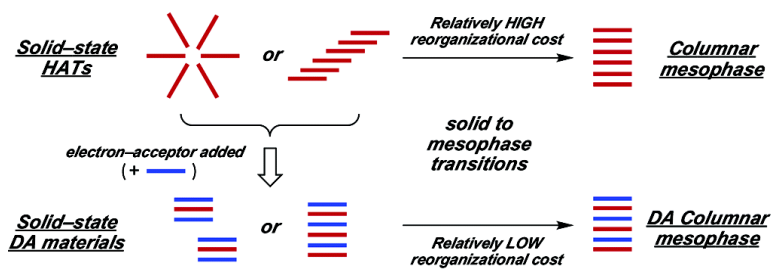


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Complementary C_3 -Symmetric Donor–Acceptor Components: Cocrystal Structure and Control of Mesophase Stability

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Abstract: The overlap of π -complementary planar organic frameworks is used to direct the assembly of extended columns of alternating donor and acceptor units. The electron-rich partner, hexaalkoxytriphenylene, is a familiar mesogen, while the electron-accepting complement is mellitic triimide, a new C_3 -symmetric building block that may be readily alkylated at its periphery without compromising its electron-accepting ability. A cocrystal of examples of the two components demonstrates π -facial overlap of the complementary aromatic surfaces. Preparation of a series of alkylated derivatives of each component allowed the study of an array of 1:1 stoichiometry mixtures. For the optimum donor–acceptor organized mesophases within this grid, temperature stability ranges of well over 100 °C are observed, some of which extend below room temperature. X-ray analysis confirms the formation of hexagonally packed, alternating, donor–acceptor columns within each of the observed mesophases. The dramatic effect on mesophase formation and stability engendered via donor–acceptor organization within discrete columns is discussed in terms of the interplay of forces leading to mesophase formation, and the potential to tune mesophase characteristics via manipulation of these factors.

Introduction

Alternating stacks of π -rich and π -poor aromatic systems offer a design principle for the formation of extended linear columns. This approach has been used successfully in catenane and rotaxane systems where self-assembly has been directed by the centrosymmetric overlap of π -electron-deficient bipyridinium or aromatic diimide cores with π -electron-rich aromatic diethers.^{1,2} In other work, the introduction of π -electron acceptors into homomolecular stacks of π -rich mesogens has been recognized as a means of modifying phase behavior in liquid crystalline materials³ and is important in the development of p-doped materials for one-dimensional charge transport. One limitation in these endeavors has been the relative scarcity of suitable electron-acceptor components available for study. Researchers have been largely limited to tetracyanoquinodimethane and fluorenone-based electron acceptors, systems which typically do not provide a good symmetry match with the disk-shaped donors and are not easily derivatized to optimize phase behavior or donor–acceptor interactions. More recently,

some novel examples of electron-accepting discotic materials have been reported.^{4–7} In this Article, we report the pairing of a new and readily derivatized disk-shaped electron acceptor with a highly structurally complementary donor species, a representative donor–acceptor cocrystal structure, and the mesophase behavior that emerges from this system. The ability to tune mesophase characteristics, when coupled with ready synthetic access to the two components, holds promise for future studies of related materials, as well as for approaches to the design of new supramolecular systems.

A C_3 -Symmetric Donor–Acceptor Pair

Mellitic triimides are C_3 -symmetric electron acceptors whose chemistry has only recently been explored.⁸ Unlike many frequently employed electron acceptors such as those mentioned above, alkylated triimides (e.g., **1a–d**) can be very readily prepared, and such alkylation does not compromise the electron-accepting ability of the core. The first reduction potentials of these triimides are quite low, around –550 mV with respect to SCE,⁹ and therefore comparable to that reported for TNF.¹⁰ In

