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Structural Rules for the Chiral Supramolecular Organization of OPE-based Discotics: Induction of Helicity and Amplification of Chirality

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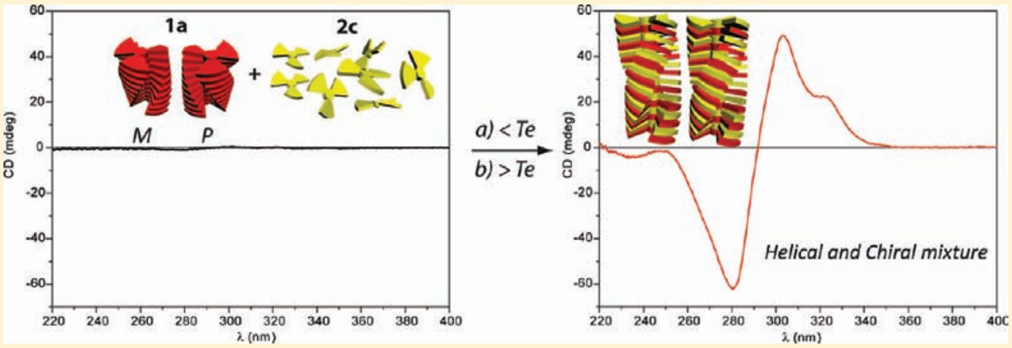
Supporting Information



ABSTRACT: A systematic study on the structural rules that regulate the chiral supramolecular organization of oligo(phenylene ethynylene) (OPE)-based discotics is presented. This study is based on the chirooptical properties of two different series of triangular shape OPEs. The first of them is composed by OPE-based trisamides with a variable number of chiral side chains (compounds **1**) that self-assemble following a cooperative mechanism. The CD experiments carried out with these desymmetrized trisamides demonstrate that only one stereogenic center is sufficient to achieve a helical organization with a preferred handedness. However, the ability to amplify the chirality decreases upon decreasing the number of stereocenters at the peripheral side chains. The second series is constituted by triangular shape OPEs with a variable number of ether and amide functional groups and constant absolute configuration of the stereogenic centers at all of the peripheral chains (compounds **2**). These compounds do not self-assemble into helical aggregates as demonstrated by the corresponding CD studies. The amplification of chirality observed in the mixtures of some of the components of both series has been investigated. The combination of chiral trisamide **1d** with chiral but nonhelical **2b** or **2c** does not produce an amplification of chirality most probably due to the mismatch between the stereogenic centers of both components. However, the combination of achiral trisamide **1a** with chiral but nonhelical bisamide **2c** generates, in a cooperative manner, helical structures with a preferred handedness in a process involving the transfer of helicity from **1a** to **2c** and the transfer of chirality from **2c** to **1a**. The structural features of the OPE discotics also exert a strong influence on the columnar aggregates. Thus, while achiral **1a** bundles into thick filaments to form an organogel, the gelation ability of these triangular OPEs decreases upon increasing the number of stereogenic centers, being totally canceled for compounds **2** in which the amide functionalities are replaced by ether linkages. Finally, we have also registered AFM images of the helical aggregates obtained from the mixture of **1a**+**2c**, which implies an efficient transfer of the chiral objects from solution to surfaces. The study presented herein increases the understanding of the structural rules that regulate the chiral supramolecular organization of discrete molecules in general and, more specifically, those based on π-conjugated oligomers.

■ INTRODUCTION

The sophistication and functionality reached by biological helices is inspiring scientists to utilize helical structures in chirality sensing,[1] enantioselective catalysis,[2] and especially to unravel the origin of homochirality.[3] The generation of chirality is directly related with an efficient transfer of chiral information from chiral units to complex supramolecular structures through noncovalent interactions. These supramolecular architectures are generally helices that are inherently chiral since right- and left-handed helices are mirror images that cannot be superimposed. Big efforts have been devoted to crystalline architectures and helical polymers to unravel the origin of homochirality.[4,5] More recently, chemical self-assembly of relative small and simple molecules has yielded hierarchically organized, complex structures in a process known as supramolecular polymerization.[6,7] Many of these supramolecular structures exhibit a preferred handedness due to the incorporation of stereocenters at the peripheral substituents.[8]

Most of the investigations dealing with amplification of chirality are based on the combination of two species that have identical chromophores but differ in the chiral or achiral nature

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of the side chains.[9] Two main experiments have been developed to control and study the amplification of the chirality phenomenon in polymers and supramolecular polymers: (a) "sergeants-and-soldiers" in which the helicity of a racemic mixture of both enantiomers (the soldiers) is biased by the addition of minute amounts of chiral units (the sargeants)[10] and (b) "majority rules", where a slight excess of one of the two possible enantiomers shifts the whole helicity to that of this enantiomer.[11] More scarce are the examples in which the strategy to achieve amplification of chirality consists of the preparation of mixtures with species of different nature. The solvation of (supramolecular) polymers with chiral solvents or the formation of complexes between achiral (supramolecular) polymers and chiral guests exemplifies this strategy based on using mixed systems.[12,13] A key issue in the generation of helical structures for both synthetic and supramolecular polymers is the synthesis of appropriate chiral building blocks. The total number of stereogenic centers at the peripheral chains and their relative position, the chemical nature of the central core supporting these side chains, the connectivity between these two units and, very importantly, the nature of the noncovalent interactions that induce the hierarchical helical organization are pivotal factors in the rational design of the chiral momoners that interact to yield the helical structure.

