

## Supramolecular chiral host–guest nanoarchitecture induced by the selective assembly of barbituric acid derivative enantiomers

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 *Nanotechnology* 27 42LT01

(<http://iopscience.iop.org/0957-4484/27/42/42LT01>)

[View the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 132.166.46.113

This content was downloaded on 15/09/2016 at 13:15

Please note that [terms and conditions apply](#).

You may also be interested in:

[Creating chiral architectures at metal surfaces](#)

R Raval

[A lifelong Odyssey: from structural and morphological engineering of functional solids to bio-chirogenesis and pathological crystallization](#)

Meir Lahav and Leslie Leiserowitz

[Moiré pattern induced by the electronic coupling between 1-octanol self-assembled monolayers and graphite surface](#)

Fabien Silly

[Monolayer self-assembly at liquid–solid interfaces: chirality and electronic properties of molecules at surfaces](#)

David B Amabilino, Steven De Feyter, Roberto Lazzaroni et al.

[Achieving chiral resolution in self-assembled supramolecular structures through kinetic pathways](#)

Jong Keon Yoon, Won-joon Son, Howon Kim et al.

[Transformations of Molecular Frameworks by Host–Guest Response: Novel Routes toward Two-Dimensional Self-Assembly at the Solid–Liquid Interface](#)

Luis Cardenas, Josh Lipton-Duffin and Federico Rosei

## Letter

# Supramolecular chiral host–guest nanoarchitecture induced by the selective assembly of barbituric acid derivative enantiomers

Xiaonan Sun<sup>1</sup>, Fabien Silly<sup>2</sup>, Francois Maurel<sup>1</sup> and Changzhi Dong<sup>1</sup>

<sup>1</sup> Université Paris Diderot, Sorbonne Paris Cité, ITODYS UMR CNRS 7086, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France

<sup>2</sup> TITANS, SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay F-91191 Gif sur Yvette, France

E-mail: [Sun.xiaonan@univ-paris-diderot.fr](mailto:Sun.xiaonan@univ-paris-diderot.fr)

Received 9 May 2016, revised 7 July 2016

Accepted for publication 11 July 2016

Published 13 September 2016



CrossMark

## Abstract

Barbituric acid derivatives are prochiral molecules, i.e. they are chiral upon adsorption on surfaces. Scanning tunneling microscopy reveals that barbituric acid derivatives self-assemble into a chiral guest–host supramolecular architecture at the solid–liquid interface on graphite. The host nanoarchitecture has a sophisticated wavy shape pattern and paired guest molecules are nested insides the cavities of the host structure. Each unit cell of the host structure is composed of both enantiomers with a ratio of 1:1. Furthermore, the wavy patterns of the nanoarchitecture are formed from alternative appearance of left- and right-handed chiral building blocks, which makes the network heterochiral. The functional guest–host nanoarchitecture is the result of two-dimensional chiral amplification from single enantiomers to organizational heterochiral supramolecular self-assembly.

 Online supplementary data available from [stacks.iop.org/nano/27/42LT01/mmedia](http://stacks.iop.org/nano/27/42LT01/mmedia)

Keywords: STM, 2D chirality, host–guest, enantiomers

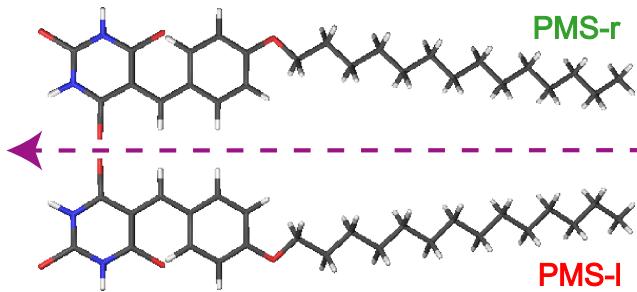
(Some figures may appear in colour only in the online journal)

## 1. Introduction

Chirality is a natural phenomenon which plays a key role in the fields of life genesis [1], enantio-selective catalysis [2], optics [3] and surface sciences [4–10]. Interest in molecular chirality started with the pioneering work of Louis Pasteur on tartaric acid [11], and his groundbreaking discovery concerning molecular symmetry.

