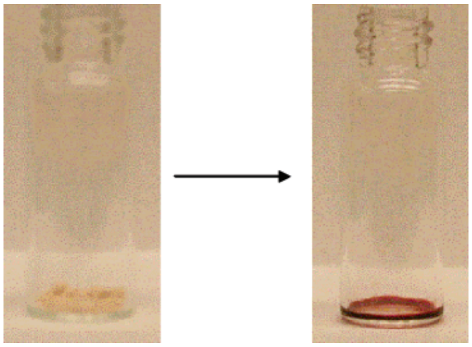


Figure 1. Color change from light yellow to deep red upon melting of the 1:1 Dan:Ndi mixture 1b:2b, which is characteristic of the Dan:Ndi mixtures reported here.

Mixtures Dan:Ndi mixtures with the desired molar equivalents were stirred during melting. In general, the Dan derivatives melted first into a liquid that dissolved the Ndi. During the dissolution of the Ndi derivative, there was usually a rapid change in color from off-white or light yellow to a deep red characteristic of the Dan-Ndi charge transfer (CT) band (Figure 1).

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was used to characterize the phase transitions of the different Dan and Ndi derivatives, as well as their mixtures. Upon heating, all crystalline Dan derivatives in pure form (1a−1f) undergo a single transition to the isotropic phase. The phase transition temperatures measured for the molecules and their mixtures are given in Table 1. Two of the pure Ndi derivatives (2c and 2d) also undergo a single transition to an isotropic phase, although the Ndi derivatives with the longest unbranched alkyl chains, 2a and 2b, exhibit a mesophase over modest temperature ranges (20−50 °C range).

The 1:1 mixtures of all Dan:Ndi combinations for which evaporation of the Dan component was not a problem produced at least two transitions, indicating mesophase formation over a sometimes relatively large temperature range (i.e., 1e:2c). Figure 2 shows representative DSC data measured for compounds 1b, 2b, and a 1:1 molar mixture of the two cooling at 5 °C/min. The mixture exhibits two phase transitions, one of lower energy at 135 °C, and one at 70 °C. Closer inspection of the phase transition at 135 °C reveals several overlapping small peaks. 1:1 mixtures of 1b with 2c and 2d exhibited transition enthalpies indicative of a liquid crystal phase along with a third phase transition, the nature of which is not clear this time.

The phase transitions of many Dan:Ndi mixtures follow an interesting trend in that the clearing point transition is generally similar to the melting point of the Ndi component (or the clearing points in the cases of Ndi 2a and 2b), whereas the crystallization temperature of the mixture is generally very similar to the Dan component melting points. Of note are the transition temperatures of Ndi enantiomers 2c and 2d with chiral derivative Dan 1e. Although 2c and 2d have identical phase behavior individually and when mixed with other nonchiral Dan derivatives, the 1e:2c mixture has phase transitions ∼20 °C higher that of the 1e:2d mixture. Combining a racemic mixture

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Table 1. Results of the Thermal Phase Behavior Characterization of Several Dan and Ndi Derivatives as Well as Their 1:1 Mixtures

	Ndi →	2a	2b	2c	2d
Dan ↓		204° → 150° 92.2 61.9	162° → 144° 72.7 19.1	159° 134.6	159° 134.6
1a	86° 460.8	146° → 78° 6.1 54.5	1a evaporated	1a evaporated	
1b	75° 175.3	143° → 68° 5.4 101.7	134° → 71° 21.4 60.0	127° → 96° → 72° 2.5 22.5 32.4	127° → 96° → 72° 2.5 22.5 32.4
1c	101° 452.7	1c evaporated	140° → 79° 4.1 16.2	129° → 81° 11.3 100.3	129° → 81° 11.3 100.3
1d	31° 212.1	1d evaporated	136° → 26° 12.5 18.7	123° → 27° 15.3 38.7	123° → 27° 15.3 38.7
1e	45° 221.6	1e evaporated	131° → 49° 10.7 39.9	115° → 17° 10.6 37.2	125° → 38° 6.8 58.1

[a] Temperatures (°C) and enthalpies (kJ/mol) for phase transitions upon cooling from the isotropic phase to the mesophase (left), and from the mesophase to the crystalline phase (right) determined by DSC (5 °C/min).

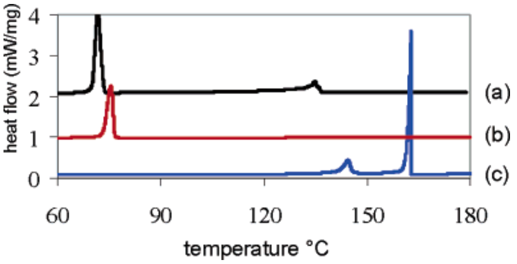

Figure 2. DSC on cooling (5 °C/min) of (a)1:1 mixture of 1b:2b (b) 1b (c) 2b.