Very recently, we have described that oligo(phenylene ethynylene) (OPE) based trisamides **1a** and **1d** (Figure 1) self-assemble into helical columnar aggregates by the operation of a 3-fold α-helical-type intermolecular amide hydrogen bonding and $\pi-\pi$ stacking of the aromatic central units. Pristine chiral trisamide **1d** and the mixture of achiral **1a** and chiral **1d** exhibit strong Cotton effects demonstrating the helical nature of the aggregates formed from these OPEs even at high diluted conditions.[14] However, the attachment of the chiral side chains to the aromatic C_3-symmetric core by an ether linkage (compound **2a** in Figure 1) results in a complete lack of dichroic response, which implies that the self-assembly of these chiral molecule produces disordered aggregates with unpreferred helicity.[15]

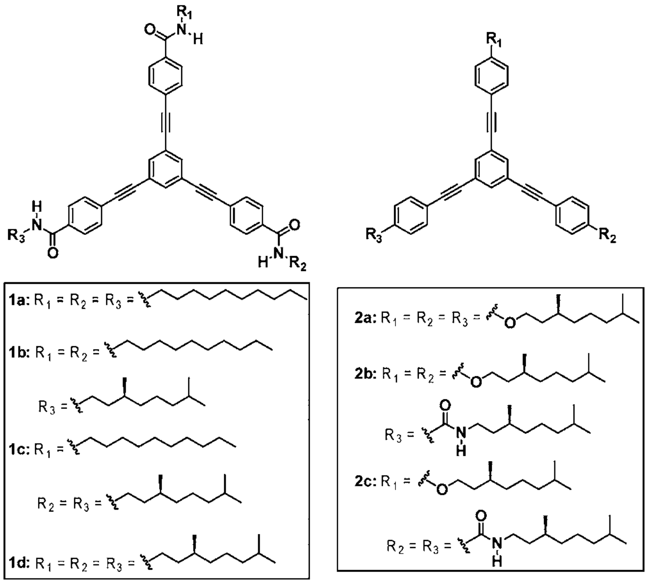


Figure 1. Chemical structure of the triangular-shape OPE-based trisamides **1** and alkoxy-amides **2**.

To establish the structural rules that regulate the chiral supramolecular organization of OPE discotics, we have synthesized OPE-based trisamides with a variable number of chiral side chains (compounds **1** in Figure 1) and new triangular shape alkoxy-substituted OPEs with a variable number of ether and amide functional groups keeping the absolute configuration of the stereogenic centers constant at all peripheral chains (compounds **2** in Figure 1). The corresponding CD studies reveal that the presence of the three amide functionalities but only one stereogenic center is sufficient to attain helical supramolecular structures although it substantially decreases the ability to amplify the chirality of the racemic mixture of **1a**. However, replacing the amide functionalities by ether linkages (compounds **2**) impedes the α-helical columnar organization and no dichroic response is observed. We have demonstrated that the combination of the racemic helical mixture formed by the achiral trisamide **1a** and the chiral but nonhelical bisamide **2c** gives rise to helical structures with a preferred handedness in a cooperative fashion. This process involves the transfer of helicity from **1a** to **2c** and the transfer of chirality from **2c** to **1a** and represents one of the very scarce examples in which chirality is obtained from the formation of host−guest complexes between structurally analogous species.

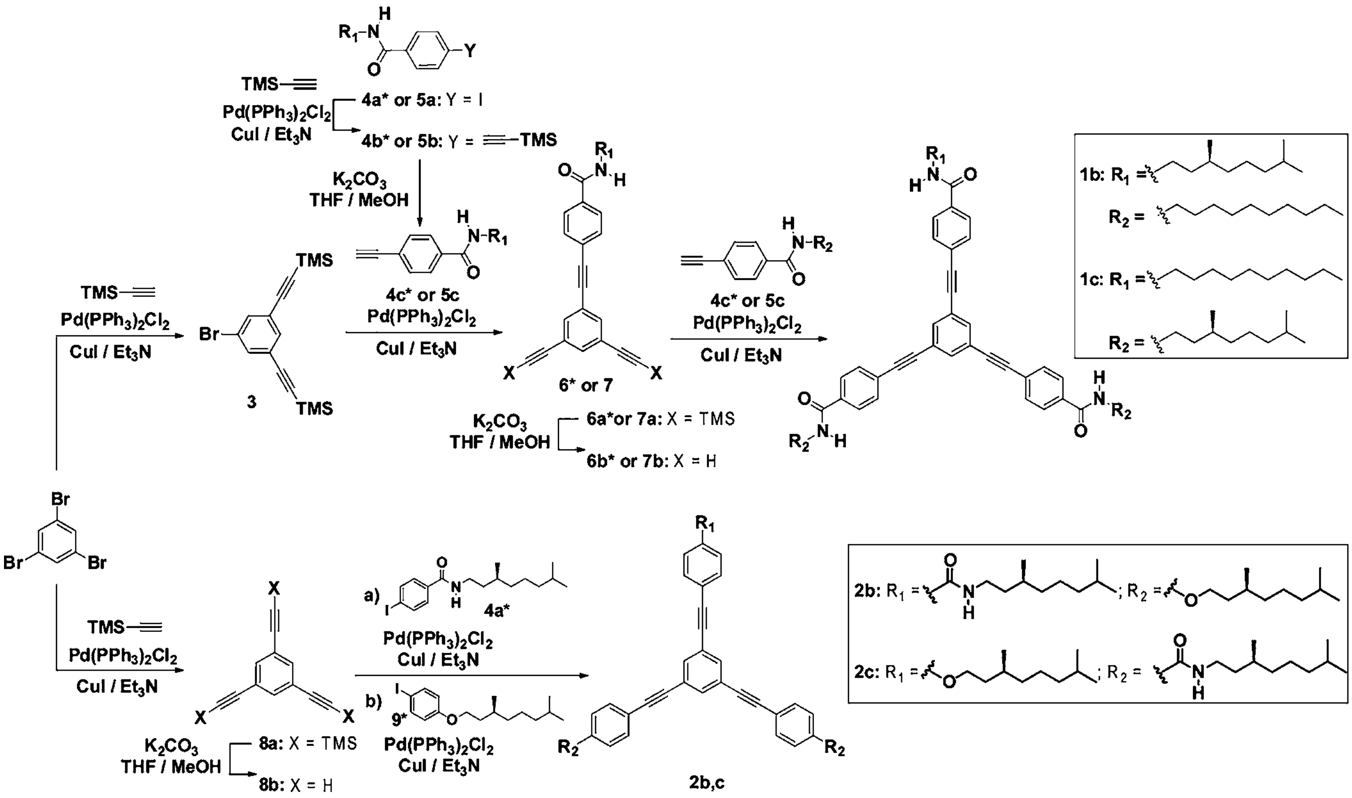
The columnar aggregates formed by the self-assembly of **1a** bundle into thick filaments that finally form an organogel in toluene as solvent. The gelation ability of this class of triangular OPE decreases upon increasing the number of stereogenic centers being totally canceled for the alkoxy OPEs **2**. The fibrillar supramolecular structures formed from trisamides **1b** and **1c** has been visualized by atomic force microscopy (AFM) imaging. Finally, we have also registered AFM images of the helical aggregates obtained from the mixture of **1a**+**2c**, which implies an efficient transfer of the chiral objects from solution to a surface.