In recent years, the study of two-dimensional (2D) chiral assemblies has been the focus of intense scientific investigations. The main scientific interest is not only concentrated on the observation and comprehension of chiral phenomena but also on the selective engineering of 2D chiral

nanoarchitectures [6, 12–16]. Molecular self-assembly opens a new route for the induction, amplification and engineering of 2D chirality. Molecular design and intermolecular interactions are play key role in chiral molecular self-assembly. Sophisticated self-assembled organic nanoarchitectures have been engineered, for example to take advantage of directional intermolecular hydrogen bonding [17–21]. Supramolecular chirality can be engineered through different methods. 2D chirality can result from the self-assembly of chiral building blocks [5, 22] as well as achiral [23, 24] and prochiral building blocks [25]. Prochiral molecules are molecules that become chiral once adsorbed on a surface. The nanoarchitecture chirality can also be tailored using a chiral modifier,



**Figure 1.** Ball and stick model of the PMS enantiomer structures. Gray, dark blue, red and white sticks represent C, N, O and H, respectively.

such as a solvent [4, 26, 27] or a surface [25, 28]. Multi-component chiral supramolecular nanoarchitectures can also be engineered by mixing a complementary chiral and achiral molecular building blocks [23, 29, 30]. Despite numerous chiral 2D organic nanoarchitectures being engineered to take advantage of the assembly of prochiral molecules, the fabrication of structures resulting from the self-assembly of the different molecular enantiomers in one single continuous domain has been rarely observed [31, 32].

In this paper we report on the self-assembly of prochiral babitric derivatives at the 1-phenyloctane/graphite interface. Scanning tunneling microscopy (STM) reveals that the molecules self-assemble into a sophisticated supramolecular chiral guest–host nanoarchitecture. The moelcular host structure appears to result from the selective arrangement of the two molecular enantiomers.