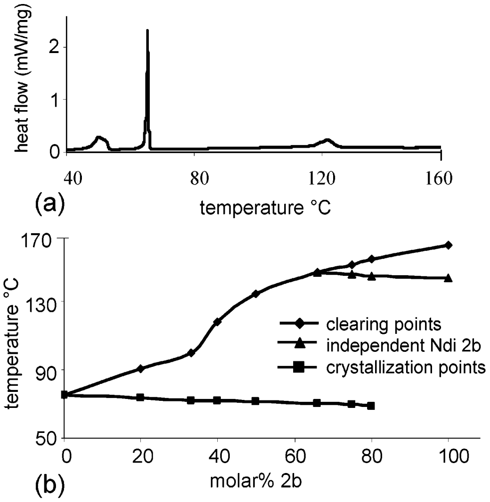

Figure 3. (a) DSC showing the three phase transitions of the 1:1:2 mixture of 1c:1d:2c. (b) Phase Behavior on Cooling of the Titration of Dan 1b with Ndi 2b.

of Ndi 2c and 2d with Dan 1e results in no mesophase, only an isotropic to crystalline phase transition at 25 °C upon cooling.

Mixing two Dan components,1c and 1d, with Ndi 2c in a 1:1:2 ratio resulted in three phase transitions, shown in Figure 3. The clearing point is consistent with other 1:1 mixtures involving Ndi 2c. The middle temperature transition is 15 °C lower than the crystallization transition of 1:1 1c:2c, and the lower temperature transition is correspondingly 15 °C higher in temperature than the crystallization temperature of a 1:1 mixture of 1d:2c. Similar results were seen with a 1:1:2 mixture of 1b:1d:2c.

Titrations. Both the clearing and crystallization points were monitored as titrations were carried out with mixtures of 1b:2b and 1c:2c. For both titrations, a relatively slow linear increase was seen in the clearing point with increasing concentration of the Ndi component until 33% of the mixture was the Ndi derivative, at which point a steeper increase in clearing point was seen until 66% was reached, after which there was a return to the slower linear increase. For the crystallization point, only a relatively slow decrease in temperature with increasing amounts of the Ndi derivative was seen. Data are shown for the molar titration of 1b with 2b (Figure 3). Note the two clearing points at high molar ratios of 2b, no doubt due to the fact that this Ndi derivative has its own mesophase in the pure state.

Optical Microscopy. The bulk optical characteristics of the Dan:Ndi mixtures were observed by melting small amounts of sample between glass coverslips, then cooling slowly (5 °C/min) under a polarizing microscope. Cooling from the isotropic liquid, dendritic domains were seen to grow over about a 10 °C temperature range. Onset of domain growth occurred at a temperature corresponding to the clearing point measured by DSC. Shearing pressure was applied to the slides upon completion of the phase transition and the coverslips slid past each other with little resistance. Upon reaching the crystallization point, the coverslips could no longer move relative to each other. Shown in Figure 4 are representative polarizing microscope images of textures of several different mixtures in their respective mesophase temperature regions. Complexes involving chiral Ndi 2c (or 2d) exhibit long, thin, sheetlike patterns of various size and order with all of the Dan derivatives (panels a−c in Figure 4) characteristic of a columnar liquid crystals. Complexes involving Ndi 2b gave a mosaic of small or elongated rectangles also representative of a columnar mesophase (panels d−f in Figure 4).

Thermochromic Behavior. For most mixtures exhibiting mesophase behavior in the DSC studies, the characteristic deep red color of the Dan:Ndi CT absorbance was seen throughout the isotropic liquid phase, the mesophase, and the crystalline

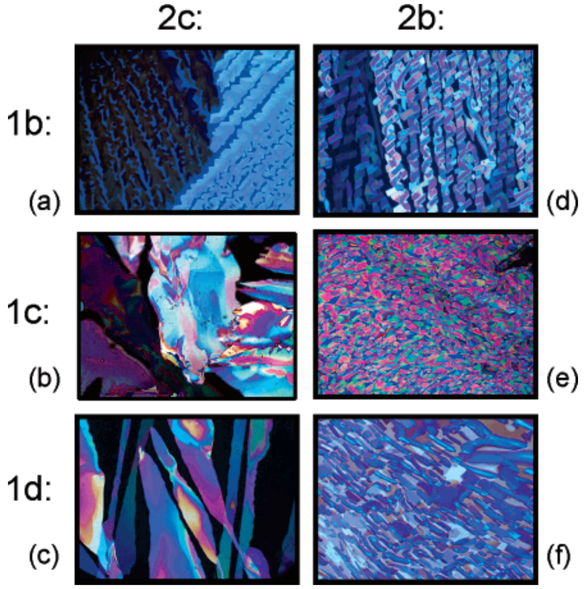

Figure 4. Optical texture of 1:1 mixtures at 110 °C of (a) 1b:2c, (b) 1c:2c, (c)1d:2c, (d) 1b:2b, (e) 1c:2b, (f) 1e:2b.