■ RESULTS AND DISCUSSION

Synthesis. Symmetric trisamides **1a** and **1d** as well as trialkoxy-OPE **2a** have been prepared by a 3-fold Sonogashira C−C cross coupling reaction catalyzed by palladium.[14,15] However, the synthesis of the asymmetrical trisamides **1b** and **1c** and also the OPE decorated with a variable number of amide and alkoxy functional groups (**2b**−**c**) requires the desymmetrization of the central aromatic ring. To accomplish this purpose, we have followed two general procedures starting from 1,3,5-tribromobenzene. For the case of trisamides **1b** and **1c**, a stoichiometrically controlled Sonogashira reaction yields 1-bromo-3,5-bis(2-(trimethylsilyl)ethynyl)benzene (**3**),[16] which allows controlling the attachment of the achiral or chiral chains. A further Sonogashira cross-coupling between **3** and the chiral 4-ethynyl-*N*-((*S*)-3,7-dimethyloctyloxy))benzamide (**4c***) or achiral 4-ethynyl-*N*-decyllbenzamide (**5c**) yields compounds **6a*** or **7a**, respectively. The deprotection of the trimethylsilyl group and subsequent Sonogashira cross-coupling of the resulting alkyne derivatives **6b*** or **7b** with **5c** or **4c***, respectively, afford asymmetrical trisamides **1b** and **1c** (Scheme 1).

The asymmetrical compounds **2b** and **2c** have been readily obtained by following a one-pot Sonogashira cross-coupling protocol in which one or two equivalents of **4a***[14] units are first attached to the central aromatic fragment.[17] The reaction was monitored by TLC until all starting materials **8b**[18] and **4a***

Scheme 1. Synthesis of the Asymmetric Trisamides and Alkoxy-OPEs 1 and 2



disappeared. After that, an excess of 1-((*S*)-3,7-dimethyloctyloxy)-4-iodobenzene (**9***)[19] was added to the reaction mixture to yield compounds **2b** and **2c** (Scheme 1).

All the compounds and intermediates were characterized by means of analytical and spectroscopic techniques (see Supporting Information). The ^{1}H NMR spectra of **1b** and **1c** show only three aromatic resonances: two doublets at δ ~7.7 and 7.5, and a singlet at δ ~7.6. The presence of the stereogenic centers is unambiguously probed by the apparition of two sharp doublets at δ ~0.9 and 0.8 adscribable to the methyl groups of the chiral (*S*)-3,7-dimethylocyl side chains. However, the asymmetry of **2b** and **2c** induces the anisochrony of the two different *para*-substituted aromatic fragments and the corresponding ^{1}H NMR spectra show two different sets of resonances ascribable to an AA′BB′ spin system typical of para-substituted aromatic compounds, the first one at δ ~7.7 and 7.5, and the second one at δ ~7.4 and 6.8. Additionally, the central aromatic protons appear as a singlet at δ ~7.6.

IR Spectroscopy. A first indication of the characteristic 3-fold intermolecular hydrogen-bonding motif that yields helical columnar stacks in supramolecular polymers endowed with amide functional groups is IR spectroscopy. More specifically, the α-helix arrangement can be inferred from the N−H, and Amide I (C=O) stretching bands as well as the Amide II (C−N) bending band.[20] The FTIR spectra of asymmetric trisamides **1b** and **1c** show well-defined bands at ~3290, 1636, and 1547 cm^{-1} diagnostic of a helical columnar stack, in good agreement with the previously data reported for the symmetric trisamides **1a** and **1d** (Table S1, Supporting Information, and Figure 2).[14] Compounds **2b** and **2c**, endowed with one or two amide functional groups, respectively, present different IR features. In these triangular OPEs, the N−H stretching appears at higher wavenumber (~3314 cm^{-1}) being the Amide I and Amide II vibrations at 1638 and 1547 cm^{-1}, respectively (Table S1, Supporting Information, and Figure 2). These values correspond to H-bonded amide functionalities but are deviated from those values reported for α-helical columnar stacks.[20] Therefore, the presence of lateral H-bonds between the amide groups of molecules of different columnar stacks could justify these experimental findings for compounds **2b** and **2c**.

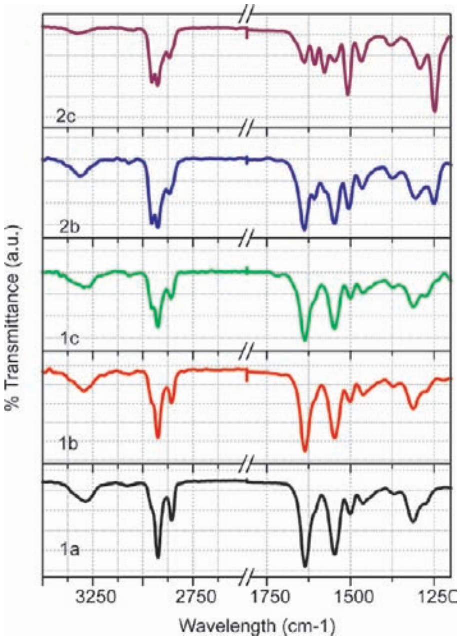


Figure 2. Partial FTIR spectra of trisamides **1a−c** and alkoxy-amides **2b,c**.

In addition, the FTIR of all the triangular OPEs studied herein exhibit well-defined bands at ν ~2925, 2860, and 1465 cm^{-1} corresponding to the stretching of the paraffinic $-CH_2-$ groups that suggest the interdigitation of the paraffinic side chains (Table S1, Supporting Information, and Figure 1).[21]

Self-assembly in Solution. The formation of stacked organized columns in solution from the compounds reported herein has been investigated by circular dichroism (CD). This technique is very sensitive to detect chiral supramolecular structures. The CD spectra of trisamides **1b** and **1c** show a bisignated Cotton effect identical to that reported for the symmeric trisamide **1d**, that is, negative at high energy (λ_{max} = 280 nm), positive at low energy (λ_{max} = 303 nm) and with a zero crossing at 291 nm.[14] These chiroptical characteristics can be assigned to right-handed helically organized structures and demonstrate that only one stereogenic center at the peripheral side chains is able to regulate the helical sense of the aggregates formed by the self-assembly of C_3-symmetric OPE trisamides (Figure 3).[22] These results are in good correlation with those reported for benzene-1,3,5-trisamides (BTAs).[23]