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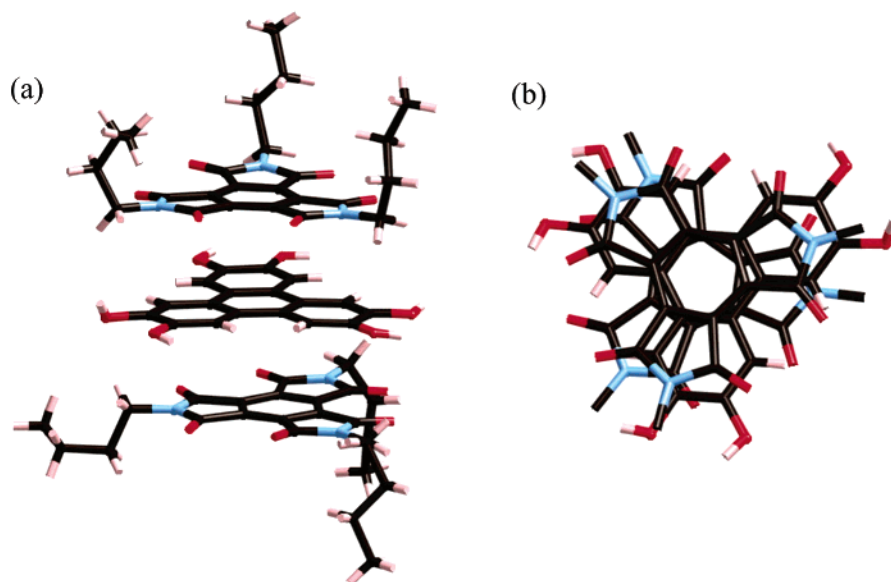


Figure 1. Side (a) and top (b) views of the acceptor–donor–acceptor triad revealed in the X-ray crystal structure of **1a**·hexahydroxytriphenylene. The triimide side chains (truncated for purposes of clarity in the top view) extend above and below the triads and interpenetrate with those of vertically adjacent triads. Triimides from vertically adjacent triads are separated by around 8.5 Å, while the separation of triphenylene cores is around 15 Å.¹⁸

addition, the reduction potential of this species may be modulated by inclusion of the triimide in a simple hydrogen bonding matrix.⁹ Accordingly, triimides are ideal candidates for application in the area of donor–acceptor stacking with a suitable π -electron-rich partner; hexahydroxytriphenylene and its alkylated derivatives (e.g., **2a–d**) are an obvious choice due to the match with the acceptor species in both relative size and symmetry. Stoichiometric mixtures of examples of these two components exhibit intense solution coloration, characterized by a broad charge-transfer (CT) absorption band at around 510 nm, indicative of some degree of interaction between the two component molecules. It is worth noting that charge-transfer interactions, which have often been interpreted as a signature of a π -facial interaction, are more correctly viewed as a possible result of, rather than a primary driving force for, the proximity of complementary π -systems.¹¹

A mixture of tri-*n*-butyl mellitic triimide (**1a**) and hexahydroxytriphenylene was isolable as deep purple X-ray quality cocrystals. The crystal structure reveals discrete acceptor–donor–acceptor triads with essentially complete overlap of π -faces (Figure 1). The relative disposition of the respective π -rich and π -poor aromatic systems in the cocrystal correlates well with reported modeling studies of the interaction between hexaalkoxytriphenylenes (HATs) and several well-established π -electron acceptors, including a fluorenone system.¹² For these calculations, an extended electron distribution force field was employed to determine the π -system interaction via a consideration of the properties of atoms at their points of intermolecular contact; these calculations therefore build on the seminal work of Hunter and Sanders whose original model successfully predicted slipped stack or edge-to-face interaction geometries for π -rich systems.¹³ In contrast, for mixtures of π -rich and π -poor aromatic systems, energetically favorable association is

most satisfactorily modeled as the result of net attractive van der Waals' and Coulombic forces¹² and is predicted to give rise to significant facial overlap of the π -faces, as observed in this structure.

The formation of discrete acceptor–donor–acceptor triads is most likely the result of repulsive interactions between the *n*-butyl triimide substituents and the hydroxyl groups on the triphenylene; the crystal structure reveals that the butyl groups extend away from (above and below) the plane of the hexahydroxytriphenylene core. However, the fact that this structure does not reveal extended, alternating, columns of 1:1 donor/acceptor constitution, despite the fact that the crystals were grown from a solution containing equimolar amounts of the two components, does not preclude the possibility of 1:1 stack formation in a subtly altered environment. Indeed, for both the aromatic diether/4,4'-bipyridinium stacking system exploited by Stoddart and co-workers in catenane and rotaxane syntheses,¹⁴ and the aromatic diether/diimide complement employed in the assembly of related charge-neutral topologies,¹⁵ there are examples of prototype cocrystals that have 1:2 ratios of complementary components, while derivative supramolecular assemblies exhibit a 1:1 ratio.^{16,17} Even if subtle forces relating to packing in the crystal may on occasion inhibit extended stack formation, some important structural features are generally conserved, including the relative orientation of the respective π -systems, and their degree of mutual overlap. When coupled with the facility for ready substitution of our acceptor,⁸ this observation suggested that the triimide–HAT complementary pair could provide an ideal vehicle for probing mesophase behavior in extended stacks of a donor–acceptor system.