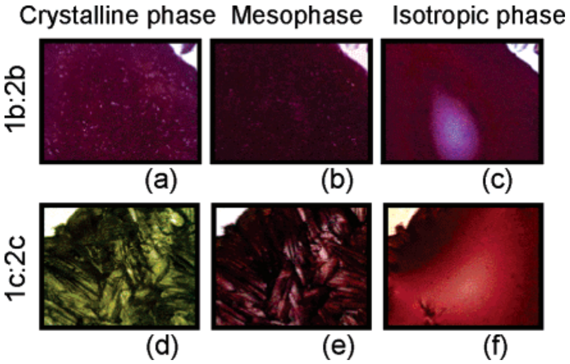

Figure 5. Color of bulk samples of 1:1 mixtures. (a) deep red 1b:2b crystalline phase (60 °C). (b) deep red 1b:2b mesophase (110 °C). (c) deep red 1b:2b liquid phase (160 °C). (d) light yellow 1c:2c crystalline phase (60 °C). (e) deep red 1c:2c mesophase (110 °C). (f) deep red 1c:2c liquid phase (160 °C).

solid phase during cooling. The top three panels of Figure 5 show representative colors of all three phases, in this case a 1:1 1b:2b mixture.

On the other hand, a dramatic color change was observed for mixtures involving the Dan derivative 1c. In these cases, the isotropic phase and mesophase exhibited the characteristic deep red color of the Dan:Ndi CT absorbance. However, upon cooling to the crystallization point, an instant change to a light yellow color was observed (Figure 5d). This dramatic color change is not accompanied by any significant distortions of the texture at low magnification (i.e., 10×), but inspection under greater magnification (100×) revealed that the transition to the yellow color was accompanied by extensive small fractures and blurring of once sharp boundaries.

UV−Vis Spectroscopy. The Dan:Ndi CT band was further investigated using UV−vis spectroscopy. Data were acquired by sandwiching premelted samples of the 1:1 mixtures between glass coverslips. The samples were then subjected to several melt and cool cycles while taking spectra continuously, monitoring temperature with a thermocouple. Representative spectra from the isotropic liquid phase, mesophase, and crystalline phase of mixtures 1b:2b and 1c:2c are shown in Figure 6a−f. Note the loss of a CT band in mixture 1c:2c upon crystallization (Figure 6d).

The absorbance of the CT band at the $\lambda_{\max}$ was compared to the Ndi absorbance in the various phases. In general, the 1:1 Dan:Ndi isotropic phases exhibited Ndi:CT absorbance ratios of 3:1. This ratio is observed regardless of the side chains on either component. Upon cooling to the mesophase, these ratios shifted to an average of 1.7:1, again regardless of the particular mesogens involved. The Ndi:CT absorption ratios did not change significantly when crystallizing from the mesophase, remaining at about 1.7:1, with the noted exception of mixtures including Dan 1c in which evidence of the CT band disappears completely upon crystallization.

X-ray Crystallography. Single crystal data were obtained for the homo-crystals of 1c, 1d, and 2c (Figure 7). In these homo-crystals, 1c and 1d adopt a herringbone structure, while 2c shows an offset face-to-face packing. Both of these solid state arrangements are as expected based either on previously reported structures or electrostatic considerations.[6c]

A cocrystal of suitable quality for single crystal determination could not be grown from solution using any combination of Dan:Ndi derivatives with hydrocarbon side chains. Likewise, when slowly cooled from melts, no suitable crystal could be isolated. We have previously reported that hydrophilic side chains yielded diffracting 1:1 cocrystals of 1f:2e from 20% DMF in water (Figure 7d-f).[3] The resulting structure shows a monoclinic cell, with columns of alternating Dan and Ndi molecules stacked in a face-centered orientation.

For comparison purposes, UV−vis spectra were taken of a 1:1 mixture of 1f:2e in both the isotropic and crystalline phases (Figure 6g,h). The Ndi:CT absorbance ratio is once again 3:1 in the isotropic phase, and 1.7:1 in the crystal. These measurements are significant because single crystal X-ray analysis confirmed essentially complete alternating Ndi-Dan, face-centered stacking in this crystalline phase.

X-ray Powder Diffraction. X-ray powder diffraction studies were carried out on the 1f:2e cocrystal for which the structure was known from single-crystal data. In addition, X-ray powder diffraction was used to investigate the mesophase and crystalline phases for two different mixtures (1c:2c and 1d:2c) for which the single-crystal data are not available. For the 1f:2e sample (Figure 8h), the two most intense peaks in the X-ray powder pattern, (100) and (10−2), correspond to the planes between columns. Mapping these reflections to the single crystal data, they are seen to represent the short plane (smaller distance between side chains within a column) and the long plane (greater distance between side chains within a column) as shown in Figure 7f. Importantly, the short plane corresponds closely with the (001) of Ndi 2e, which is essentially the length of the Ndi molecule, while the long plane similarly corresponds to the length of Dan 1f. In other words, the spacing between inter-column planes (100 and 10−2) of the cocrystal appear to be dictated by the lengths of the Ndi and Dan units, respectively.