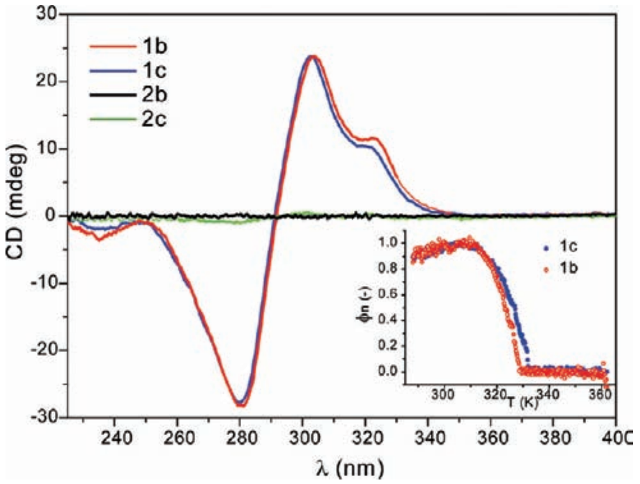


Figure 3. CD spectra of **1b** (red line), **1c** (blue line), **2b** (black line) and **2c** (green line) (MCH, 1.5 × 10^{-5} M). (Inset) Nonsigmoidal melting curves of **1b** (red) and **1c** (blue) from 363 to 288 K at intervals of 0.5 K min^{-1}.

We have previously demonstrated that achiral **1a** and chiral **1d** form supramolecular polymers following a nucleation-elongation or cooperative mechanism.[14,24] Analogously, the cooperative supramolecular polymerization of **1b** and **1c** is inferred from the nonsigmoidal shape of the curves obtained by variable temperature CD experiments performed in methylcyclohexane (MCH). These experiments were carried out at diluted conditions and applying a slow cooling rate of 0.5 K min^{-1} to suppress possible kinetic effects during the polymerization process (inset in Figure 3). The melting curves also present an abrupt change between the nucleation regimen, in which the corresponding trisamide is molecularly dissolved and no CD signal is observed, and the elongation regimen, in which the supramolecular polymer grows rapidly (Figures 3 and S1, Supporting Information).

To extract the thermodynamic parameters that define the cooperative supramolecular polymerization of **1b** and **1c**, we have fitted the temperature dependent CD response at 303 nm to the nucleation-elongation model proposed by Van der Schoot.[25] This model allows calculating the elongation temperature (T_e), the enthalpy release in the elongation regimen (h_e) and the degree of cooperativity expressed by the activation constant K_a. These thermodynamic parameters for **1b** and **1c** are collected in Table 1 together with that reported previously for symmetric **1a** and **1d**. The stability of the aggregates, determined by the T_e values, decreases for the asymmetric trisamides **1b** and **1c** in comparison to the symmetric **1a** and **1d**. The lower stability of the aggregates could be accounted for by considering a less efficient interdigitation of the achiral and the chiral side chains that decorate the desymmetrised trisamides. The low value calculated for K_a expresses a high degree of cooperativity. The melting curves of **1b** and **1c** also show that the CD response diminishes at low temperatures. This phenomenon can be reasonably assigned to the scarce solubility of these compounds in MCH.

Table 1. Thermodynamic Parameters Corresponding to the Supramolecular Polymerization of Trisamides 1a–d and the Mixture of 1a+2c (MCH, 1–1.5 × 10^{-5} M)

compound	h_e (kJ mol^{-1})	T_e (K)	K_a
1a	−61.0	348	2.1 × 10^{-3}
1b	−114.3	328	4.9 × 10^{-4}
1c	−100.1	332	1.2 × 10^{-4}
1d	−97.1	344	5.0 × 10^{-4}
1a+2c	−107.0	332	4.4 × 10^{-4}

The cooperative mechanism that governs the supramolecular polymerization of trisamides **1b** and **1c** has been confirmed by the nonsigmoidal curves obtained in the corresponding temperature dependent UV–vis experiments in MCH. Similarly to compounds **1a** and **1d**, asymmetric compounds **1b** and **1c** present two absorption maxima at around 300 and 314 nm at high temperature (363 K) whose intensity decreases upon cooling appearing a new shoulder at 325 nm (Figure S2, Supporting Information).

The replacement of the amide functional groups by alkoxy linkages strongly conditions the helical organization of the triangular OPEs. Similarly to the symmetrical, chiral trialkoxy derivative **2a**, asymmetric **2b** and **2c** endowed with one or two amide functionalities, respectively, showed no CD response in the same experimental conditions as trisamides **1b–d**. The lack of dichroic signal confirms that these triangular OPEs are not able to self-assemble into helical columnar stacks, as already suggested by the corresponding FTIR data. Therefore, the operation of the three highly directional H-bonds between the amide functional groups plays a pivotal role in the hierarchical self-assembly of triangular shape OPEs.

Amplification of Chirality in Mixed Systems. The systematic variation of the chemical structure of the reported OPE discotics allows investigating of the influence of the chemical structure on the amplification of chirality. Considering the above rationalized structural requirements necessary for triangular OPEs to self-assemble into helical aggregates, we have investigated the chiral behavior of mixed systems by following “sergeants-and-soldiers” experiments. We have reported that the chirality of self-assembled **1a** is amplified upon the addition of chiral **1d** and the maximum handedness value is reached when a 20% of the chiral sergeant **1d** is added (Figure 4, bottom).[14] Taking into account the chiroptical features of asymmetric trisamides **1b** and **1c**, we have also performed “sergeants-and-soldiers” experiments by mixing

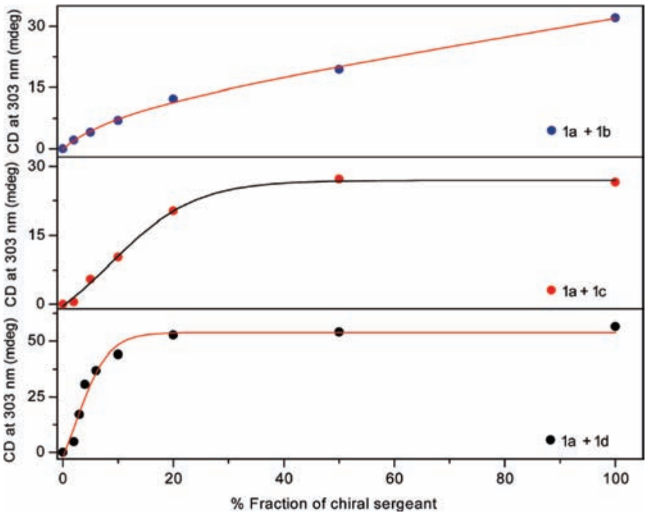


Figure 4. Amplification of chirality experiments for achiral **1a** upon mixing with chiral **1b** (top), **1c** (middle), and **1d** (bottom) (298 K, MCH, total concentration 1×10^{-5} M, 298 K).

