Mirror Helices and Helicity Switch at Surfaces Based on Chiral Triangular-Shape Oligo(phenylene ethynylenes)

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Abstract: The self-assembly of triangular-shaped oligo(phenylene ethynylenes) (OPEs), peripherally decorated with chiral and linear paraffinic chains, is investigated in bulk, onto surfaces and in solution. Whilst the X-ray diffraction data for the chiral studied systems display a broad reflection centered at $2\theta \sim 20^{\circ}$ ($\lambda = Cu_{K\alpha}$), the higher crystallinity of OPE 3, endowed with three linear decyl chains, results in a diffractrogram with a number of wellresolved reflections that can be accurately indexed as a columnar packing arranged in 2D oblique cells. Compounds (S)-1a and (R)-1b—endowed with (S)- and (R)-3,7-dimethyloctyloxy chains-transfer their chirality to the supramolecular structures formed upon

Introduction

DNA, collagen or tobacco mosaic virus are paradigmatic natural molecules in which weak supramolecular interactions operate to create helical structures and condition their specific biological function. The presence of stereogenic centers at the molecular building blocks is responsible for the helicity of such natural compounds. Mimicking the natural process of creating helical supramolecular structures has prompted researchers to synthesize artificial helical ensembles with the primary goal of contributing to unravel the mechanisms followed by Nature in the generation of such chiral superstructures. Interestingly, the chiral organization of unnatural molecules holds potential applicability in supramolecular electronics and chirotechnology.^[1] The properties

their self-assembly, and give rise to helical nanostructures of opposite handedness. A helicity switch is noticeable for the case of chiral (S)-2 decorated with (S)-2-methylnonyloxy chains which forms right-handed helices despite it possesses the same stereoconfiguration for their stereogenic carbons as (S)-1**a** that self-assembles into left-handed helices. The stability and the mechanism of the supramolecular polymerization in solution have been investigated by UV/Vis experiments in methylcyclohexane. These studies demonstrate

Keywords: chirality • helical structures • nucleation-elongation • pi interactions • self-assembly that the larger the distance between the stereogenic carbon and the aromatic framework is, the more stable the aggregate is. Additionally, the self-assembly mechanism is conditioned by the peripheral substituents: whereas compounds (S)-1a and (R)-1b self-assemble in a cooperative manner with a low degree of cooperativity, the aggregation of (S)-2 and 3 is well described by an isodesmic model. Therefore, the interaction between the chiral coil chains conditions the handedness of the helical pitch, the stability of the supramolecular structure and the supramolecular polymerization mechanism of the studied OPEs.

(mechanical, optical, electrical) exhibited by the aggregates could be directly related with the mechanism followed by the building blocks to self-assemble.^[2-4] This self-assembly process strongly depends on thermodynamic parameters such as concentration or temperature and it is possible to establish three different mechanisms: a) isodesmic, b) ringchain, and iii) cooperative or nucleation-elongation.^[3] An isodesmic aggregation presents a single binding constant (K)for each assembly step. For a ring-chain mechanism, the connection of two reversibly associating units by a flexible spacer is a must. Concentration is crucial in this mechanism to switch rings into linear chains. The cooperative mechanism can be simplified as a two-state model in which an unfavored nucleus needs to be formed prior to the fast and energetically favored elongation of the polymeric chain. This circumstance implies that two different binding constants are necessary to describe the nucleation-elongation mechanism.^[3,5]

 π -Conjugated molecules—many of them exhibiting a strong tendency to aggregate—are playing a prominent role in the integration of organic materials into optoelectronic devices.^[4a,6] Regarding the self-assembly of π -conjugated systems, two end groups are electronically coupled and π - π stacking interactions are the main driving force for these systems to self-assemble. If an isodesmic mechanism oper-



