Reversing the Handedness of Self-Assembled Porous Molecular Networks by the Number of Identical Chiral Centres

Kazukuni Tahara,^{*,[a,b]} Aya Noguchi,^[a] Ruri Nakayama,^[b] Elke Ghijsens,^[c] Steven De Feyter,^{*,[c]} and Yoshito Tobe^{*,[a,d,e]}

Abstract: Scanning tunnelling microscope observations at the 1-phenyloctane/graphite interface reveal how chiral structural information at the molecular level is transferred and expressed structurally at the 2D supramolecular level for a porous system. Chirality of self-assembled molecular networks formed by chiral dehydrobenzo[12]annulene (cDBA) derivatives having three chiral chains and three achiral chains, alternatingly, is compared with those of cDBAs having six chiral chains reported previously. While for all cDBAs homochiral surfaces are formed, an intriguing finding is that their handedness is not simply a reflection of the absolute configuration of the stereogenic centres. Both the number of stereogenic centres as well as the length of the achiral chains determine the supramolecular handedness, providing deep insight into the supramolecular chirality induction mechanisms at play. Moreover, these cDBAs act to induce chirality in porous networks formed by achiral DBAs.

Supramolecular chirality is an area of intense interest, in solution, gels, as well as on surfaces.¹ How molecular chirality is translated into supramolecular chirality and the different hierarchical steps that are involved in such process is at the heart of many studies.² However, systematic studies addressing how efficient chiral structural information at molecular level is transferred and expressed structurally into supramolecular objects are rare, and have mainly been addressed for supramolecular fibre formation in solution.³

Surface-confined supramolecular self-assemblies, and the way their handedness is induced and amplified, generate a lot of interest, as scanning tunnelling microscopy (STM) techniques offer visualization at the nanoscale with submolecular resolution,

providing a level of detail which is hard to achieve for solution based systems.⁴ Among various systems, control and induction of chirality of two-dimensional (2D) porous molecular self-assemblies have attracted a great deal of attention.⁵

Here we show for the first time that in addition to the absolute configuration of the stereogenic centres, the number of stereogenic centres as well as other subtle structural changes define the handedness of the supramolecular networks in a non-trivial way. We focus thereby on alkoxy-substituted dehydrobenzo[12]annulene (DBA) derivatives, as many aspects defining chirality in self-assembled monolayers of both achiral and chiral DBA (cDBA) derivatives at the liquid/solid interface (Figure 1a) are well-understood.⁶

First we summarize some key features of relevance to this study. DBAs form chiral honeycomb type porous monolayer structures through van der Waals interactions of the interdigitated alkyl chains. The chirality of the DBA honeycomb networks is expressed at different structural levels. The mode of interaction of two adjacent molecules can be classified as “+ type” or “– type”, depending on the relative position of the four interdigitated alkyl chains (Figure 1c). Typically, the same type of interaction, so + or –, is repeated up to the hexamer level for the formation of the honeycomb pores. Consistent – type interdigitations lead to so-called *clockwise* (CW) pores, while + type interdigitations produce *counterclockwise* (CCW) pores (Figure 1d).⁷

The handedness of the monolayer formed by achiral DBA molecules is domain specific and overall the surface remains globally achiral.⁸ In contrast, the chirality of the DBA networks is controlled for cDBAs that comprise stereogenic centres at the 2-positions of all alkyl chains. Namely, **cDBAOC12(S)** or **cDBAOC13(R)** having six chiral OC12(S) or OC13(R) chains exclusively form CW or CCW pores because of steric interactions of the methyl groups attached to the stereogenic centres in the interdigitation pattern (Figure 1a).⁷ In each set of four interdigitated alkyl chains, two chiral methyl groups inevitably point to the graphite substrate, while the other two orient away from the substrate (Figure 2a). The energetically most favourable condition is when the facing-down methyl groups are situated in the outer alkyl chains of an interdigitated cDBA dimer and are directed towards the interior of the nanopore to avoid steric compression. This leads to the – type interdigitation pattern of **cDBAOC12(S)** forming CW pores and + type interdigitation pattern of **cDBAOC13(R)** forming CCW pores, respectively, rendering the surface globally chiral.⁹

Moreover, cDBAs also act as chiral inducers. Adding **cDBAOC12(S)** to **DBAOC12** leads to the preferential formation of CW domains, but yet the induction efficiency remains moderate, which in part is attributed to the low adsorption energy of this cDBA. Using **cDBAOC12(S)OC13(R)**, having alternating OC12(S) and OC13(R) chains, where all chiral methyl groups point away from the surface, leads to a stronger molecule-surface interaction, a more efficient co-adsorption with **cDBAOC12**, and therefore better induction by the *sergeant-soldiers* effect.⁷