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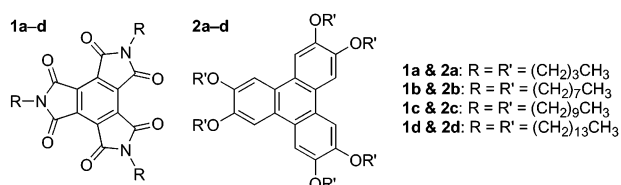
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Chart 1. Acceptor and Donor Components Used in This Study



Mesophases from a Matched Donor–Acceptor System

The tri-*n*-alkyl triimides used in this study, **1a–d**, were prepared by alkylation of a crude sample of the unsubstituted triimide core using a published procedure (see Experimental Section), while HATs **2a–d** were prepared by standard methods, either alkylation of hexahydroxytriphenylene or oxidative trimerization of the appropriate 1,2-dialkoxybenzene (Chart 1).^{8,19–21} Synthetic access to the triimide derivatives is currently limited by problems of solubility and isolation to *N*-alkylated systems bearing chains of four or more carbons; we therefore chose *n*-butyl as the lower alkyl chain length for each series. We selected three other alkyl chain lengths for this study: octyl, decyl, and tetradecyl; these were chosen because **2b** and **2c** are well-known discotic mesogens,^{22,23} while **2d** was not expected to display a mesophase on its own. The range of HATs employed in this study thus spans a window of mesophase behavior and was chosen to offer the best opportunity to probe the induction or modification of mesophase behavior in the HATs by mixing with triimides of varying alkyl substituent chain length.

The pure triimides, **1a–d**, are not discotic in their own right, exhibiting crystalline to isotropic transitions by DSC and optical microscopy. Of the HATs, **2a–c** exhibit columnar mesophases as reported previously,^{22,23} while, as expected, **2d** melts cleanly from the crystalline to the isotropic phase. All 16 possible 1:1 stoichiometric mixtures of the donors and acceptors were prepared in methylene chloride solution and subsequently evaporated. Both in solution, and after evaporation of the solvent, the mixtures exhibited the characteristic deep red coloration associated with the charge-transfer absorption band (510 ± 1 nm) in these materials. The CT interaction, while not the driving force in this system, may perhaps be viewed instead as a signature of the donor–acceptor interactions in these materials;²⁴ the fact that the maximum of the CT band is consistent within our series of mixtures suggests that the nature and strength of the donor–acceptor interactions remain relatively constant despite the variation in the chain length of the substituents.

Table 1. Results of Thermal and XRD Characterization of the Phase Behavior of the Pure Triimides and HATs, and Their 1:1 Complexes^a

Triimide	1b (R=C ₈)	1c (R=C ₁₀)	1d (R=C ₁₄)
HAT	170° (35.1) $C \rightleftharpoons I$	117° (69.2) $C \rightleftharpoons I$	103° (26.9) $C \rightleftharpoons I$
2b (R'=C ₈) 56° (47.1) 78° (2.2) $C \rightleftharpoons Col_h \rightleftharpoons I$	<40° 170° (3.3) $C \rightleftharpoons Col_h \rightleftharpoons I$ 17.33 (100) 10.09 (110) 8.73 (200) a = 20.01, 30°	5° (12.6) 155° (2.0) $C \rightleftharpoons Col_h \rightleftharpoons I$ 17.95 (100) 10.51 (110) 9.08 (200) a = 20.06, 30°	<40° 95° (0.4) $C \rightleftharpoons Col_h \rightleftharpoons I$ 19.89 (100) 11.50 (110) a = 22.87, 30°
2c (R'=C ₁₀) 56° (53.0) 64° (0.4) $C \rightleftharpoons Col_h \rightleftharpoons I$	30° (31.6) 130° (3.5) $C \rightleftharpoons Col_h \rightleftharpoons I$ 19.36 (100) 10.31 (110) 9.82 (200) a = 22.27, 30°	40° (17.5) 136° (3.6) $C \rightleftharpoons Col_h \rightleftharpoons I$ 19.75 (100) 11.45 (110) 9.99 (200) a = 22.72, 75°	19° (25.4) 107° (2.1) $C \rightleftharpoons Col_h \rightleftharpoons I$ 20.59 (100) 11.99 (110) 10.43 (200) a = 23.68, 60°
2d (R'=C ₁₄) 66° (85.5) $C \rightleftharpoons I$	60° (16.2) $C \rightleftharpoons I$	29° (33.0) 41° (2.9) $C \rightleftharpoons Col_h \rightleftharpoons I$ 23.04 (100) 13.55 (110) a = 26.63, 34°	48° (54.9) 60° (3.6) $C \rightleftharpoons Col_h \rightleftharpoons I$ 23.60 (100) 13.98 (110) 11.83 (200) a = 27.14, 55°