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ates in the self-assembly of such π -conjugated systems, the strength of π - π interactions is unaffected upon aggregation. Nonetheless, if some additional contribution-conformational changes or other secondary attractive interaction-takes place upon, or participates in the self-assembly, a nucleation-elongation mechanism will describe the corresponding aggregation process. Different classes of achiral π -conjugated molecules, like phenyl-acetylene macrocycles,^[7] hexakis-(phenylethynyl)triindoles,^[8] tris(phenylisoxazolyl)benzenes,^[9] hexa-peri-hexabenzocoronenes (HBCs)^[10] or perylene bisimide derivatives,^[11] have been reported to form electronically coupled, linear supramolecular structures following an isodesmic or equal-K mechanism. More interestingly, the incorporation of chiral peripheral substituents to some of these aromatic platforms-specially phenylenevinylenes, phenyleneethynylenes or phenylenes-gives rise to helical structures in which a simple stereogenic center bias the overall stacking in a hierarchical manner.^[11-15]

We have recently reported on the self-assembly of a variety of amphiphilic radial oligo(phenylene ethynylenes) (OPEs) that self-assemble to form hollow vesicles or toroids, nanosheets or wires.^[16] Concentration dependent UV/Vis studies carried out with all these aromatic systems demonstrate an isodesmic mechanism for the corresponding supramolecular aggregation process in solution. Herein we report on the formation of mirror helices from chiral triangular OPEs—compounds (S)-1a, (R)-1b and (S)-2, see Scheme 1



Scheme 1. Synthesis of chiral OPEs (S)-1a, (R)-1b and (S)-2.

and formula below—and compare their self-assembly mechanism with the previously reported triangular OPE endowed with three linear decyl peripheral chains (compound **3**).^[9] The nature of the peripheral chiral chains conditions the helicity of the aggregates and also the association mechanism of the studied OPEs.

Results and Discussion

Synthesis: The synthesis of chiral OPEs (S)-1a, (R)-1b and (S)-2 has been carried out by following a multistep protocol,



in analogy to previous amphiphilic OPEs reported by our research group and is depicted in Scheme 1.^[16] The first synthetic step to obtain triangular-shape OPEs (S)-1a and (R)-**1b**, endowed with peripheral (S)- or (R)-3,7-dimethyloctyloxy chains, respectively, requires the catalytic hydrogenation of commercially available (S)- and (R)-citronellol.^[17] The peripheral aromatic units decorated with the corresponding chiral chains ((S)-6a, (R)-6b and (S)-7) were prepared by utilizing a bimolecular nucleophilic substitution $(S_N 2)$ Mitsunobu's reaction^[18] between the corresponding chiral alcohols (S)-4a, (R)-4b or (R)-decan-2-ol ((R)-5) and commercial 4-iodophenol. The S_N2 mechanism of the Mitsunobu's reaction completely inverts the R absolute configuration of the stereogenic center of commercial (R)-decan-2-ol ((R)-5) and ensures the same stereoconfiguration for the chiral peripheral chains of both compounds (S)-**6a** and (S)-7. Finally, compounds (S)-6a, (R)-6b and (S)-7 were reacted with 1,3,5-triethynylbenzene (8)^[19] by following a C-C cross-coupling Sonogashira-type reaction catalyzed by palladium^[20] to yield the target OPEs (S)-1a, (R)-1b and (S)-2 in 82, 68 and 55%, respectively. All new compounds reported in this study ((R)-6b, (S)-7, (S)-1a, (R)-1b and (S)-2) have been fully characterized by using NMR and FTIR spectroscopy, and mass spectrometry (see the Supporting Information). The C_3 symmetry of the synthesized OPEs (S)-1a, (R)-1b and (S)-2 results in simple ¹H NMR spectra, in which only three aromatic resonances appear ($\delta \sim 7.6, 7.4,$ and 6.8). In the aliphatic region, the signals at $\delta \sim 4$ ppm corresponding to the methylene group next to the oxygen atom and at $\delta \sim 0.9$ ppm ascribable to the methyl group present at the stereogenic center, confirm the structure of the final compounds. As expected, the enantiomeric character of (S)-1a and (R)-1b yields identical spectroscopic features for both of them.