The X-ray powder pattern of the mesophases of 1:1 mixtures of 1c:2c and 1d:2c (Figure 8a,b) both show at least two-dimensional order. Additionally, the mesophase of the 1d:2c mixture produced sharp reflections at wide angles possibly indicating three-dimensional ordering.[13] Strong 100 reflections are seen

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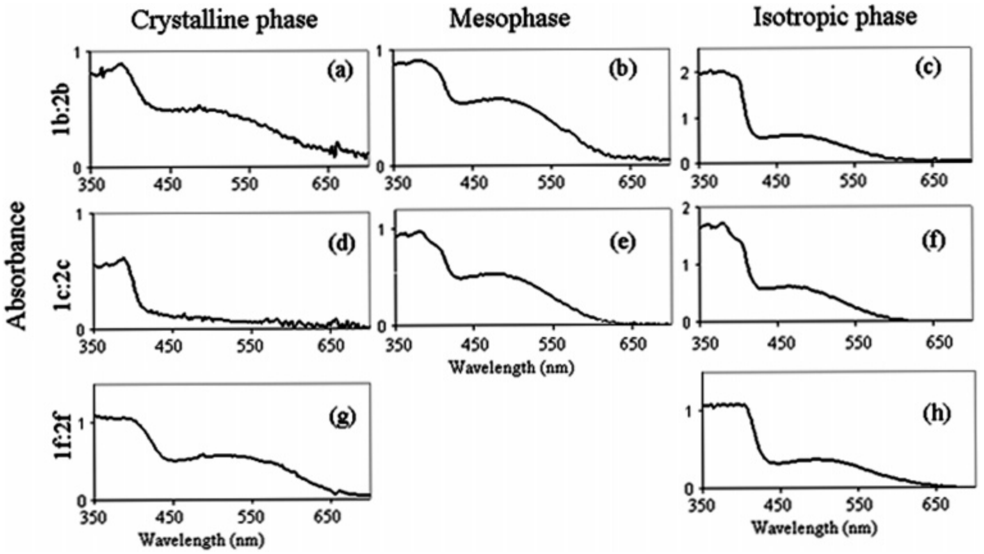

Figure 6. UV−vis Spectra comparing Ndi adsorption (380 nm) to CT band adsorption (475 nm) of 1:1 mixtures. (a) 1b:2b crystalline phase (60 °C). (b) 1b:2b mesophase (110 °C). (c) 1b:2b liquid phase (160 °C). (d) 1c:2c crystalline phase (60 °C). (e) 1c:2c mesophase (110 °C). (f) 1c:2c liquid phase (160 °C). (g) 1f:2e crystalline phase (60 °C). (h) 1f:2e liquid phase (180 °C).