^a Temperatures (°C) and enthalpies (J/g) for phase transitions (upon heating) as determined by DSC (10 °C/min) and optical microscopy are given above the arrows. Observed spacings and lattice constants (Å), as well as Miller indices, are given for samples where a mesophase was observed, at the specified temperature.

No clear liquid crystalline behavior was observed for any of the mixtures containing either **1a** or **2a**. Most of these displayed crystalline to isotropic transitions, although **1a:2a** gave rise to biphasic behavior. Of the remaining nine mixtures (involving **1b–d** and **2b–d**), all but one displayed significantly enhanced enantiotropic columnar mesophases with respect to those observed for either of the pure parent species; in several cases, these phases are stable over very wide temperature ranges (Table 1). From the table, it is clear that the thermal stability of the enhanced mesophase for a given HAT may be adjusted by varying the length of the alkyl substituent on the triimide.

A representative optical texture of one of these 1:1 mixtures is shown in Figure 2a; the homeotropic (black) regions clearly suggest hexagonal columnar ordering. DSC traces of the mixtures exhibited no features ascribable to either of the individual parent components. Similarly, X-ray diffraction of each of these samples indicated the presence of a single hexagonal columnar phase; there was no evidence of coexisting phases. A reflection at $d = 3.43\text{--}3.49$ Å is due to the intracolumnar spacing; this value is similar to that observed in the structure of the cocrystal (3.45 Å), but slightly smaller than that reported for pure HAT LC materials (typically slightly greater than 3.5 Å),²² as would be expected from the additional influence of attractive $\pi\text{--}\pi$ interactions. The presence of an additional weak reflection at $d = 6.9$ Å confirms the formation of extended columns composed of alternating donors and acceptors in the mesophase,^{3b} rather than the HAT–triimide–HAT triads observed in the cocrystal described earlier. Unsurprisingly, intercolumnar spacings increase with increasing length of the alkyl chains. The intercolumnar distances are slightly smaller than those reported for pure HATs; we hypothesize that this is most likely due to a greater coiling of the HAT alkyl chains to better fill space when mixed with the triimides, which possess a lower peripheral chain density. The XRD and DSC data therefore confirm the formation of hexagonally packed columns of alternating donor and acceptor units in the observed mesophases (Figure 2b).

Crystallographic studies of a number of short chain HATs reveal packing modes that share little structural similarity with

- (18) Crystal data for **1a**·hexahydroxytriphenylene cocrystal: (C₁₈H₁₂O₆):2(C₂₄H₂₇N₃O₆):(C₃H₇NO):6.2(H₂O), $M_r = 1416.04$, $T = 183(2)$ K, $\lambda = 0.71703$ Å, triclinic, $a = 12.8563(8)$, $b = 15.5927(9)$, $c = 18.9159(11)$ Å, $\alpha = 105.6470(10)$, $\beta = 100.8910(10)$, $\gamma = 91.5280(10)^\circ$, $V = 3573.6(4)$ Å³, space group *P*-1, deep purple crystal ($0.21 \times 0.17 \times 0.07$ mm), $Z = 2$, $\rho_{\text{calcd}} = 1.316$ g cm⁻³. The crystal contains 1 DMF and 6.2 water molecules per unit cell and also exhibits substantial disorder in the triimide *n*-butyl substituents. Accordingly, the final *R* value was 10%.
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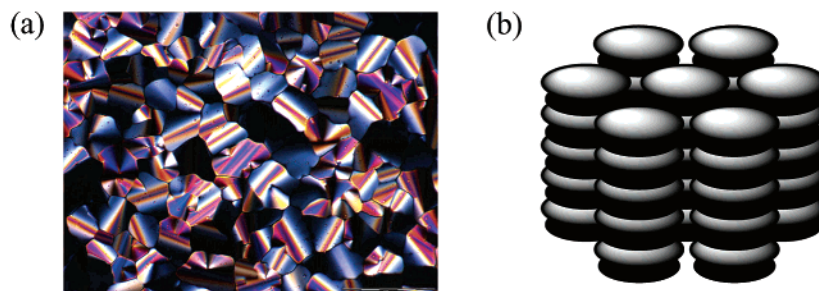