Besides the structural information provided by MALDI-TOF (matrix assisted laser desorption ionization-time-offlight) spectrometry, these studies are a powerful tool to evaluate the capability of organic compounds to interact non-covalently.^[21] Thus, compound (S)-1a shows an intense peak at m/z at 846 corresponding to the molecular peak together with less intense peaks at m/z 1693, 2539 and 3386 diagnostic of the aggregation of two, three or four units (Figure 1). The closer proximity of the stereogenic center to the aromatic backbone in (S)-2 could reduce the stability of the supramolecular polymer and only the peaks correspond-

ing to the molecular ion $(m/z \ 846)$ and the dimer $(m/z \ 1693)$ appear in its MALDI-TOF spectrum (Figure S1).^[22]



Figure 1. MALDI-TOF mass spectra of OPE (S)-1a in a ditranol matrix.

Organization in bulk: The organization of triangular-shape OPEs (S)-1a, (S)-2 and 3 in the bulk-state has been analyzed by X-ray diffraction experiments ($\lambda = Cu_{Kq}$). Both chiral (S)-1a and (S)-2 display a diffuse halo in the wideangle region at $2\theta \sim 20^{\circ}$ (Figure 2a,b). In addition, (S)-2 presents also some crystalline peaks at 7.296, 4.220 and 3.656 Å, being the result of some degree of order. To investigate a potential increasing in the crystallinity of (S)-1a, we have carried out a temperature-dependent X-ray scattering analysis (Figure S2). Unfortunately, no changes appear in the range of studied temperatures (263–298 K) and only the above mentioned diffuse halo at $2\theta \sim 20^{\circ}$ is discernible. Similarly to (S)-1a and (S)-2, the X-ray diffractogram of OPE 3 shows the diffuse halo centered at 2θ ~20° together with a high number of well-resolved reflections (Figure 2c) which can be accurately indexed as a twodimensional oblique unit cell with typical parameters of a =2.8, b=2.7 nm, and $\gamma=71.4^{\circ}$ (Table S1 and Figure 2c). These X-ray scattering data for 3 suggest a columnar packing of 2D oblique cells with the decyl chains interdigitated and interacting by van der Waals forces (Figure 2d).

Self-assembly on surfaces: The self-assembling features of the triangular OPEs (*S*)-**1a**, (*R*)-**1b**, (*S*)-**2** and **3** on surfaces have been firstly investigated by atomic force microscopy (AFM). Tapping-mode AFM images from a spin-coated solution of chiral OPE (*S*)-**1a** in methylcyclohexane (MCH, $\sim 10^{-4}$ M) on highly ordered pyrolytic graphite (HOPG) exhibit isolated rod aggregates of several micrometers long (Figure 3a and S3). These rods clearly present a rope-like structure with ~ 3.2 nm in height in good agreement with the molecular dimensions calculated for all these triangular-



Figure 2. X-ray diffraction patterns (298 K) plotted against the angle 2θ for OPEs a) (S)-1a, b) (S)-2, and c) 3. The inset in c) shows the expanded region of large angles. d) Schematic representation of the 2D oblique unit cell.



Figure 3. Tapping-mode AFM images (air, 298 K) of a spin-cast MCH solution (~ 10^{-4} M, 2000 r.p.m., HOPG) of a) (*S*)-**1a** showing a *M*-type helix (*Z* scale = 10 nm), and b) (*R*)-**1b** showing a *P*-type helix (*Z* scale = 10 nm). The insets depict the corresponding height profile and the helical pitch along the black line in a) and b).