these chiral OPEs with racemic **1a**. The addition of increasing amounts of chiral **1c**—endowed with two sterogenic centers—into a solution of achiral **1a** keeping the total concentration constant and further heating above the T_e value leads to the appearance of a chirooptical response that increases nonlinearly (Figure 4, middle and Figure S3, Supporting Information). In this case, the maximum handedness is obtained upon adding a larger amount of the chiral sergeant **1c** (around 40%), which suggests the strong dependence of the amplification of chirality with the number of stereogenic centers present in the chiral sergeant.

This dependence is confirmed in the sergeants-and-soldiers experiments carried out with trisamides **1a** and **1b**, which possess only one stereogenic center and the peripheral side chains. The chirooptical response obtained for the mixture **1a**+**1b** increases almost linearly which indicates that the amplification of chirality in this mixture is negligible. These results demonstrate the increasing the number of stereocenters per monomeric unit increases the ability to transfer the chiral information reaching a fully amplified state. A plausible explanation on the influence of the number of sterogenic centers at the peripheral positions of the OPE-based trisamides on the amplification of chirality can be extracted by utilizing the concepts of helix reversal penalty (HRP) and mismatch penalty (MMP), recently investigated for BTAs.[26] HRP is directly related to the strength of the intermolecular hydrogen bonds and penalizes a helix reversal within a columnar stack, while MMP penalizes the mismatch induced when a chiral monomer is introduced into a stack of its unpreferred helicity. Since the four trisamides **1a**−**d** exhibit equally strong intermolecular H-bonding arrays, as suggested by the FTIR features, remarkable HRP deviations can be ruled out and the weaker sergeants-and-soldiers effect could be justified by a lower MMP.

After these sergeants-and-soldiers experiments in which we only changed the (a)chiral nature of the peripheral side chains of the two components of the mixture, we have also investigated the chirooptical behavior experienced by systems formed by mixing both OPE-based discotics **1** and **2**. Considering that compounds **2b** and **2c** are inherently chiral but do not form helical supramolecular structures, we have utilized them as achiral soldiers and we have added increasing amounts of symmetric **1d** as chiral sergeant thus forming chiral host−guest complexes (Figures 5 and S4, Supporting Information). The CD response of the mixtures formed by **2b** and **1d** as well as **2c** and **1d** increases linearly upon the ratio of the chiral counterpart increases (insets in Figures 5 and S4, Supporting Information) which implies that there is no amplification of chirality in these mixtures. On the contrary, the CD intensity of **2b**+**1d** and **2c**+**1d** is smaller than the CD signal observed for pristine chiral **1d** at the same range of concentration (Figure S5, Supporting Information). These data suggest that both alkoxy-OPEs **2b** and **2c** interact with **1d** diminishing the helicity of the whole sample most probably due to a mismatch between the stereogenic centers at the side chains in both types of triangular OPEs.

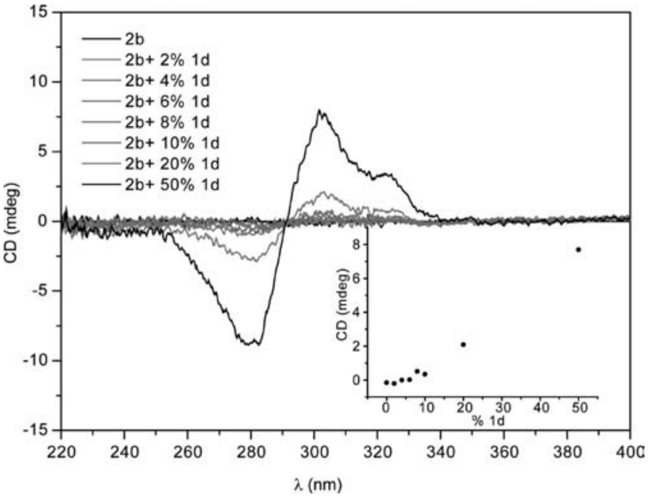


Figure 5. CD spectra of **2b** upon addition of increasing amounts of **1d** (MCH, total concentration 1×10^{-5} M, 298 K). (Inset) Variation of the CD signal upon increasing the amount of **1d**.

The interaction between alkoxy-OPEs **2b**−**c** and symmetric trisamide **1d** prompted us to evaluate the induction of helicity and amplification of chirality in mixtures formed by trisamide **1a** and triangular OPEs **2b** and **2c**. The former self-assembles into an equimolar mixture of right- and left-handed helices whereas the latter are inherently chiral but do not self-assemble into helical aggregates in diluted conditions. The complexation of these compounds, structurally close but not identical, could produce the transfer of helicity from **1a** to **2b** or **2c**, and the transfer of chirality from chiral **2b** or **2c** to achiral **1a** thus generating helical supramolecular polymers. The interaction between **1a** and **2b** or **2c** has been monitored by CD experiments. The addition of increasing amounts of **2b** to a diluted solution of **1a**, keeping the total concentration constant of the mixture (1×10^{-5} M) and heating the mixture above the T_e did not show any dichroic signal (Figure S6, Supporting Information). The lack of chirooptical properties in the mixture of **1a** and **2b** demonstrates that the interaction of the only amide functionality of **2b** with the amide functional groups of **1a** is not efficient and the α-helix H-bonding array between these groups, responsible of the helical organization of triangular OPEs, is not operating in these diluted conditions.