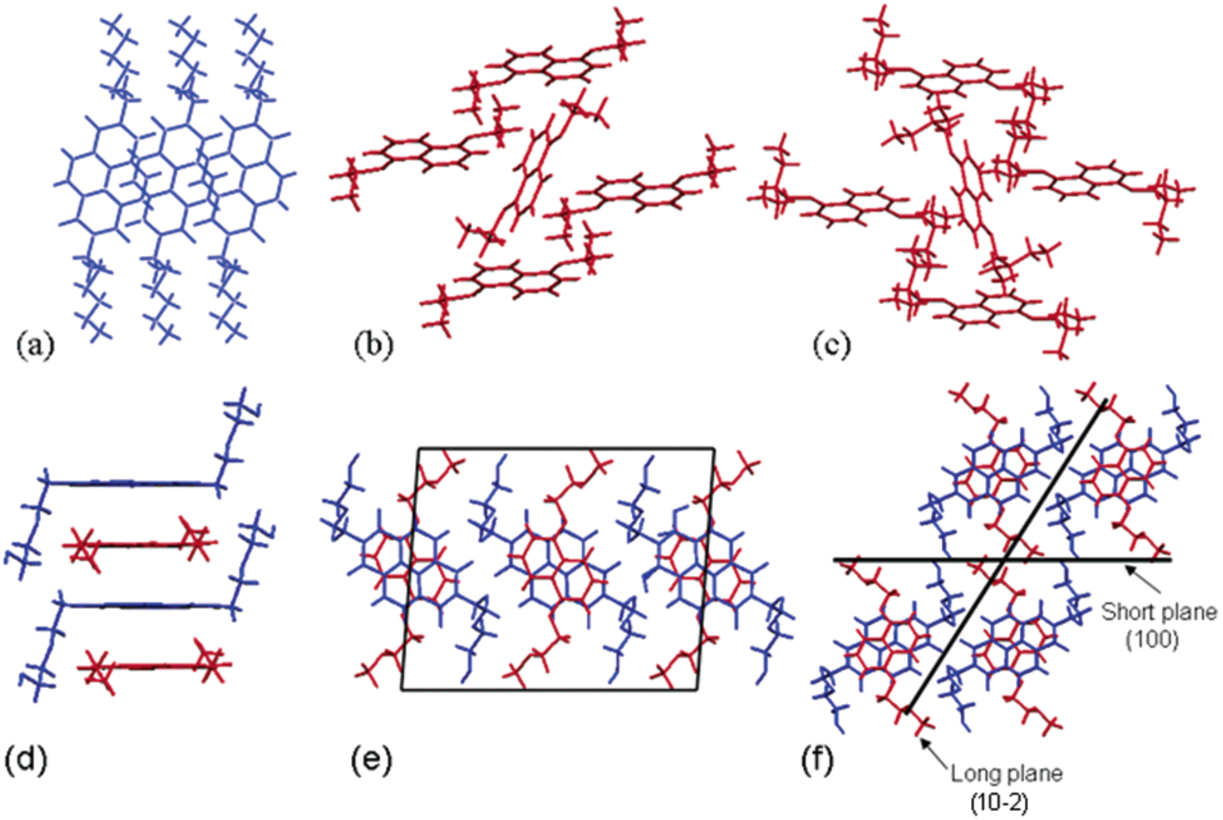

Figure 7. X-ray single-crystal structure of (a) 2b, (b) 1c, (c) 1d, (d) 1f:2e cocrystal, alternating face-centered columns (e) 1f:2e cocrystal, oblique monoclinic cell (f) 1f:2e cocrystal, planes between columns, and their Miller indices.

for both mesophases that are similar to the 200 reflection seen in the X-ray powder pattern of the Ndi component 2c (Figure 8g), corresponding to essentially the length of the Ndi molecule. In addition, less intense 010 reflections are seen in both mesophases corresponding to the 100 reflections of the component Dan molecules 1c and 1d, respectively (Figure 8e,f), which in turn reflect the length of the Dan component. Beyond these two prominent reflections, neither mesophase contains the remaining diffraction patterns of the individual components.

In the 1d:2c crystalline phase (Figure 8d), the low angle 100 and 010 reflections seen in the mesophase remain. Again, these correspond to essentially the lengths of the Ndi and Dan components, respectively. However, the remaining reflections measured for the 1d:2c crystalline phase are distinct from either component.

For the 1c:2c crystalline phase (Figure 8c), the positions of reflections closely resemble the sum of the two components, the only independent peak being the broad one at $\sim 2\theta = 6$. In