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shape OPEs (Figure S4).^[23] Additionally, the rope-like structures present a left-handed helicity (Figure 3a) due to the transfer of the chiral information embedded in the alkyl peripheral chains of (*S*)-**1a** to the columnar stacks. The *M*-type helical wound arrangement of (*S*)-**1a** results in an average pitch of 35 nm, in good correlation with many other helices formed upon the self-assembly of a variety of organic scaffolds.^[24] An optimal packing of molecules of triangular (*S*)-**1a** involves a face-to-face π -stacking with all the peripheral wedges rotated in the same direction. This columnar packing gives rise to preferred stable chiral objects (Figure 4a and S5a).^[25]



Figure 4. Schematic illustration of the self-assembly of a) (S)-1a, b) (R)-1b and c) (S)-2. The yellow line depicts the helicity of the aggregates. The ellipsoids indicate the steric hindrance between the peripheral substituents or the lack of such steric interaction.

AFM images of (*R*)-1b (MCH, ~ 10^{-4} M, HOPG) also reveal rope-like aggregates with ~3 nm in height and ~32 nm of pitch, in good correlation with the calculated molecular dimensions and the above mentioned pitch observed for (*S*)-1a. Interestingly, the nanostructures formed upon the self-assembly of (*R*)-1b are mirror images of those obtained form (*S*)-1a (Figure 3b and S6) and right-handed helices can be visualized as a consequence of the change in the stereoconfiguration of the chiral coiled chains from *S* to *R*. The change in the helicity, scarcely reported for small organic compounds,^[24d] implies that to achieve an optimal π stacking between the aromatic backbones, all the peripheral chiral wedges are oppositely rotated in (*R*)-1b than for compound (*S*)-1a (Figure 4a, b and S5).

Spin-casting (2000 r.p.m.) a $\sim 10^{-4}$ M solution of chiral OPE (S)-2 in MCH onto HOPG also results in the appearance of linear rods with lengths of several micrometers and height of ~ 3 nm (Figure 5). Expanded AFM images of the wires formed from (S)-2 also show rope-like structures, simi-



Figure 5. a) Tapping-mode and b) 3D AFM images (air, 298 K, HOPG) of a spin-cast solution (MCH, $\sim 10^{-4}$ M, 2000 r.p.m.) of (S)-2 showing a *P*-type helix (Z scale = 10 nm).

more pronounced rotation of the peripheral aromatic units in the stacks, giving rise to helical structures with lower pitches.

We have also investigated the morphology of the supramolecular structures formed from achiral **3**. The AFM images obtained upon spin-casting a $\sim 10^{-4}$ M MCH solution

pounds (S)-1a and (R)-1b appear as non-superimposable mirror images due to the opposite absolute configuration of the stereogenic centers (to guide the eye we have placed the methyl substituent of the stereogenic center in green and pointing to the reader in Figure S4a, S4c, and S4e). Chiral (S)-2 presents an opposite distribution of the methyl groups of the stereogenic center than (S)-1a which finally results in contrary rotation turns when stacks on top of each other to

and S5c). The difference in the magnitude of helical pitches is ascribable to the closer localization of the chiral center in (S)-2 in comparison with (S)-1a and (R)-1b (Figure 4c and S5c). The closer proximity of the stereogenic center in (S)-2 exerts a bigger steric demand in the optimal packing and induces a

attain stable helices (Figure 4c

larly to (S)-1a and (R)-1b. However, two sharp differences

are observed when both OPEs (S)-1a and (S)-2 are com-

pared: a) the helicity of the arrangement of (S)-2 is right-

handed (*P*-type), and b) the pitch of the *P* helix is of ~ 28 nm, a smaller value than that found for (*S*)-**1a**. The hel-

icity switch between (S)-1a and (S)-2 is consequence of the

change in the position of the chiral substituent along the

paraffinic chain. A plausible explanation of this behaviour

can be extracted from the calculated molecular geometry of

OPEs, (R)-1b and (S)-2 (Figure S4). As expected, com-

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of OPE 3 clearly show long monodimensional filaments a) with opposite handedness (Figure S7). Despite the achiral character of compound 3, AFM images show the presence of left- and right-handed columnar stacks, which suggests that 3 behaves as an enantiomeric mixture that upon self-assembly gives rise to helices of opposite helicity. Taking into account that compound 3 lacks any additional attractive secondary interaction or chiral substituent to induce the helicity, its helical organization could be justified by the local dipole moments present between the C–O bonds of the peripheral wedges.^[26] To the best of our knowledge, this is the first time that a mixture of M and P columnar stacks is visualized by AFM from the deposition of an achiral molecule onto a surface.