Figure 2. (a) Optical texture of the 1:1 stoichiometry **1b**:**2c** mixture at approximately 160 °C. (b) Cartoon representation of hexagonal packing of alternating donor–acceptor stacks.

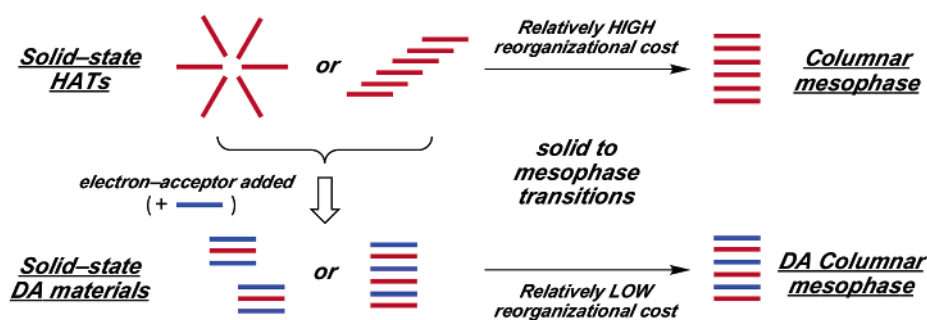


Figure 3. Cartoon schematic of the reorganizational processes required in the solid to mesophase transitions of pure HAT (red boxes) and mixed triimide/HAT mixtures (mixed red/blue boxes). The solid-state structure cartoons for HATs loosely represent frequently observed packing modes (paddle wheel or slipped stack),²⁵ while for the DA materials we present both isolated triads (as in our cocrystal) and the possibility of extended alternating stacks.

their corresponding mesophases. In particular, the substantial overlap of planar aromatic cores that characterizes a columnar mesophase is absent from the packing of HATs in the solid state. Rather, the steric requirements of accommodating the alkyl chains appear to dominate solid-state organization.²⁵ In the absence of alkyl substituents, slipped stacks of aromatic cores are often observed, a familiar packing mode for π -electron-rich aromatics and one predicted by the application of the Hunter and Sanders model of interaction.¹³ With the addition of even very short alkyl substituents to the periphery, the degree of aromatic core overlap drops to zero as the requirements of alkyl chain packing become the significant force dictating solid-state structure, resulting in paddle wheel-like packing arrangements.²⁵ From these facts, it follows that the solid state to mesophase transition for HATs, whether from a slipped stack or paddle-wheel packing mode, must involve substantial conformational reordering, with an associated energetic cost (Figure 3). Therefore, for those pure HATs that exhibit columnar mesophases, the repulsive interactions between stacked π -rich components that dominate in the solid state have been successfully offset with favorable van der Waals' contacts between interpenetrating alkyl substituents in the mesophase.

For the mixed triimide/triphenylene system, however, our cocrystal structure, supported by previous modeling predictions, indicates an energy minimum involving essentially complete π -system overlap. Therefore, the mixed DA materials are inherently more ordered, in a columnar sense, than the HATs alone. Whether the solid state is composed of extended columns (as in our mesophases), or discrete triads (as in the cocrystal), a comparatively small energy input is required to generate an extended, alternating, columnar mesophase, leading to a decrease in the melting temperature. At the same time, the π -rich/ π -poor interactions provide an additional attractive component, leading

to an increase in the isotropization (clearing) temperatures. The mesophases for the mixed systems are therefore considerably broader than the mesophases observed for the pure HATs.