[a] Prof. Dr. K. Tahara, A. Noguchi, Prof. Dr. Y. Tobe
Division of Frontier Materials Science
Graduate School of Engineering Science, Osaka University
Toyonaka, Osaka 560-8531 (Japan)
E-mail: tobe@chem.es.osaka-u.ac.jp

[b] Prof. Dr. K. Tahara, R. Nakayama
Department of Applied Chemistry
School of Science and Technology, Meiji University
1-1-1 Higashimita, Tama-ku, Kawasaki, 214-8571 (Japan)
E-mail: tahara@meiji.ac.jp

[c] Prof. Dr. S. De Feyter, Dr. E. Ghijsens
Division of Molecular Imaging and Photonics
Department of Chemistry, KU Leuven
Celestijnenlaan 200F, 3001 Leuven (Belgium)
E-mail: steven.defeyter@kuleuven.be

[d] Prof. Dr. Y. Tobe
The Institute of Scientific and Industrial Research, Osaka University
Ibaraki, Osaka 567-0047 (Japan)

[e] Prof. Dr. Y. Tobe
Department of Applied Chemistry
National Chiao Tung University
1001 Ta Hsueh Road, Hsinchu 30030 (Taiwan)
Supporting information and the ORCID identification numbers for the authors of this article can be found under:
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In order to evaluate if the number of stereogenic centres affects the extent of amplification and induction of chirality, we designed **cDBAOC12(S)OC12** and **cDBAOC12(S)OC13** with alternating chiral OC12(S) chains and achiral OC12 chains or achiral OC13 chains, respectively, with in total three chiral centers per molecule (Figure 1a). By molecular design, we expected that in contrast to **cDBAOC12(S)**, in both molecules the three chiral methyl groups would adopt the same orientation with respect to the DBA core, and when adsorbed on the graphite substrate would face away from it (Figure 2). We anticipated that this would stabilize the interaction with the surface, and potentially affect the extent of chiral amplification, or chiral induction when mixed with achiral DBAs. We show that the number of chiral groups has indeed an effect on the 2D chirality, but in a way different from hypothesized: while supramolecular handedness is controlled by the absolute configuration of the chiral centres, a change in the number of the chiral centres can lead to a reversal of the supramolecular chirality.

Figure 1. (a) Chemical structures of achiral DBAs, DBAOCns, and chiral DBAs, **cDBAOC12(S)**, **cDBAOC12(S)OC12**, **cDBAOC12(S)OC13**, and **cDBAOC12(S)OC13(R)**. (b) Chiral + and - type alkyl chain interdigitation patterns formed by achiral DBAOC12. (c) Chiral clockwise (CW) and counter-clockwise (CCW) honeycomb structures of DBAOC12. The CW and CCW hexagonal structures are formed by combining six - or + type alkyl chain interdigitation patterns.

Figure 2. Chiral clockwise (CW) and counter-clockwise (CCW) hexagonal structures of **cDBAOC12(S)** (a), **cDBAOC12(S)OC12** (b), and **cDBAOC12(S)OC13** (c). Red boxes are zoomed images of four interdigitated alkyl chains. The model under a zoomed image is a side view of the four interdigitated alkyl chains. "Up" and "down" refers to the orientation of methyl groups attached to the stereogenic centres with respect to the molecular plane (and with the substrate underneath which is not shown). In the molecular models, methyl groups on the stereogenic centres are indicated in green. C13 chains are coloured in pink. Experimentally, CCW pore is preferred for **cDBAOC12(S)OC12** and CW pore for **cDBAOC12(S)** and **cDBAOC12(S)OC13**.

Self-assembled molecular networks were prepared by dropping a solution of compound(s) in 1-phenyloctane onto the basal plane of graphite. All STM observations of the monolayers were performed at the 1-phenyloctane/graphite interface at room temperature. Total solute concentration was set to 3.0×10^{-6} M to ensure the formation of the honeycomb structures.^{6b,10} When annealing treatment was applied, a solution was poured into a liquid cell placed on the graphite substrate and this setup was annealed at 80 °C for 1 h or 3 h.

Both new cDBAs produce monolayers (Figures 3a,c). In both STM images, bright features correspond to the π -conjugated cores of DBAs, while striped features connecting the DBA cores are composed of four interdigitated alkyl chains,¹¹ revealing the formation of honeycomb structures. Moreover, the alkyl chains lie parallel to the main symmetry axes of the underlying graphite surface.