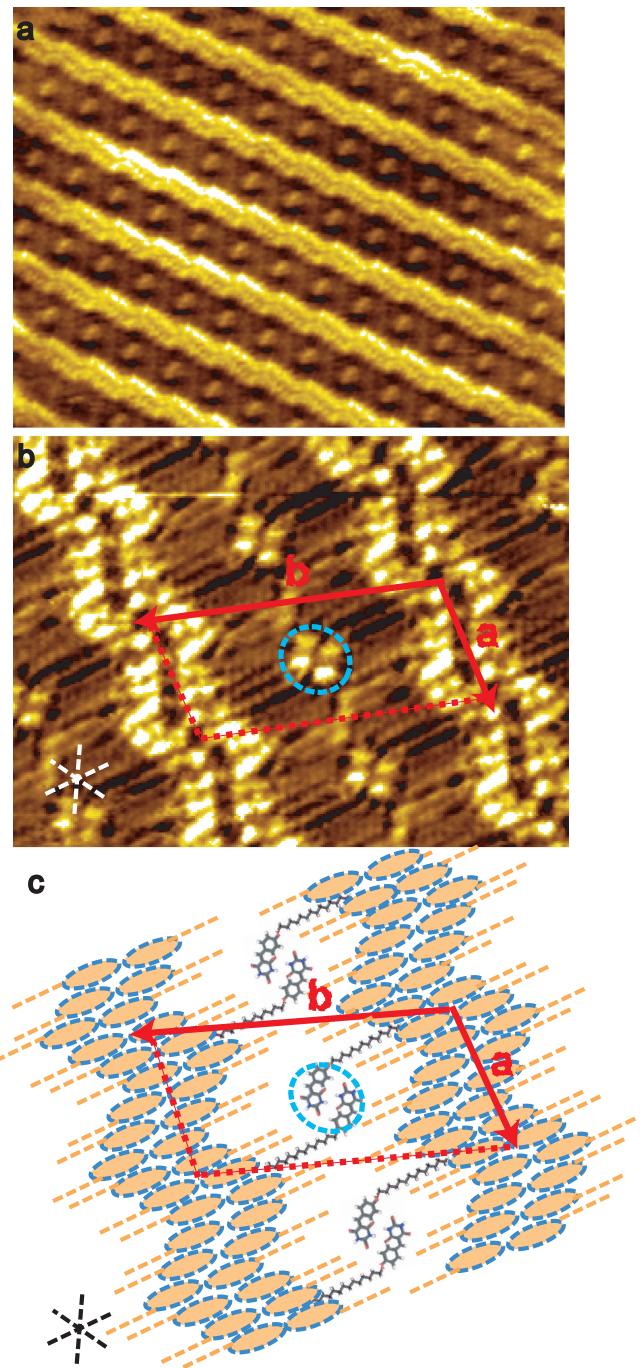
## 2. Experimental

Solutions of 5-(4-(tetradecyloxy)benzylidene)pyrimidine-2,4,6(1H,3H)trione (PMS) molecules in 1-phenyloctane (Aldrich) were prepared with a concentration around  $10^{-4}$  mol/l. A droplet of this solution was then deposited on a highly oriented pyrolytic graphite (HOPG) substrate. STM imaging of the samples is performed at the liquid–solid interface using a SPM Nanoscope III (Veeco, Bruker) scanning tunneling microscope. Cut Pt/Ir tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample. STM images were processed and analyzed using the application FabViewer [33].

## 3. Results and discussion

### 3.1. Molecule scheme

The PMS molecule has a formula of  $C_{25}H_{36}N_2O_4$ . The structure of PMS is shown in figure 1 with a stick-ball model. The molecule by itself is not planar; we draw it as planar as a guide for the eye for readers. The molecules are synthesized and the details of the synthesis are introduced in the attached supporting information. PMS is a prochiral molecule. It becomes chiral upon absorption on a surface [25]. The two



**Figure 2.** (a) Large-scale STM image of PMS molecular network.  $47 \times 36 \text{ nm}^2$ ,  $I_t = 15 \text{ pA}$ ,  $U_S = 500 \text{ mV}$ . (b) High resolution STM image,  $13 \times 10 \text{ nm}^2$ ,  $I_t = 15 \text{ pA}$ ,  $U_S = -600 \text{ mV}$ . The red parallelogram shape highlights the unit cell of the supramolecular host structure. Guest molecules are highlighted by the blue circle. (c) Organizations of the wavy architecture are shown where two hydrogen-bonded guest molecules are nested inside each of the cavities.

enantiomers are defined as PMS-I (left-handed) and PMS-r (right-handed) chiral phases, see figure 1.

### 3.2. Molecular self-assembly

The large-scale STM image in figure 2(a) shows that PMS molecules self-assemble into a sophisticated 2D architecture

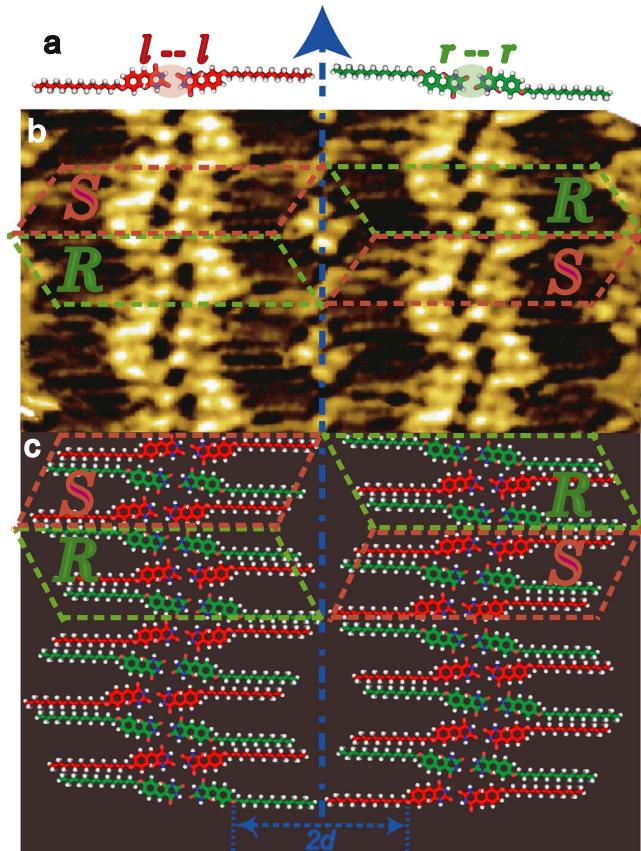
at the 1-phenyloctane/graphite interface immediately after droplet deposition at room temperature. The PMS architecture is a long range ordered network composed of parallel wavy molecular stripes. Bright spots are observed periodically between the neighboring stripes.