A sharp contrast is observed in the experiments carried out in the mixture formed by the achiral but helical trisamide **1a** and the chiral but nonhelical bisamide-alkoxy OPE **2c**. The direct mixture of both components at room temperature and at total constant concentration of 1×10^{-5} M did not result in any dichroic response, due to the kinetic inertness of the aggregates formed by **1a** at these experimental conditions that impedes the intercalation of the chiral guest **2c**. However, heating the mixture above the T_e value leads the solution to a molecularly dissolved state that allows the coassembly of both components of the mixture upon cooling. In fact, the slow cooling of the mixture results in the apparition of a clear bisignated Cotton effect with a negative and a positive maxima at 280 and 303 nm, respectively, and a zero crossing at 290 nm identical to that exhibited by chiral trisamides **1b−d** (Figure 6a). Unlike the mixture **1a+2b**, the interaction between the three amides of **1a** and the two amides of **2c** is very efficient and the α-helix H-bonding array between them together with the $\pi-\pi$ interactions between the aromatic units generates stable chiral and helical complexes even at diluted conditions. Additionally, the lack of stereogenic centers in **1a** cancels the possible mismatch effect between the two triangular OPEs as occurs in the mixture **1d+2c**.

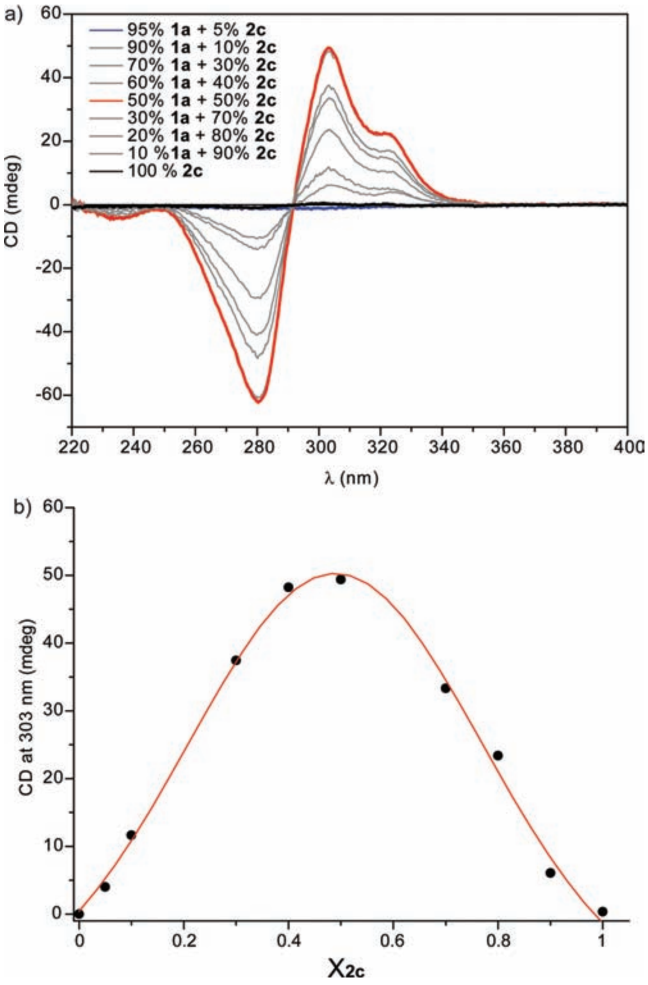


Figure 6. (a) CD spectra of **1a** upon addition of increasing amounts of **2c** (MCH, total concentration 1×10^{-5} M, 298 K). (b) Job plot of the mole fraction of **2c** versus CD intensity at 303 nm (MCH, 298 K, and 1×10^{-5} M as total concentration).

The stoichiometry of the complex formed by the interaction of **1a** and **2c** has been determined by a Job plot experiment monitoring the CD intensity at 303 nm. The maximum intensity is achieved for a molar fraction of 0.5 but the Job plot also presents a bell shape with inflections in the region close to mole fractions of 0 and 1. These features of the Job plot are consistent with the interaction of *n* molecules of **1a** with *n* molecules of **2c** to form the complex $\mathbf{1a_n2c_n}$ with an estimated constant of around 10^6 M^{-1}.[27] The generation of the complex $\mathbf{1a_n2c_n}$ would start with the formation of chiral dimeric species that further elongate to give rise to helical supramolecular polymers (Figure 7).

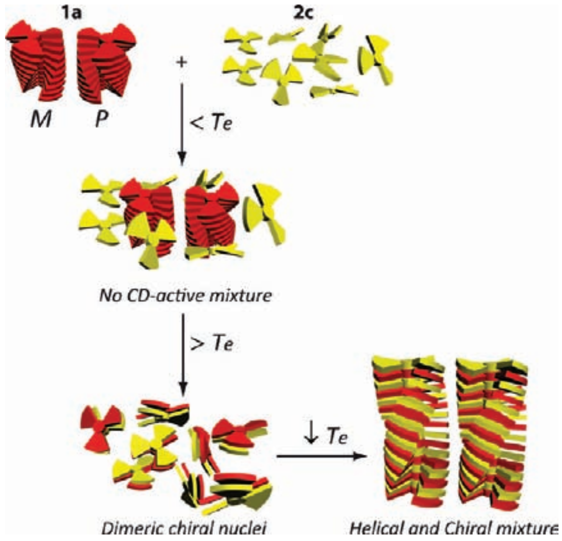


Figure 7. Schematic illustration of the transfer of helicity and amplification of chirality in the mixture of trisamide **1a** and bisamide-alkoxy-OPE **2c**.

The stability of the helical aggregates formed by the mixture **1a+2c** has been explored by temperature dependent CD experiments at different concentrations and compared with the results previously reported for pristine achiral **1a**.[14] The CD spectra of the mixture **1a+2c** shows the typical bisignated Cotton effect with the negative and the positive maxima at 280 and 303 nm, respectively, even at a concentration as low as 1×10^{-6} M (Figure 8a). The normalized CD cooling curves of the mixture **1a+2c** at different concentrations are not sigmoidal in shape with an abrupt drop in the dichroic response at around 320 K for the more concentrated samples, due to the scarce solubility of the resulting mixture (Figure 8b). Despite the different supramolecular processes taking place in the aggregation of the mixture **1a+2c**, it is possible to simplify the mechanism of this aggregation considering a cooperative supramolecular polymerization, analogously to pristine compounds **1**. Similar thermodynamic parameters to those calculated for **1a−d** (T_e =332 K, h_e = −107 kJ mol^{-1}, and K_a = 4.4×10^{-4}; see Table 1) has been determined for the mixture **1a+2c** at 1×10^{-5} M applying the above-mentioned cooperative model proposed by Van der Schoot.[25] The lower T_e value calculated for the mixture **1a+2c** (T_e = 332 K) in comparison to pristine **1a** (T_e = 348 K) is indicative of the weaker character of the aggregates formed by the mixture. Additionally, eq 1 allows determining the average number of molecules required to form the active chiral nucleus ($\langle N_n(T_e)\rangle$) that further elongates giving rise to the final supramolecular polymer.[25] For a K_a value of 4.4×10^{-4}, the parameter $\langle N_n(T_e)\rangle$ for the mixture **1a+2c** is of around ten molecules, that is, around five pairs of **1a** and **2c**.