Figure 3. STM images of CCW honeycomb structures of **cDBAOC12(S)OC12** (a, b) and CW honeycomb structures of **cDBAOC12(S)OC13** (c, d) at the 1-phenyloctane/graphite interface. Blue triangles in (c) indicate *distorted pores*. White arrows in (b) and (d) indicate the orientation of the main symmetry axes $\langle 100 \rangle$ of the graphite underneath, and light blue and yellow dotted lines indicate directions of the normal $\langle 110 \rangle$ to one of the substrate's symmetry axes and one of the vectors of the unit cells, respectively. In (b, d), molecular models are superimposed. Image (b) was taken after annealing. Tunnelling parameters are $I_{\text{set}} = 200$ pA and $V_{\text{set}} = -0.20$ V for (a), $I_{\text{set}} = 110$ pA and $V_{\text{set}} = -0.30$ mV for (b), $I_{\text{set}} = 150$ pA and $V_{\text{set}} = -0.35$ V for (c), and $I_{\text{set}} = 300$ pA and $V_{\text{set}} = -0.35$ V for (d).

The chirality of each hexagonal structure, classified as *CW* pore, *CCW* pore, and *distorted pores*, was analysed. The *distorted pores* consist of a mix of + and – type interdigitation patterns within each pore.⁷ Statistical analysis of the pore chirality for the honeycomb structure of **cDBAOC12(S)OC12** gives the following distributions: *CW* pore, 4.2%; *CCW* pore, 94.3%; *other (distorted) pores*, 1.6% (Table S1). Obviously, the *CCW* pore is the dominant structural feature. In the case of **cDBAOC12(S)OC13**, the distribution of the three pore types is 85.4% for *CW* pore, 0% for *CCW* pores and 14.6% for *distorted pores*. *CW* pores are observed dominantly. Statistical analysis on the distribution of different patterns of the *distorted pores* is summarized in Figure S4. Annealing resulted in enlarged domains sizes, and the almost exclusive *CCW* pore formation for **cDBAOC12(S)OC12** and *CW* honeycomb structure for **cDBAOC12(S)OC13**, indicating these are the thermodynamically most stable phases (Table S1, Figure S1).¹² Unit cell parameters of the *CCW* honeycomb structure of **cDBAOC12(S)OC12** are $a = b = 4.5 \pm 0.1$ nm, $\gamma = 60 \pm 2^\circ$ (Figure 3b). An average angle α between the unit cell vector and a normal of graphite is $4.1 \pm 0.8^\circ$, which is consistent with that of achiral **DBAOC12**.⁸ Unit cell parameters of the *CW* honeycomb structure of **cDBAOC12(S)OC13** are $a = b = 4.5 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$ (Figure 3d). An average angle α is $4.7 \pm 1.0^\circ$. We also analysed the number of the pores having bright fuzzy features. Such bright

features are most likely due to mobile guest cDBA molecules in those pores.¹³ Respectively $9.3 \pm 1.2\%$ and $9.5 \pm 1.3\%$ of the honeycomb pores show this STM contrast feature for **cDBAOC12(S)OC12** and **cDBAOC12(S)OC13**. The absence of effect of the co-adsorbed cDBA on the chirality of the network is discussed in the Supporting Information.

These results show that by a reduction with 50% (from 6 to 3 chiral centres), homochirality can still be achieved. However, the most striking result is not the mere induction of chirality of the cDBA derivatives, but the handedness of the supramolecular structures they form, which is unexpected. Both **cDBAOC12(S)OC12** and **cDBAOC12(S)**, only differing in the number of identical chiral centres, form homochiral supramolecular structures, but of the opposite handedness. This is in contrast to self-assembly of chiral porphyrin derivatives with a varying number of stereogenic centres, in which the handedness remained the same.¹⁴ So, why does the difference in the number of chiral alkyl chains, or a difference in the length of the achiral alkyl chain, leads to a reversal in supramolecular chirality in the DBA porous system? We consider three aspects that may play a role: molecule-substrate interactions, molecule-molecule interactions, and packing density. Van der Waals interactions dominate the molecule-substrate and molecule-molecule interactions of these DBA derivatives adsorbing on graphite. Here we have to consider the orientation of the methyl groups on the chiral centres with respect to the substrate (pointing towards it or away from it), and the position of these groups in the interdigitating alkyl chains (on the outer and/or inner alkyl chains).