A high resolution STM image reveals that PMS molecules are oriented perpendicular to the molecular stripe direction, see figure 2(b). The head (benzylidene barbituric acid) [34] of the PMS molecule appears as two bright spots which are contributed by the electron DOS (density of states) from the barbituric and the phenyl rings, respectively. The molecular alkyl chain appears darker in the STM image in figure 2(b). All alkyl chains are aligned parallel along the symmetry axis of graphite substrate as shown by the white dashed lines in figure 2(b). The unit cell of the wavy supramolecular architecture has a shape of a parallelogram with 3.1 nm and 6.3 nm unit cell constants and an angle of around  $115^\circ$  between the axes. The cell is composed by 14 PMS molecules. Twelve PMS molecules are from the supramolecular wavy stripes and two molecules from the periodic bright spots nested between the wavy stripes (figures 2(b) and (c)).

The scheme in figure 2(c) represents the organization of the wavy row structure. PMS molecular heads and alkyl chains are simplified as orange ellipses and dashed lines respectively to mimic the complex supramolecular wavy patterns. PMS molecules are arranged in head-to-head fashions perpendicular to the stripe axis. The head-to-head fashion of the PMS molecules are stabilized by the formation of hydrogen bonds which will be illustrated in detail in figure 3. The molecular stripes are double row structures. The neighboring PMS double-rows have identical wavy patterns but are shifted along the direction of their main axis. They are stabilized from the van der Waals interaction of the parallel alkyl chains on the HOPG surface. The shift from the neighboring supramolecular wavy stripes leads to the periodic formation of cavities which are 1 nm in size. In between the neighboring rows, two guest molecules are nested inside each of the cavities in a side-by-side arrangement. The paired guest molecules are stabilized by N–H $\cdots$ O and C–H $\cdots$ O hydrogen bonds. The PMS supramolecular network is therefore a 2D host–guest system.

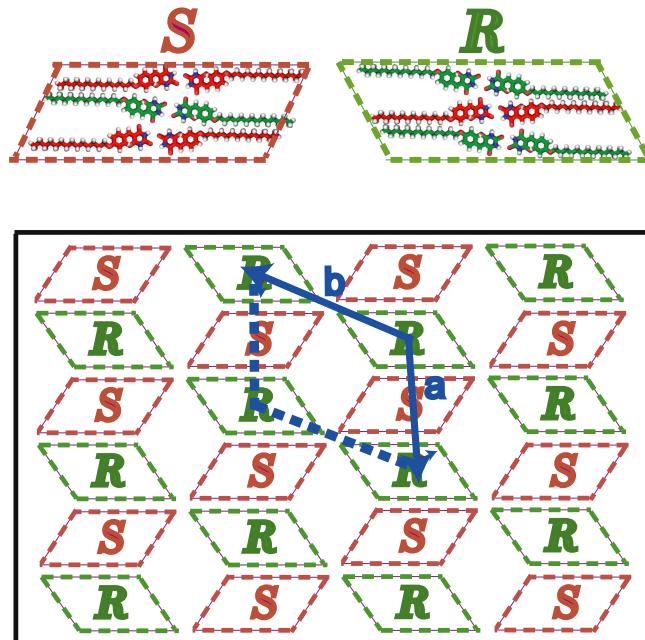
### 3.3. 2D Heterochirality

Figure 3 shows the analysis of structure symmetry from the PMS host architecture on the surfaces. Two PMS enantiomers are distinguished as red and green isomers on the surfaces due to the 2D molecular chirality, see figure 2(a). The chiral isomers form head-to-head dimers through N–H $\cdots$ O hydrogen bonds, modelled in figure 2(a). Two different dimers are formed. The red dimers (l–l dimer) are formed from two PMS-l isomers purely, whereas the green dimers (r–r dimer) are formed from two PMS-r isomers. l–l dimer and r–r dimer are chiral enantiomers on surfaces. A high resolution STM image from two neighboring wavy rows is shown in figure 3(b). The molecular model of the network structure is presented in figure 3(c). Supramolecular wavy rows are composed of both PMS l–l and r–r dimers side-by-side