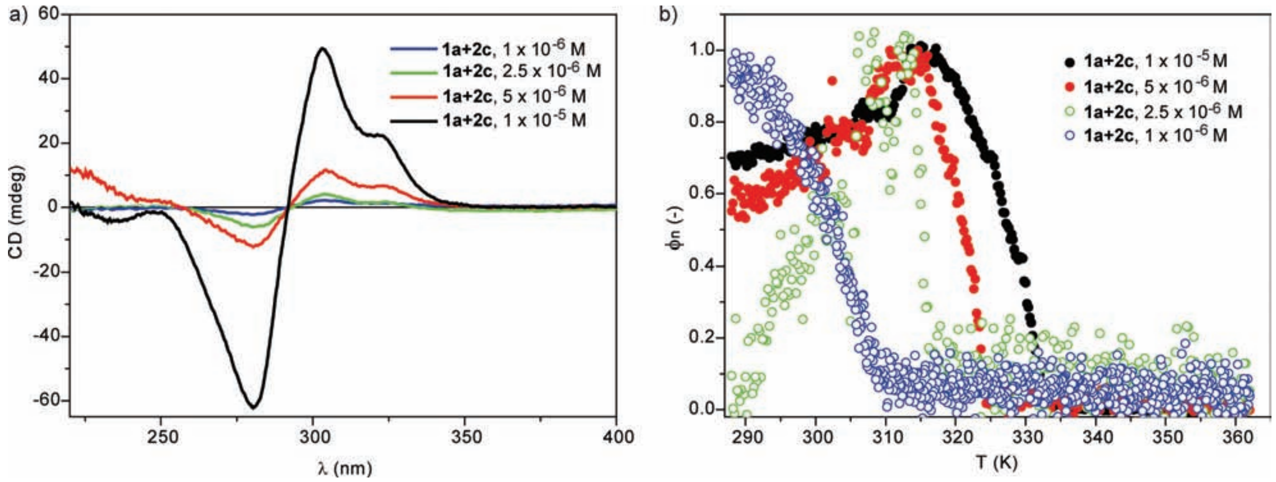


Figure 8. (a) CD spectra of the 1:1 mixture **1a+2c** at different concentrations (MCH, 298 K). (b) Melting curves of the 1:1 mixture **1a+2c** at different concentrations from 363 to 288 K at intervals of 0.5 K min^{-1}.

$$\langle N_n(T_e)\rangle = \frac{1}{\sqrt[3]{K_a}} \qquad (1)$$

$$K_a = K_2/K \qquad (2)$$

A complete determination of the thermodynamic parameters governing the supramolecular polymerization of the mixture **1a+2c** can be also calculated from the data obtained in the Van der Schoot analysis at different concentrations. The degree of cooperativity in a supramolecular polymerization process is determined by K_a that, in turn, is the quotient between the nucleation (K_2) and the elongation (K) constants (eq 2). A modified version of the Van't Hoff analysis is obtained by plotting the natural logarithm of the concentration ($\ln(C)$) versus the inverse of T_e ($1/T_e$). The critical concentration at room temperature can be calculated by simple extrapolation in the resulting straight line (Figure S7, Supporting Information). This critical concentration value is equated to the inverse of the elongation constant K, and a value of $K = 8.40 \times 10^7$ M^{-1} is extracted.[28] The high calculated value of K for the mixture **1a+2c** is in good correlation with the value estimated from the Job plot analysis for this constant. Upon calculating the elongation constant K and by utilizing eq 2, it is possible to determine that the value of the nucleation constant K_2 is 3.06×10^5 M^{-1}. The high values of K and K_2 are accounted for by considering the synergy between the H-bonding interactions established between the amide functional groups and the $\pi-\pi$ stacking between the aromatic OPEs moieties. A similar calculation has been carried out for pristine achiral **1a** utilizing the parameters deduced form temperature dependent UV−vis experiments previously reported.[14] The supramolecular polymerization process of trisamide **1a** is defined by an elongation and a nucleation constants of $K = 3.49 \times 10^7$ M^{-1} and K_2 is 1.04×10^5 M^{-1}, respectively. These values for K and K_2 are in very good correlation with those calculated for the mixture **1a+2c**. The CD investigations presented herein for **1a+2c** mixture confirm that the combination of the racemic helical mixture formed by the achiral trisamide **1a** and the chiral but nonhelical bisamide **2c** gives rise to helical structures with a preferred handedness in a cooperative manner. This process implies the transfer of helicity from **1a** to **2c** and the transfer of chirality from **2c** to **1a** and represents one of the very few examples in which the chirality is obtained from the formation of host−guest complexes between structurally analogous species.

Morphology of the Supramolecular Polymers onto Surfaces. The columnar organization of symmetric trisamides **1a** and **1d** has been visualized previously by scanning electron microscopy (SEM).[14] This columnar aggregation can favor the entangling of fibrils to give rise to organogels upon capturing molecules of solvent.[29] Achiral **1a** is able to form an organogel at a concentration relatively high (∼10 wt %) by using toluene as solvent. The formation of the organogel is envisioned by inversion of the glass vial and experience a gel-to-sol transition upon heating (inset in Figure 9). This organogel is constituted by a dense network of thick filaments of around 1 μm thick as it can be observed by SEM imaging (Figures 9 and S8, Supporting Information). The introduction of stereogenic centers at the peripheral side chains of trisamides **1** diminishes the ability of this class of compounds to form organogels. Thus, compounds **1b**, **1c** and **1d** are not able to gelify in toluene at very high concentration (>15 wt %). In fact, the formation of intertwined fibers diminishes with the increasing number of