The surface and also the deposition technique play a crucial role in the morphology of the aggregates and, especially, in the visualization of chirality. Thus, scanning (SEM) and transmission-electron microscopy (TEM) images demonstrate the formation of long fibrils (Figures 6, S8, and S9).



Figure 6. SEM image of a long fiber formed by the aggregation of (S)-2 (MCH, $\sim 10^{-4}$ M). The inset depicts the diameter of the fiber.

The diameter of the fibers seen in SEM images is in the range of ~120 nm that corresponds to several intertwined wires. To our surprise, the rope-like structures seen in the AFM images are not observed in these images which is indicative of the strong influence of the substrate and also of the deposition technique into the morphology of the aggregates.^[27]

Self-assembly in solution: The mechanism followed by the chiral OPEs (S)-1a, (R)-1b and (S)-2 to self-assemble in solution has been investigated by concentration dependent UV/Vis experiments. As in our previous reported radial OPEs, these studies disclose the interaction of compounds (S)-1a, (R)-1b and (S)-2 by π -stacking since the reduction of the high energetic band at ~284 nm is concomitant with



Figure 7. Normalized UV/Vis absorption spectra of (*R*)-**1b** (MCH, 298 K, 2×10^{-4} to 1.6×10^{-7} M). Arrows indicate the direction of change with increasing concentration. The inset depicts the experimental α_{aggr} values of chiral (*R*)-**1b** (MCH, 298 K, 2×10^{-4} to 1.6×10^{-7} M) at 318 nm plotted as a function of $Kc_{\rm T}$ with different σ values according to cooperative nucleation-elongation model (lines from left to right: σ =1, 0.2, 0.1, and 0.01).

the increase of the two lower energetic bands at ~300 and ~314 nm (Figure 7).^[16] Considering the previous results obtained for radial OPEs, we firstly considered that the aggregate formation in solution could be described by an isodesmic model. If this is the case, the molar fraction of aggregates (α_{aggr}) or the molar fraction of monomeric species (α_{mon}) are related with the binding constant K by Equation (1):^[3,5,28]

$$\alpha_{\text{aggr}} = 1 - \alpha_{\text{mon}} = 1 - \frac{2Kc_{\text{T}} + -\sqrt{2Kc_{\text{T}} + 1}}{2(Kc_{\text{T}})^2} \tag{1}$$

Plotting the variation of a_{aggr} against the concentration of chiral (S)-1a and (R)-1b fails in fitting with the isodesmic model (Figures 7, S10, and S11). This non-isodesmic aggregation process implies the operation of a nucleation-elongation mechanism in the self-assembly of these two chiral OPEs. The simplest cooperative model for self-assembly considers that the nucleation step consists in the formation of a dimer, defined by K_2 , followed by the isodesmic elongation step expressed by K. The degree of cooperativity is given by the parameter σ that is described as K_2/K . Therefore, the smaller the σ value is, the higher the cooperativity of the supramolecular polymerization is. The mathematical relation among the different binding constants (K_2 and K), σ , and α_{mon} is given by the cubic Equation (2). The impossibility to solve Equation (2) requires the utilization of Equations (3) and (4) to estimate σ , K_2 and K:^[5,28]

$$a_{\text{mon}}^{3}(Kc_{\text{T}})^{2}(\sigma-1) + a_{\text{mon}}^{2}Kc_{\text{T}}(Kc_{\text{T}}-2(\sigma-1)) -a_{\text{mon}}(2Kc_{\text{T}}+1) + 1 = 0$$
(2)