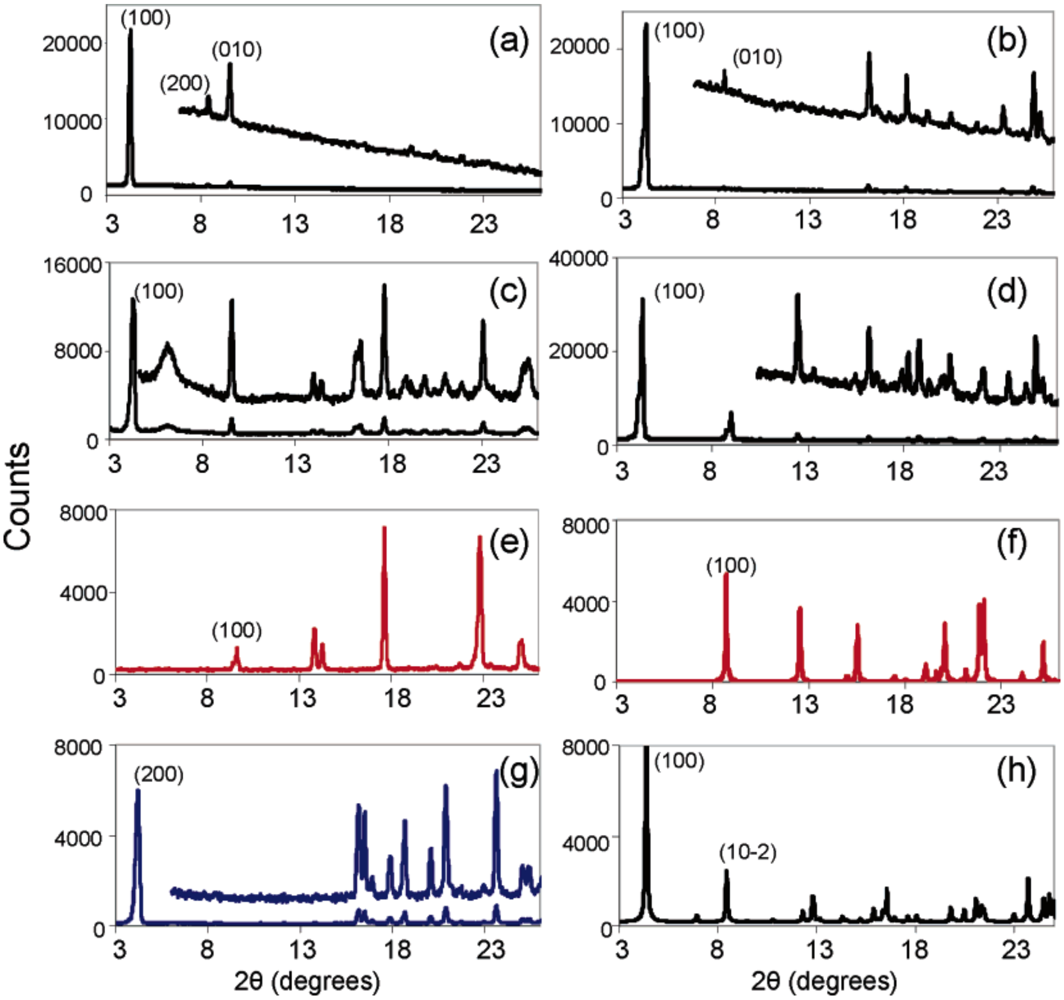

Figure 8. X-ray Powder Diffraction Data including expansions over the same degree range (top spectra) where informative for (a) 1c:2c mesophase (110 °C) (b) 1d:2c mesophase (100 °C) (c) 1c:2c crystalline phase (35 °C) (d) 1d:2c crystalline phase (27 °C) (e) 1c crystalline phase (35 °C) (f) 1d crystalline phase (27 °C) (g) 2c crystalline phase (35 °C) (h) 1f:2e crystalline phase (27 °C).

particular, the reflections corresponding to the Ndi 2c mesogen are all present, albeit less intense and broader in the mixture. The exception is the reflection corresponding to the 200 reflection of 2c, which is of similar intensity and sharpness in the mixture. Reflections in the mixture corresponding to the Dan 1c pattern are present and sharp, although the 100 reflection is significantly higher in relative intensity in the mixture. Recall that crystalline 1c:2c is yellow even though the mesophase of the same mixture is deep red.

Disscusion.

Mesophase Face-Centered Assembly of Extended Columns. The small amount of order indicated by the powder diffraction data for most Dan/Ndi mixtures in the temperature region between the clearing and crystallization points, as well as the ability to shear and deform slides of the mixtures in that region, but not below the crystallization point, are indicative of a true mesophase formation and not crystal−crystal transitions. The deep red color seen upon melting of the Dan:Ndi mixtures, interpreted as an aromatic donor−acceptor CT band, is clear evidence that the Dan and Ndi molecules are stacking in an alternating, face-centered geometry. The UV−vis spectrum of a 1:1 mixture of 1f:2e (Figure 6g), for which single-crystal X-ray data reveals a cocrystal structure consisting of alternating Dan:Ndi face-centered stacks (Figure 7d), showed an Ndi:CT absorbance ratio of 1.7:1 in the crystalline phase. This value is identical to most of the Dan:Ndi complexes investigated. We therefore associate the Ndi:CT absorbance ratio of 1.7:1 with complete face-centered columnar order in the crystalline phase, consistent with other aromatic donor−acceptor systems.[14]

Significantly, the same Ndi:CTabsorbance ratio of 1.7:1 is seen in the mesophases of the 1:1 mixtures reported here. By analogy to the crystalline phases, it is reasonable to propose that these mesophases also have columnar, alternating face-centered stacking of the Dan and Ndi molecules. Thus, it appears that the mesophase to crystalline transition of most of our mixtures does not involve a significant reorganization of our columnar stacked aromatic donor and acceptor cores, the exception being mixtures with Dan 1c.

The X-ray powder diffraction data of the two 1:1 mixtures investigated, 1c:2c and 1d:2c, are also consistent with columnar stacks in their mesophases, separated by distances corresponding to the lengths of the component Dan and Ndi molecules, just as was seen in the 1f:2e cocrystal structure. According to this interpretation, both complexes analyzed by X-ray powder

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diffraction show the short plane reflection corresponding to the length of the Ndi 2c, which has a *d* spacing calculated to be 20.5 Å. The calculated *d* spacing for the long plane of complex 1c:2c (with isopropyl side chains on the Dan) is 9.1 Å, corresponding to the length of Dan 1c, whereas the longer side chains on the Dan in the 1d:2c complex give a somewhat longer distance of 10.5 Å, corresponding to the length of Dan 1d (Figure 9).

The preceding structural analysis indicates that the mesophase of Dan:Ndi mixtures should be classified as columnar oblique rectangular ($\mathrm{Col_{Ob}}$) mesophases. This conclusion is supported by the optical textures (See Figure 4d−f) in which rectangular domains are seen.[15] The transition enthalpies, optical textures, and powder diffraction data suggest soft/plastic liquid crystals for most of the mesophases, while a few (1b:2c and 1b:2d) exhibit properties of true columnar liquid crystals. Note that with chiral Ndi 2c, evidence for a $\mathrm{Col_{Ob}}$ B1 phase comes from the more sheetlike domains in the optical texture (See Figure 4a−c).[14a,16]

Thermochromic Behavior of Mixtures Containing Dan 1c. The fact that all the complexes investigated in this study exhibit the same deep red color in the mesophase and isotropic phase suggest that the side chains investigated do not affect the aromatic stacking arrangement in these less ordered phases. However, the mixtures involving Dan 1c with various Ndi derivates all show striking thermochromic behavior in which the deep red mesophase rapidly turns to a light yellow color upon crystallization. Thus, it appears that the packing of the side chains can make a difference in the crystalline phase. Steric interactions involving the Dan 1c isopropyl chains apparently force the aromatic faces apart and thereby disrupt the CT absorbance upon freezing into a crystalline phase (yellow color), although these interactions are not significant enough to prevent face-centered interactions in the isotropic or mesophases (deep red color).