On the basis of the array of mixtures presented here, it is also clear that both effects (the lowering of the melting point and the raising of the clearing point) become less pronounced as the difference in the lengths of the alkyl substituents on the HAT and triimide increases. The donor–acceptor interactions in this system are clearly not sufficient to stabilize a mesophase as none of the HATs exhibited a mesophase upon mixing with **1a**, while other electron acceptors are known to enhance and stabilize mesophases with HATs, even in the absence of additional aliphatic substituents. It is possible in our case that the high degree of overlap between the HAT and triimide cores (due to size and symmetry) sufficiently alters the balance of forces that governs mesophase stability to render the role of the van der Waals' forces more important. Apparently, in our system, the van der Waals' contributions from the shortest alkyl groups are insufficient for mesophase formation because no mesophase is observed for mixtures involving either **1a** or **2a**. This effect is particularly stark in the case of **2a**, a material which exhibits the broadest mesophase in its pure form for any of the HATs in this study, but not in any of the triimide mixtures investigated. For mixtures involving **1b–d** and **2b–d**, the van der Waals' interactions are apparently sufficient to provide the necessary balance for mesophase formation. Furthermore, the broadest mesophases for a given HAT (**2b–d**) are observed in mixtures with triimides whose aliphatic substituents are well matched in length, thus maximizing van der Waals' interactions through extensive interdigitation of the alkyl chains.²⁶ Our results therefore indicate that the thermal range of the mesophases in this system may be tuned by adjusting the relative

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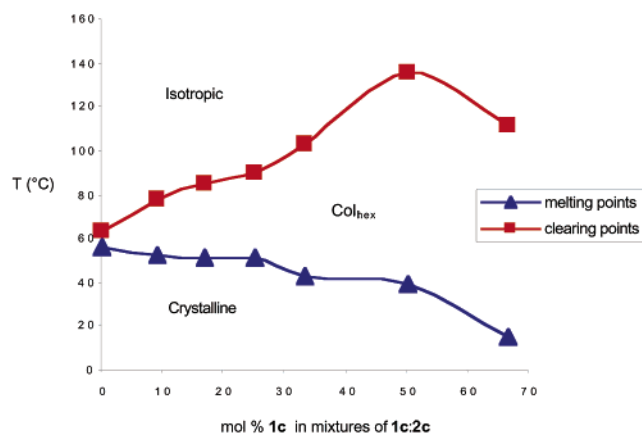


Figure 4. Evolution of phase behavior observed for mixtures of **1c:2c** of varying composition.

lengths of the aliphatic substituents on the donor and acceptor components.

Studies involving mixtures of **1c** and **2c** over a range of compositions less than 1:1 were also carried out; 1:2, 1:3, 1:5, and 1:10 mixtures of **1c** to **2c**, respectively, displayed single mesophases according to DSC analysis, tentatively assigned as Col_h (in all cases) on the basis of the optical textures. The thermal stabilities of these mesophases were significantly reduced as compared to the 1:1 mixture, with the effect on the clearing points being more dramatic than on the melting points, as illustrated in Figure 4. As the mole percentage of triimide in these mixtures increased, the clearing points climbed smoothly; this is not surprising, as the percentage of acceptor in the donor–acceptor stacks should be closely correlated with the energy required to enter the isotropic phase. Likewise, the melting points decrease smoothly with increasing triimide percentage, suggesting that even with a relatively low percentage of acceptor present the intermolecular interactions have rearranged from the slipped stack or paddle wheel formation favored by pure HATs to the more aligned stacks expected for the donor–acceptor material. The results also indicate that at low percentages of triimide the donor–acceptor composition of the material is relatively homogeneous; there is no evidence for phase separation of pure **2c** from a mixed **1c:2c** aggregate. Similar to the TNF/HAT system,^{3b} there is no apparent lower limit on the amount of triimide required to induce the changes in mesophase behavior described here. However, when the percentage of the triimide component was increased beyond 50%, the evolution of the phase behavior changes; a 2:1 mixture of **1c** and **2c** gives rise to a single mesophase by DSC whose melting point and clearing point were both lower than that observed for the 1:1 mixture (the mesophase was again tentatively identified as Col_h on the basis of microscopy). At a composition of 3:1, the mixture was clearly biphasic, thus defining the upper limit on the amount of triimide tolerated in this system.