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$$Kc_{\rm T} = (1 - \sigma)Kc_{\rm mon} + \frac{\sigma K c_{\rm mon}}{(1 - K c_{\rm mon})^2}$$
(3)

$$\alpha_{\rm aggr} = 1 - \alpha_{\rm mon} = 1 - \frac{Kc_{\rm mon}}{Kc_{\rm T}} \tag{4}$$

Plotting Kc_{mon} vs Kc_{T} according to the nucleation–elongation model for a number of σ values [Eq. (3)] allows calculating the theoretical α_{aggr} values for cooperative processes by applying Equation (4) (Figure S12). The experimental α_{aggr} values found for (*R*)-**1b** fit quite well with the calculated curve for a σ value of 0.2, and binding constants of K_2 = $2.5 \times 10^4 \text{ M}^{-1}$ and $K = 1.25 \times 10^5 \text{ M}^{-1}$ can be extracted. Similar results have been obtained for chiral (*S*)-**1a** being the parameters corresponding to a nucleation–elongation mechanism of $\sigma = 0.2$, and binding constants of $K_2 = 2.6 \times 10^4 \text{ M}^{-1}$ and $K = 1.3 \times 10^5 \text{ M}^{-1}$ (Figure S11).

Unexpectedly, the variation of the molar extinction coefficient with increasing concentration observed for chiral OPE (S)-2 results in a sigmoidal curve that fits with Equation (1)with an R^2 value of 0.99687 (Figure S13) indicating that the supramolecular polymerization of this chiral system is well described by an isodesmic model, that is, with a σ value of 1, and a binding constant of $K = 4.8 \times 10^4 \,\mathrm{m}^{-1}$. These results are in clear contrast with those obtained for (S)-1a and (R)-1b that self-assemble cooperatively. All these data suggest the influence exerted by the peripheral substituents on the supramolecular polymerization mechanism (Figure 4). The closer proximity of the stereogenic center in (S)-2 in comparison with compounds (S)-1a and (R)-1b, induces a more pronounced rotation of the peripheral aromatic units in the stacks that generates helical structures with low pitches (Figure 4c and S5c) and also a less efficient overlap of the aromatic frameworks when the molecules of (S)-2 stack on top of each other. The smaller contact surface results in a lower binding constant.

The different degree of rotation of the π -stacked molecules induced for the stereogenic center in the studied chiral OPEs could also justify the dissimilar supramolecular polymerization mechanism observed for chiral (S)-1a and (R)-1b in comparison with chiral (S)-2 and achiral 3.^[16b] Considering that, first, all the studied OPEs present an identical aromatic skeleton and, second, there are no additional secondary interactions operating in the aggregation of any of these systems, the cooperative character of the supramolecular mechanism determined for (S)-1a and (R)-1b can only be justified by considering the branched nature of their peripheral coil segments. We postulate that the steric constraints exerted by the 3,7-dimethyloctyloxy chains difficult the aggregation of (S)-1a and (R)-1b. A conformational change should operate in these coil segments that releases the steric hindrance between them and induces the formation of a nucleus of two molecules that interact by π - π stacking forces, as clearly suggests the calculated value of the nucleation K_2 . Once this nucleus is formed the system elongates to form the helical supramolecular polymer.