These considerations were used previously to explain the *CW* handedness of **cDBAOC12(S)** nanopores. For the – type interdigitation pattern of **cDBAOC12(S)**, both methyl groups on the stereogenic centres of the two middle alkyl chains of an interdigitated cDBA dimer point away from the substrate. In this way, the facing-down methyl groups are situated in the outer alkyl chains of an interdigitated cDBA dimer and are directed towards the interior of the nanopores.⁷ A situation where the methyl groups on the stereogenic centres of the two middle alkyl chains of an interdigitated cDBA dimer are facing down would cause a distortion of the alkyl chains in which some methylene units would be prevented from adopting the *anti* conformation. This would prevent optimal van der Waals interactions between the two adjacent alkyl chains, and would therefore destabilize the assembly. For **cDBAOC12(S)OC12**, we expect that all methyl groups are facing away from the graphite substrate, to optimize van der Waals interactions with the substrate (vide infra). In the preferred *CCW* pore of **cDBAOC12(S)OC12**, the achiral chains are the middle alkyl chains and the chiral alkyl chains are the outer ones. This suggests that “bulky” alkyl chains preferentially face nanopore, but this does not seem to be line with the results for **cDBAOC12(S)OC13**, that form preferentially *CW* pore, and where the achiral alkyl chains are located at the outer positions.

To gain further insight into the factors that determine chirality of these structures, we performed molecular mechanics (MM) simulations using model compounds. For the construction of one hexagonal pore, the two alkoxy chains at the DBA edge not involved in the alkyl chain interdigitation, were replaced by methoxy groups to reduce computational cost. Details on the MM simulations are in Supporting Information.

Figures 4a,b show optimized geometries of *CW* and *CCW* pores of a model compound of **cDBAOC12(S)OC12** (see also Figure S6 and Table S3). The non-bonding interactions ($E_{\text{non-bonding}}^{\text{total}}$) dominate the differences between the *CW* and the *CCW* pores, with the main contribution coming from the intermolecular interactions. As a result, the *CCW* pore is stable over the *CW* pore. These MM analyses agree the experimental observation.

Optimized geometries of the *CW* and *CCW* pores consisting of the six molecules of the model compound of **cDBAOC12(S)OC13** are shown in Figures 4c,d. Both E_{internal} and $E_{\text{non-bonding}}^{\text{total}}$ values indicate that the *CCW* pore is stable over the *CW* pore (Figure S7 and Table S3), contrary to the experimental observation. The *CW* pore is favoured by intermolecular interactions (by 7.1 kcal/mol) while molecule-substrate interactions are in favour of the *CCW* pore (by 44.0 kcal/mol). Note that the surface molecular density is different for the *CW* and *CCW* pores due to different position of the alkyl chains of unequal lengths. We estimate the unit area per hexagon as defined by connecting the six gravity centres of the triangular DBA cores in the optimized hexamer models. These are 18.2 nm² and 19.0 nm² for the *CW* and *CCW* pores, respectively. Dividing the E_{internal} and $E_{\text{non-bonding}}^{\text{total}}$ values by the respective unit area affords surface energy densities. As a result, the *CW* pore becomes favourable for the E_{internal} value and there is no difference in $E_{\text{non-bonding}}^{\text{total}}$ value. The above analyses suggest that the difference in surface density is one of the factors for the dominant formation of the *CW* structure for **cDBAOC12(S)OC13**.

Figure 4. (a, b) Optimized molecular models of *CW* (a) and *CCW* (b) pores formed by models of **cDBAOC12(S)OC12** and (c, d) *CW* (c) and *CCW* (d) pores formed by models of **cDBAOC12(S)OC13** by MM simulations. Black arrows refer to the main symmetry directions of the graphene sheets underneath.

Next, we investigated the ability of these cDBAs as chiral inducers. Supramolecular chirality induction of the honeycomb structure of achiral **DBAOC12** by the cDBAs was carried out by premixing chiral and achiral DBAs at different ratios while maintaining a total concentration of 3.0×10^{-6} M. Statistical analysis on the *CW* and *CCW* structures at different ratios of cDBA is summarized in Figure 5. In the case of

cDBAOC12(S)OC12, the fraction of the *CCW* structure increased with increasing cDBA molar ratio (Table S4). However, perfect chiral induction was not achieved even at 20 mol% of the cDBA. The degree of chirality induction is similar to **cDBAOC12(S)**,⁷ yet the induced chirality is opposite, but in line with the handedness of the nanopores formed by **cDBAOC12(S)OC12**. Chirality induction to the *CW* structure was observed for **cDBAOC12(S)OC13**. The fraction of the *CW* structure reaches $93.4 \pm 2.0\%$ at 9 mol% of cDBA, and increased gradually with increasing cDBA molar ratio. In contrast, **cDBAOC12(S)OC13(R)** showed already perfect chiral induction at 9 mol% of the cDBA, though the induction efficiency decreased for higher cDBA content.⁷