Conclusions

Recent literature points to the relative scarcity of electron-accepting discotic molecules and their importance in developing liquid crystalline systems that display effective charge transport.^{4–7} The triimides used here are particularly intriguing for a number of reasons. Although not liquid crystalline on their own, they can induce broad liquid crystalline phases when mixed with suitable electron donors such as HATs. The key feature of the

triimide core is ready access to a series of alkylated derivatives, thereby giving rise to several means of tuning mesophase behavior. For the series of mixtures described here, variation in the match between the alkyl substituents on the electron-accepting and -donating cores, as well as the percent composition of the donor–acceptor material, provide independent means of tuning mesophase characteristics.

Experimental Section

General Methods. NMR spectra were recorded as solutions in CDCl₃ and referenced to residual solvent impurities. All starting materials were obtained from commercial sources and were used without further purification. Optical microscopy was carried out using standard covered glass microscope slides on an Olympus BX50 polarizing microscope equipped with a Linkam LTS350 heating stage and digital camera. DSC experiments were performed on a TA Instruments 2920 Modulated DSC. Variable temperature X-ray data were collected using an Inel CPS 120 position sensitive detector using an XRG 2000 generator (Cu K α) and a Minco CT137 temperature controller; solid samples were packed into 1.5 mm glass capillary tubes and sealed. Triimide–HAT mixtures were formed by mixing appropriate amounts of the two species in methylene chloride solution (with the characteristic deep red coloration forming immediately upon mixing) followed by evaporation of the solvent in air. The **1a**-hexahydroxytriphenylene dco-crystal was grown by vapor diffusion of water into an equimolar DMF solution of the two components.

Triimides **1b–d** were prepared by Mitsunobu alkylation of a crude sample of the unsubstituted triimide core with the appropriate *n*-alcohol using a previously reported procedure.⁸ The preparation and characterization of triimide **1a** is also reported therein. The triimides were isolated by column chromatography on SiO₂ in ethyl acetate/hexane mixtures and recrystallized from aqueous DMF to give the respective tri-*n*-alkyl triimides as white crystalline solids in 25–30% yield.

***N,N,N'*-Tri-*n*-octylmellitic Triimide (**1b**).** Mp 127.5–128.5 °C; *R_f* = 0.30 (SiO₂, 1:4 EtOAc:hexanes); ¹³C NMR (126 MHz, CDCl₃) δ 162.49, 133.54, 39.31, 31.69, 29.02 (two coincident peaks), 28.09, 26.75, 22.55, 14.00 ppm; ¹H NMR (300 MHz, CDCl₃) δ 3.79 (t, *J* = 7 Hz, 6H), 1.57 (m, 6H), 1.27 (m, 30H), 0.85 (t, *J* = 7 Hz, 9H) ppm; ESI-MS (positive-ion) 622 ([M + H]⁺), 644 ([M + Na]⁺, 100%).

***N,N,N'*-Tri-*n*-decylmellitic Triimide (**1c**).** Mp 116–117.5 °C; *R_f* = 0.56 (SiO₂, 1:4 EtOAc:hexanes); ¹³C NMR (126 MHz, CDCl₃) δ 162.65, 133.52, 39.61, 32.10, 29.72, 29.65, 29.47, 29.33, 28.36, 27.03, 22.91, 14.35 ppm; ¹H NMR (270 MHz, CDCl₃) δ 3.80 (t, *J* = 7 Hz, 6H), 1.56 (m, 6H), 1.24 (m, 42H), 0.86 (t, *J* = 7 Hz, 9H) ppm; ESI-MS (positive-ion) 706 ([M + H]⁺), 728 ([M + Na]⁺, 100%).

***N,N,N'*-Tri-*n*-tetradecylmellitic Triimide (**1d**).** Mp 102–103 °C; *R_f* = 0.43 (SiO₂, 1:4 EtOAc:hexanes); ¹³C NMR (126 MHz, CDCl₃) δ 162.49, 133.35, 39.32, 31.88, 29.64, 29.61 (two coincident peaks), 29.57, 29.52, 29.38, 29.31, 29.09, 28.11, 26.77, 22.65, 14.07 ppm; ¹H NMR (270 MHz, CDCl₃) δ 3.80 (t, *J* = 7 Hz, 6H), 1.58 (m, 6H), 1.26 (m, 66H), 0.82 (t, *J* = 7 Hz, 9H) ppm; ESI-MS (positive-ion) 875 ([M + H]⁺), 897 ([M + Na]⁺, 100%).

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Supporting Information Available: Crystallographic information (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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