**Figure 3.** (a) Chiral dimers are formed from two enantiomers where PMS-l and PMS-r isomers are shown as red and green molecules. (b) An STM image of the wavy supramolecular structure. S (left-handed) and R (right-handed) chiral building blocks are highlighted by red and green dashed parallelograms respectively. (c) A molecular model shows the wavy shape supramolecular organization from both PMS-l and PMS-r enantiomers, the distance between the two nearest molecular rows is shown with a value  $2d$ .

through N–H $\cdots$ O and C–H $\cdots$ O hydrogen bonds. Comparing the neighboring wavy rows, each red (green) dimer is facing an opposite chiral green (red) dimer horizontally. Two chiral blocks are highlighted between the two neighboring supramolecules by the red and green dashed lines, see figures 3(b) and (c). The red block is composed of four PMS-l and two PMS-r enantiomers and has a left-handed diamond shape. The PMS-l/PMS-r ratio is 2:1 and it is a left-handed (S) chiral block. The green block is composed of two PMS-l and four PMS-r enantiomers and has a right-handed diamond shape. The PMS-l/PMS-r ratio is 1:2 and it is a right-handed (R) block, see figure 3(c). The S and R building blocks are therefore enantiomeric pairs, see figure 3(a). The supramolecular wavy structures are composed of a periodic alternation of R and S blocks along the row axis. Neighboring wavy rows are shifted along the row axes with one building block length, see figure 2. Each of the S(R) building blocks are organized close to an opposite R(S) building blocks along or perpendicular to the row axes. PMS rows are composed of building blocks with a RS organization. Neither an SS nor RR sequence is observed. The supramolecular wavy network is a



**Figure 4.** Heterochiral organization from the PMS supramolecular architecture is presented by S and R building blocks. The unit cell of the supramolecular structure is superimposed on the building block organization (blue dashed parallelogram).

2D heterochiral structure. The PMS-l to PMS-r ratio is 1:1 for the 2D network.

In this structure the alkyl chains of all PMS molecules are parallel to each other. The organization of the alkyl chains is not homogeneous due to the alternative appearance of the two enantiomers. PMS molecules are stabilized by van de Waals interactions from the alkyl chains between the neighboring rows. The nearest tail-by-tail distance between the neighboring wavy-row is around 3.3 nm (figure 2(c)). This value is twice the length of C<sub>14</sub>H<sub>29</sub> alkyl chains ( $2d = 3.3$  nm). There is therefore no intercrossing between alkyl chains from neighboring PMS molecular rows.

PMS is a prochiral molecule. It becomes chiral upon adsorption on surface because of the adsorption-induced symmetry loss. PMS-l (left) and PMS-r (right), figure 1, are the two molecular PMS enantiomers with a 2D mirror symmetry on surfaces. Two isomers from the same chiral phase (l+l or r+r) form chiral left or right dimers. These dimers self-assembled into enantiomeric building blocks S and R, presented in figure 4. The organic wavy lines observed in figure 2 result from the sequential succession of R and S chiral blocks. The unit cell of the wavy network is superimposed to the building blocks organization, see the blue parallelogram in figure 4. Each unit cell is composed of one S plus one R building block. This means that the PMS-l to PMS-r ratio is 1:1 among the supramolecular wavy networks. That verifies the equal probability of PMS molecule to adsorb in the r or l configuration. The supramolecular wavy host is organized from the building blocks in a SR sequence on 2D surfaces, see figure 4. It therefore has an organizational 2D heterochirality. The wavy supramolecular network is an enantiomeric-mixed structure and is racemic. The

supramolecular wavy-structure and its 2D heterochirality are the results of 2D chiral self-assembly from single chiral molecule.

#### 4. Conclusion

To summarize, we investigated the self-assembly of the pochiral PMS molecules on graphite at the solid–liquid interface using scanning tunneling microscopy. Molecules self-assemble into a wavy-shape guest–host structure from both of the enantiomers. The wavy double-row host structure has an organizational 2D heterochirality. The heterochirality is transferred from single chiral molecules to 2D networks through chiral self-organization. Paired guest molecules are trapped periodically in the host wavy structures. The supramolecular organization of the network reveals that this nanoarchitecture is enantiomeric-mixed and is racemic. Our results show molecular self-assembly can be used to fabricate functional chiral guest–host nanoarchitectures through chiral induction and amplification. These observations contribute in improving the controllability, predictability, and stability of chiral nanoarchitectures at the molecular scale.