Finally, we tried to corroborate the mechanism of the selfassembly of (S)-1a, (R)-1b, and (S)-2 by circular dichroism (CD) (Figure S14). CD studies of chiral (*S*)-**1***a*, (*R*)-**1***b*, and (*S*)-**2** resulted in a very weak response in all the range of concentrations utilized ($\sim 5 \times 10^{-4} - \sim 10^{-5}$ M). The planarity of the aromatic framework^[29]—that results in no conformational changes upon self-assembly—and the lack of any secondary non-covalent interaction—that efficiently direct the rotation in only one sense during the aggregation—could form disordered columnar stacks of nonpreferred helicity and would justify the lack of a clear dichroic response.^[14b]

Conclusion

In conclusion, we report herein the helical aggregation of chiral C_3 -symmetric OPEs. Chiral (S)-1a and (R)-1b self-assemble into supramolecular polymers of mirror helicity, being left-handed for (S)-1a and right-handed for (R)-1b, to avoid the steric constraints exerted by the stereocenter present in the peripheral coiled chains. Interestingly, a helical switch is observed for chiral (S)-2 despite it possesses the same stereoconfiguration as (S)-1a. In addition, the closer proximity of the chiral center to the aromatic framework in (S)-2 results in a smaller value for the pitch of the P-helix. C-dependent UV/Vis investigations demonstrate that the supramolecular polymerization mechanism depends upon the chemical nature of the peripheral, paraffinic chains. An isodesmic aggregation mechanism applies for the case of chiral (S)-2 and achiral 3. Contrary to that, chiral (S)-1a and (R)-1b self-assemble by following a cooperative nucleationelongation mechanism with values of $\sigma = 0.2$, $K_2 \sim 2.5 \times$ 10^4 m^{-1} , and $K \sim 1.5 \times 10^5 \text{ m}^{-1}$. The dissimilar aggregation mechanism followed by the studied triangular-shape OPEs could be explained by considering the steric demand exerted by the 3,7-dimethyloctyloxy groups that decorate the periphery of (S)-1a and (R)-1b. Our overall results bring to light that minute variations in the molecular structure of the supramolecularly interacting species-as it occurs in naturecan decisively alter the outcome of a self-assembly process. The comprehension of the variables that control the self-organization processes in artificial systems would certainly help to create supramolecular systems that exhibit the complexity of their natural counterparts.

Experimental Section

1,3,5-Tris(2-(4-((S)-3,7-dimethyloctyloxy)phenyl)ethynyl)benzene [(S)-1a]: Compound (*S*)-**6a** (1.18 g, 3.3 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.05 mmol) and copper(I) iodide (0.011 mg, 0.06 mmol) were dissolved in triethylamine (16 mL). The mixture was subjected to several vacuum/argon cycles and compound **8** (0.15 g, 1 mmol) was added. The mixture was heated at 60 °C overnight. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, hexane/dichlorometane 4:1) affording (*S*)-**1a** as a yellow oil (0.69 g, 82 %). ¹H NMR (CDCl₃, 300 MHz, TMS): δ =7.58 (s, 3 H; H_a), 7.46 (d, ³/(H,H) = 8.8 Hz, 6 H; H_c), 4.01 (m, 6 H; H_d), 1.83 (m, 3 H; H_d), 1.75–1.48 (br, 9 H; H_{k+e}), 1.40–1.12 (br, 18H; H_{h+i+i}), 0.96 (d, ³/(H,H) = 6.4 Hz, 9 H; H_g), 0.89 ppm (d, ³/(H,H) = 6.6 Hz, 18H; H_{1+m}); ¹³C NMR

(CDCl₃, 75 MHz, TMS): $\delta = 159.5$, 133.4, 133.2, 124.3, 114.8, 114.6, 90.5, 86.7, 66.5, 39.3, 37.3, 36.2, 29.9, 28.0, 24.7, 22.7, 22.6, 19.7 ppm; FTIR (neat): $\tilde{\nu} = 683$, 832, 878, 1020, 1051, 1109, 1174, 1249, 1292, 1385, 1471, 1510, 1580, 1608, 2211, 2870, 2928, 2955 cm⁻¹; MALDI-TOF-MS: *m*/*z*: 864.4; HRMS: *m*/*z*: calcd for C₆₀H₇₈O₃ [*M*⁺]: 846.595; found: 846.594.