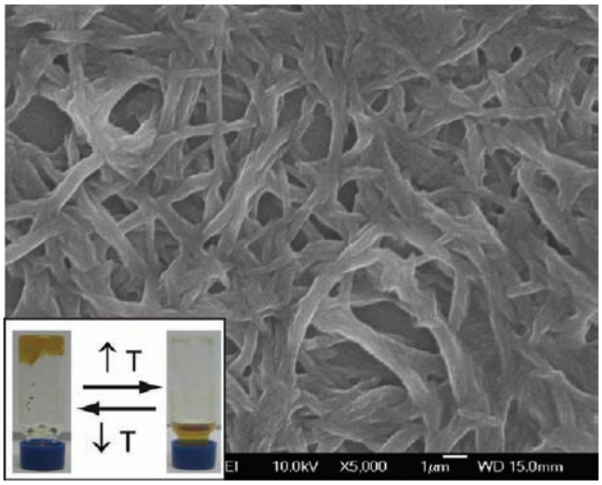


Figure 9. SEM image of the organogel formed by **1a** in toluene (glass substrate, ∼10 wt %). (Inset) Picture of the gel−sol transition of the organogel formed by **1a** in toluene.

sterogenic centers, most probably due to a poorer interdigitation between the peripheral chains.

AFM images of the aggregates formed in toluene at 1×10^{-4} M solutions are shown in Figure S9 (Supporting Information). Trisamide **1b**, endowed with only one stereogenic center at the peripheral chains, self-assemble into a dense network of fibrils that resembles to an organogel (Figure S9a, Supporting Information). However, the introduction of a second stereogenic center in trisamide **1c** reduces the efficient interdigation of the peripheral side chains and smaller fibrils of ~3 nm height are observed in the corresponding AFM images (Figure S9b, Supporting Information).

Unlike trialkoxy **2a** which forms isolated chiral rods,[15] compounds **2b** and **2c** are not able to form fibrillar structures and only amorphous material is visualized by AFM imaging. These findings are in good correlation with that observed in the corresponding FTIR spectra in which the amide functional groups are not forming an α-helix H-bonding array. However, the morphology of the supramolecular structures formed by the combination of **2c** with racemic **1a** can be visualized by AFM imaging (Figures 10 and S10, Supporting Information).

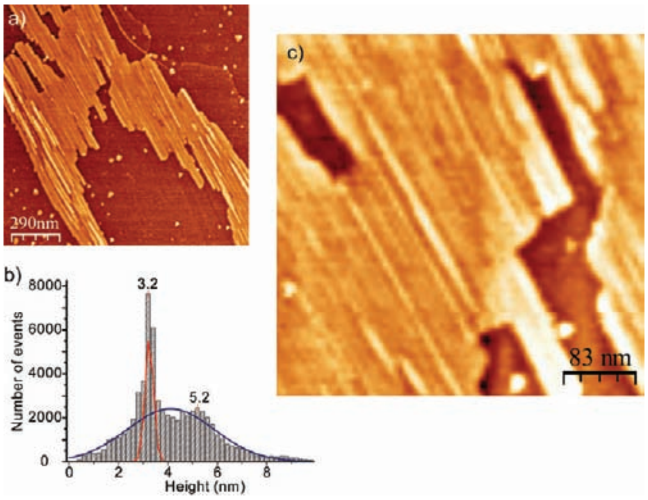


Figure 10. AFM height images (a and c) of the helical columnar aggregates obtained by the mixture **1a**+**2c** onto HOPG (z scale = 35 nm for (a) and 15 nm for (c); toluene, 1×10^{-5} M). (b) Histogram of the height distribution of the columnar aggregates shown in (a).

AFM images of a drop-casted toluene solution at 1×10^{-4} M of the mixture show long fibers that bundled to form thicker filaments (Figure S10, Supporting Information). The fibrils formed by this mixture are stable even at diluted conditions and stacks of right-handed filaments are observed in the AFM images after depositing a 1×10^{-5} M solution of the mixture in toluene. The histogram determined for the stacks height shows two distributions of aggregates centered the most populated at 3.2 nm, and the less populated at 5.2 nm (Figure 10b). The smaller effective height fits with the calculated size for a single trisamide,[14] which clearly suggests that the columnar π-stacked aggregates are deposited perpendicular to the substrate and can bundle to form thicker deposits. These images confirm that it is possible to efficiently transfer the supramolecular polymers formed by the mixture of **1a**+**2c** onto surfaces, which is a great advantage in the potential application of these aggregates.

CONCLUSIONS

The self-assembly of two different series of OPE-based discotics has been extensively studied. The first of these series consists of OPE-based trisamides with a variable number of chiral side chains (compounds **1**) that self-assemble cooperatively. The CD experiments carried out with these desymmetrized discotics demonstrate that only one stereogenic center at the peripheral side chains is sufficient to achieve a helical organization with a preferred handedness. However, the ability of the chiral trisamides **1b**–**d** to bias the chirality of the racemic mixture formed by the self-assembly of achiral **1a** decreases upon decreasing the number of stereocenters at the peripheral side chains. In the second series, we have investigated triangular shape OPEs with a variable number of ether and amide functional groups keeping the absolute configuration of the stereogenic centers at all peripheral chains constant (compounds **2**). The CD studies performed with these mixed triangular OPEs indicate that there is no helical organization. We have also investigated the amplification of chirality experienced by mixing some of the components of the two series. Thus, while the mixture of chiral trisamide **1d** with chiral but non helical **2b** or **2c** does not result in an amplification of chirality, the combination of achiral trisamide **1a** with chiral but nonhelical bisamide **2c** generates helical structures with a preferred handedness in a cooperative fashion in a process involving the transfer of helicity from **1a** to **2c** and the amplification of chirality from **2c** to **1a**. These studies represent one of the very scarce examples in which chirality is obtained from the formation of host–guest complexes between structurally analogous species that separately are CD-silent. The gelation ability of this class of triangular OPE decreases upon increasing the number of stereogenic centers being totally canceled for compounds **2** in which the amide functionalities are replaced by ether linkages.

The systematic study on the effect of the number of stereogenic centers at the side chains and the connectivity between those side chains and the central aromatic moiety in OPE-based discotics presented herein increases the understanding of the structural rules that regulate the chiral supramolecular organization of discrete molecules in general and, more specifically, those based on π-conjugated oligomers.

ASSOCIATED CONTENT

Ⓢ Supporting Information

FTIR data, UV–vis and CD melting curves, sergeants and soldiers experiments, SEM and AFM images, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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