The cDBAs, **cDBAOC12(S)OC12** and **cDBAOC12(S)OC13**, form *CCW* and *CW* structures as single components respectively, and the chirality induction experiments confirm that the *sergeant-soldier* pathway prevails. For cDBAs, under favourable imaging conditions the bright DBA part is sometimes surrounded by a black rim, allowing to distinguish them from achiral DBAs. The peculiar image contrast is attributed to the methyl groups attached to the stereogenic centres.¹⁵ While this contrast feature is less pronounced than for DBAs with six chiral side chains (Figures S2,S3), visualization of these so-called “black-contour DBAs” allows for a more detailed analysis. In the first place, it shows that **cDBAOC12(S)OC12** molecules appear mostly in *CCW* domains and **cDBAOC12(S)OC13** in *CW* domains, confirming the *sergeant-soldier* effect. Furthermore, statistical analysis shows that the solution composition and surface composition are the same (Table S5).

The reason for the chirality induction to the *CCW* structures for **cDBAOC12(S)OC12** via the *sergeant-soldier* pathway is attributed to steric factors of the methyl groups attached to the stereogenic centres in the interdigitated four alkyl chains. Indeed, MM simulations of hexamer models consisting of one cDBA and five achiral DBA molecular models indicate that a *CCW* pore is stable over a *CW* pore (Figures S8a,b and Table S3). In the case of **cDBAOC12(S)OC13**, the *CW* structure is induced through preferred formation of the – type interdigitation pattern at a dimer level and also hierarchical structural recognition at a hexamer level.⁷ This is supported by MM simulations (Figures S8c,d and Table S3).

Figure 5. Chirality of the honeycomb structures of DBAs by increasing composition (mol%) of the chiral DBAs, **cDBAOC12(S)OC12** (a) and **cDBAOC12(S)OC13** (b) in a solution containing **DBAOC12**. Relative area (%) of CW pore, CCW pore and distorted hexagonal pores are coloured in blue, red, and green, respectively.

Two cDBAs, **cDBAOC12(S)OC12** and **cDBAOC12(S)OC13**, having three chiral chains were synthesized to investigate the impact of the number of chiral centres on the expression of 2D chirality at the 1-phenyloctane/graphite interface. STM observations revealed the formation of porous honeycomb structures. **cDBAOC12(S)OC12** and **cDBAOC12(S)OC13** preferentially form CCW and CW honeycomb structures, respectively, and macroscopic chirality was achieved after annealing treatment. Of particular interest is the fact that both compounds form supramolecular nanostructures of the opposite handedness, which is also the case for the compounds with three and six identical chiral groups. A small (chiral) structural variation at a single molecular level dramatically affects the chirality at a supramolecular level, the result of molecular-substrate, molecule-molecule, and molecular packing density effects. In addition, chiral induction experiments using **cDBAOC12(S)OC12** and **cDBAOC12(S)OC13** as chiral sources to influence the handedness of achiral **DBAOC12** revealed the *sergeant-soldier* effect as a main induction pathway.

A counterintuitive finding is that the number of chiral centres on the alkylated monomers has a much more dramatic impact on the handedness of the supramolecular structures, than on the extent of chiral amplification. Furthermore, the chiral molecules with three stereogenic centres are equally good chiral inducers when

mixed with achiral molecules compared to the molecules with the maximum amount of chiral centres. The effect of the chiral solvent on the chirality of self-assembled structures of the present chiral DBAs would be an interesting future topic of this study. Present study provides useful information for chirality control and induction of porous molecular self-assembled systems, thereby illustrating the different effects the number of chiral groups may have, which is of importance in the field of 2D crystal engineering.

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Conflict of interest

The authors declare no conflict of interest.

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Kazukuni Tahara,* Aya Noguchi, Ruri Nakayama, Elke Ghijsens, Steven De Feyter,* Yoshito Tobe*

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Reversing the Handedness of Self-Assembled Porous Molecular Networks by the Number of Identical Chiral Centres

Scanning tunnelling microscope observations at the liquid/graphite interface reveal chirality of self-assembled porous molecular networks formed by chiral molecules having three chiral chains and three achiral chains, alternatingly. While homochiral surfaces are formed for all chiral molecules, the number of stereogenic centres as well as the length of the achiral chains determine the supramolecular handedness.