The X-ray powder diffraction data for the 1c:2c mixture are consistent with crystallization-induced phase separation in mixtures containing Dan 1c. In the crystalline phase of the 1c:2c mixture, reflections corresponding to those seen in the Dan 1c homo-crystal appear as sharp peaks, and reflections corresponding to those seen in the Ndi 2c homo-crystal appear as well, although they are of low intensity and diffuse. These data are consistent with the Dan molecules forcing themselves out of contact with the Ndi molecules in what is likely a steric induced phase separation. The Dan molecules reorganize and pack with themselves in what appears to be the homo-crystal herringbone arrangement, and the Ndi molecules are forced to reorganize and pack with themselves as well. This leads to many structural defects seen at high magnification. The only new peak in the 1c:2c crystal phase is a very broad one at $2\theta = 6.2°$ that could be due to the boundaries between phase separated Dan and Ndi molecules.

Note that the steric effect proposed to be responsible for the thermochromic behavior seen with Dan 1c is highly sensitive to structure. Moving the branch one methylene unit farther from the aromatic ring, as in derivative 1d, eliminates the thermochromic behavior.

Tuning Phase Transition Temperatures. As seen in Table 1, the relative clearing points of the various donor−acceptor mixtures track with the relative melting/clearing points of the Ndi component. For example, in 1:1 mixtures containing Dan 1b as the donor, the clearing points range from 143 °C with 2a to 127 °C with enantiomers 2c and 2d, with 2b coming in between. This relative order coincides with the relative melting/clearing points of the Ndi components.

Along the same lines, the relative crystallization points of the 1:1 mixtures track with the melting points of the Dan derivatives. For example, with Ndi 2b, the crystallization points range from 79 °C with 1c to 26 °C with 1d, with the other derivatives coming between; again in the same relative order as their individual melting points. In the case of the crystallization points, the values for the mixtures are also similar (within ∼5 °C) in absolute magnitude to the Dan component melting points. The exception is the derivative 1c, in which the crystallization points of the 1:1 mixtures are around 20 °C lower than the melting point of 1c, presumably a phenomenon that is related to the phase separating behavior seen in these mixtures upon crystallization.

A straightforward interpretation of these trends is that the 1:1 Dan:Ndi mixture clearing points track in a relative way with restriction of motion of the Ndi side chains, and the crystallization points track with restriction of motion of the Dan side chain component. In other words, there is more order associated with Ndi long axes because the Ndi side chains have more restricted motion in the mesophase, and less order along the Dan long axes because the Dan residues maintain greater freedom of motion in the mesophase. Consistent with this, the mesophase X-ray powder diffraction data for both the 1c:2c and 1d:2c mixtures show substantially more order (much more intense reflection) corresponding to the short plane, due to the long axis of the Ndi component. The ability to tune phase transition temperatures based on knowledge of component melting/clearing points is a relatively unique and highly desirable feature of Dan:Ndi mixtures.

Further temperature tuning of the clearing point was affected by altering the molar ratios of the component mixtures as was exhibited in the titration of 1b with 2b. While the crystallization temperature remained fairly constant, the clearing point ranged from 95 °C at 66% 1b to 140 °C at 33% 1b. Presumably, the 66% and 33% values indicate 2:1 and 1:2 stoichiometries, in which each aromatic unit is still interacting with at least one complementary unit, and there is still long-range face-centered stacking. At mixtures with more extreme molar compositions (>66% or < 33%), this arrangement is not possible, and the clearing temperatures of the mixtures change more gradually, taking on more the characteristics of the aromatic unit in highest concentration.

Chiral Side Chains. Phase transition temperatures were further modulated by manipulating the chirality of the side chains. While Ndi enantiomers 2c and 2d behave identically by themselves and with any achiral Dan, the diastereomeric mixtures they create with chiral Dan 1e produced similar mesophase textures, but their phase transition temperatures differed significantly. In particular, the 1:1 mixture of 1e:2d (the *S,S*:*S,S* diastereomeric complex) displayed clearing and crystallization points of 125 °C and 38 °C, respectively. The