1,3,5-Tris(2-(4-((R)-3,7-dimethyloctyloxy)phenyl)ethynyl)benzene [(R)-1b]: Compound (R)-6b (0.20 g, 0.56 mmol), bis(triphenylphosphine)palladium(II) chloride (0.006 g, 0.008 mmol) and copper(I) iodide (0.002 mg, 0.01 mmol) were dissolved in triethylamine (3 mL). The mixture was subjected to several vacuum/argon cycles and compound 8 (0.02 g, 0.17 mmol) was added. The mixture was heated at 60 °C overnight. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, hexane/dichlorometane 8:2) affording (R)-1b as a yellow oil (0.098 g, 68%); ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 7.58$ (s, 3 H; H_a), 7.46 (d, ${}^{3}J(H,H) = 8.8$ Hz, 6H; H_b), 6.88 (d, ${}^{3}J(H,H) = 8.8 \text{ Hz}$, 6H; H_c), 4.01 (m, 6H; H_d), 1.83 (m, 3H; H_f), 1.75–1.48 (br, 9H; H_{k+e}), 1.40–1.12 (br, 18H; H_{h+i+j}), 0.96 (d, ${}^{3}J(H,H) =$ 6.4 Hz, 9H; H_o), 0.89 ppm (d, ${}^{3}J(H,H) = 6.6$ Hz, 18H; H₁); ${}^{13}C$ NMR (CDCl₃, 75 MHz, TMS): δ = 159.5, 133.4, 133.2, 124.3, 114.8, 114.6, 90.5, 86.7, 66.5, 39.3, 37.3, 36.2, 29.9, 28.0, 24.7, 22.7, 22.6, 19.7 ppm; FTIR (neat): $\tilde{\nu} = 683, 832, 878, 1020, 1051, 1109, 1174, 1249, 1292, 1385, 1471,$ 1510, 1580, 1608, 2211, 2870, 2928, 2955 cm⁻¹; HRMS: *m/z*: calcd for C₆₀H₇₈O₃ [*M*⁺]: 846.595; found: 846.594.

1,3,5-Tris(2-(4-((S)-decan-2-yloxy)phenyl)ethynyl)benzene [(S)-2]: Compound (S)-7 (0.87 g, 2.42 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.05 mmol) and copper(I) iodide (0.007 mg, 0.04 mmol) were dissolved in triethylamine (20 mL). The mixture was subjected to several vacuum/argon cycles and compound 8 (0.12 g, 0.78 mmol) was added. The mixture was heated at 60 °C for 12 h and then was allowed to reach room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, hexane/chloroform 2:1) affording (S)-2 as a brown oil (0.36 g, 55%); ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 7.60$ (s, 3H; H_a), 7.47 (d, ${}^{3}J(H,H) = 8.8 \text{ Hz}, 6\text{ H}; H_{b}), 6.88 \text{ (d, } {}^{3}J(H,H) = 8.8 \text{ Hz}; 6\text{ H}; H_{c}), 4.40 \text{ (sxt,}$ ${}^{3}J(H,H) = 6.0 \text{ Hz}, 3 \text{ H}; H_{d}), 1.82-1.30 \text{ (br, } 51 \text{ H}; H_{e+f+g+h+i+j+k+l});$ 0.91 ppm (t, ${}^{3}J(H,H) = 6.6$ Hz, 9H; H_m); ${}^{13}C$ NMR (CDCl₃, 75 MHz, TMS): $\delta = 159.0, 133.7, 133.6, 124.7, 116.1, 114.9, 90.9, 87.1, 74.4, 36.8,$ 32.3, 30.0, 29.9, 29.7, 25.9, 23.1, 20.1, 14.5 ppm; FTIR (neat): $\tilde{\nu} = 684$, 745, 832, 878, 915, 1011, 1063, 1123, 1173, 1246, 1287, 1377, 1461, 1506, 1576, 1606, 2210, 2856, 2927 cm⁻¹; HRMS: m/z: calcd. for C₆₀H₇₈O₃ [M^+]: 846.5945; found: 846.5980.

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