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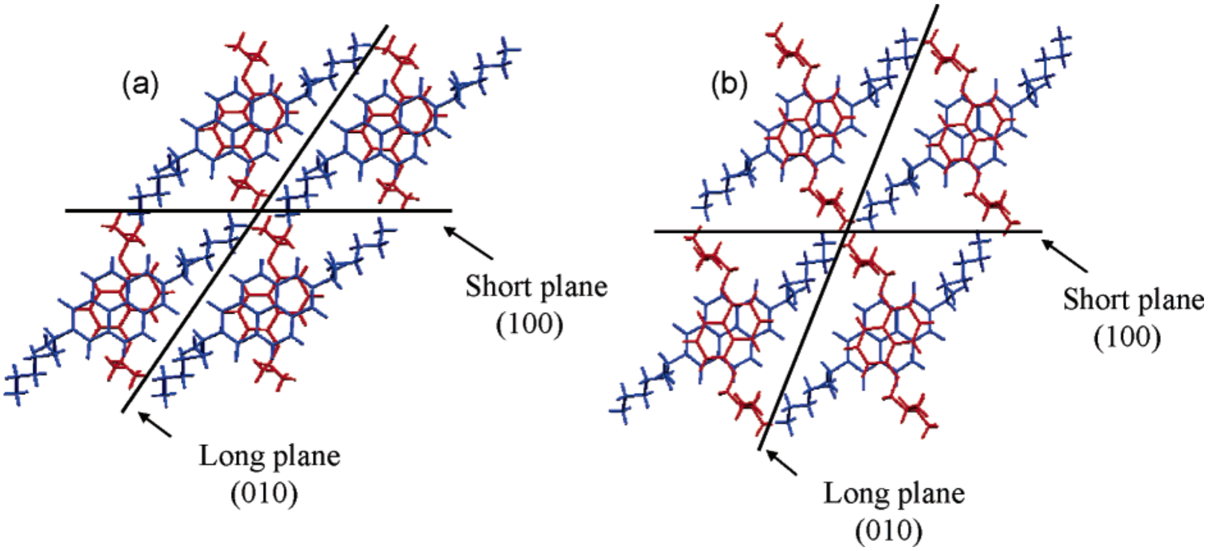

Figure 9. Computer models of the proposed oblique rectangular packing for the mesophase of (a) 1c:2c, (b) 1d:2c (Hyperchem, Hypercube, Inc.).

1:1 mixture of 1e:2c (the *S,S:R,R* diastereomeric complex) exhibited clearing and crystallization points of 115 °C and 17 °C, respectively. These latter two values represent the lowest transition temperatures measured of any Dan:Ndi complex in the present study. Interestingly, using a racemic mixture of 2c and 2d with 1e (in a 1:1:2 ratio) resulted in no mesophase being formed. The single isotropic to crystal phase transition occurs at 25 °C, between the crystallization temperatures of the single diastereomeric mixtures implying that the crystallization event is an average of the two. However, it appears that any long range order at higher temperature is disrupted by the opposing chirality of the Ndi units, disallowing the existence of a mesophase.

Terniary Mixtures. To investigate an alternate method of controlling phase transition temperatures, more than one Dan was mixed with a particular Ndi; for example a 1:1:2 mixture of 1b:1c:2c. The result was not a single mesophase with intermediate temperature crystallization points, but rather, two separate sets of crystallization points (Figure 3a) corresponding roughly to the crystallization points of independent 1b:2c and 1d:2c mixtures, respectively. The clearing point was that expected for a mixture containing Ndi 2c. Similar results were obtained with a 1:1:2 mixture of 1b:1d:2c.

Taken together, our results indicate that a surprising amount of predictable control can be exerted over the phase transition temperatures of 1:1 Dan:Ndi mixtures. The success of this approach is no doubt related to not only their complementary geometries (both aromatic units are of a similar size) but also their C2 symmetries that facilitate alternating, face-centered stacks with side chains oriented in orthogonal directions. This orthogonal directionality apparently allows the side chain motions of individual Dan and Ndi units to behave independently, as well as retain their behaviors in homo-crystalline materials. Such independent behavior is probably the basis for the general correspondence of mixture phase transition temperatures with the component melting/clearing points. Note that the orthogonal directionality of the side chains also makes it possible to predict inter-stack distances in the columnar mesophases and crystalline phases of 1:1 mixtures.

Conclusion

As a logical extension of our efforts to use the preferred alternating, face-centered stacking of Dan and Ndi donor and acceptor units to control folding and recognition in aqueous solution, we have explored their use in the formation of novel mesophases. Detailed characterization of 1:1 mixtures indicated that long, alternating stacks of Dan and Ndi derivatives produced columnar mesophases with a deep red color and inter-stack distances predictable in a straightforward way from the side chains of the Dan and Ndi components. Importantly, we found that the temperatures of the crystallization and clearing point phase transitions correlated with the melting/clearing points of the Dan and Ndi components, respectively, allowing for what we believe may be an unprecedented degree of predictable control over the tuning of these important properties.

Several interesting materials were produced, including ones based on mixtures containing Dan 1c that undergo a rapid color change from deep red to yellow upon crystallization from the mesophase, due to separation of the components into domains presumably due to steric interactions caused by the isopropyl side chains of 1c. This change not only affects the color of the material, but should have a dramatic influence over other properties such as conductivity. Current efforts are directed toward elucidating these and other practical properties, as well as characterizing other mesophases produced by novel mixtures of Dan and Ndi derivatives.

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Supporting Information Available: Experimental section, spectral data, and Crystallographic information (CIF).This material is available free of charge via the Internet at http://pubs.acs.org.

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