#### Acknowledgments

The research leading to these results has received funding from the European Research Council under the European Union’s Seventh Framework Programme (FP7/2007-2013)/ERC grant agreement No. 259297. The authors thank the CNRS, the Université Paris Diderot for financial support.

#### References

- [1] Bailey J, Chrysostomou A, Hough J H, Gledhill T M, McCall A, Clark S, Menard F and Tamura M 1998 Circular polarization in star-formation regions: Implications for biomolecular homochirality *Science* **281** 672–4
- [2] Hoen R, Boogers J A F, Bernsmann H, Minnaard A J, Meetsma A, Tiemersma-Wegman T D, De Vries A H M, De Vries J G and Feringa B L 2005 Achiral ligands dramatically enhance rate and enantioselectivity in the rh/phosphoramidite-catalyzed hydrogenation of -disubstituted unsaturated acids *Angew. Chem. Int. Ed.* **44** 4209–12
- [3] Ogoishi T, Yamafuji D, Akutsu T, Naito M and Yamagishi T 2013 Achiral guest-induced chiroptical changes of a planar-chiral pillar[5]arene containing one-conjugated unit *Chem. Commun.* **49** 8782
- [4] Chen T, Yang W-H, Wang D and Wan L-J 2013 Globally homochiral assembly of two-dimensional molecular networks triggered by co-absorbers *Nat. Commun.* **4** 1389
- [5] Fasel R, Parschau M and Ernst K-H 2006 Amplification of chirality in two-dimensional enantiomorphous lattices *Nature* **439** 449–52
- [6] Tahara K, Yamaga H, Ghijssens E, Inukai K, Adisoejoso J, Blunt M O, De Feyter S and Tobe Y 2011 Control and induction of surface-confined homochiral porous molecular networks *Nat. Chem.* **3** 714–9

- [7] Barlow S M and Raval R 2003 Complex organic molecules at metal surfaces: bonding, organisation and chirality *Surf. Sci. Rep.* **50** 201–341
- [8] Pawin G 2006 A homomolecular porous network at a Cu(111) surface *Science* **313** 961–2
- [9] Rivera J M, Craig S L, Martín T and Rebek J J 2000 Chiral guests and their ghosts in reversibly assembled hosts *Angew. Chem. Int. Ed.* **39** 2130–2
- [10] Raval R 2009 Chiral expression from molecular assemblies at metal surfaces: insights from surface science techniques *Chem. Soc. Rev.* **38** 707
- [11] Pasteur L 1905 Researches on the molecular asymmetry of natural organic products *Alembic Club Reprints* **14** 1–46
- [12] Elemans J A A W, De Cat I, Xu H and De Feyter S 2009 Two-dimensional chirality at liquid-solid interfaces *Chem. Soc. Rev.* **38** 722
- [13] Xu H, Wolfs M, Tomović Z, Meijer E W, Schenning A P H J and De Feyter S 2011 A multivalent hexapod having 24 stereogenic centers: chirality and conformational dynamics in homochiral and heterochiral systems *Cryst. Eng. Commun.* **13** 5584
- [14] Gutzler R, Ivasenko O, Fu C, Brusso J L, Rosei F and Perepichka D F 2011 Halogen bonds as stabilizing interactions in a chiral self-assembled molecular monolayer *Chem. Commun.* **47** 9453
- [15] Kühne D, Klappenberger F, Decker R, Schlickum U, Brune H, Klyatskaya S, Ruben M and Barth J V 2009 Self-assembly of nanoporous chiral networks with varying symmetry from sexiphenyl-dicarbonitrile on Ag(111) *J. Phys. Chem. C* **113** 17851–9
- [16] Robin A, Iavicoli P, Wurst K, Dyer M S, Haq S, Amabilino D B and Raval R A 2010 Racemic conglomerate nipped in the bud: a molecular view of enantiomer cross-inhibition of conglomerate nucleation at a surface *Cryst. Growth Des.* **10** 4516–25
- [17] Ouchi H, Lin X, Kizaki T, Prabhu D D, Silly F, Kajitani T, Fukushima T, Nakayama K and Yagai S 2016 Hydrogen-bonded oligothiophene rosettes with a benzodithiophene terminal unit: self-assembly and application to bulk heterojunction solar cells *Chem. Commun.* **52** 7874–7
- [18] Silly F 2012 Two-dimensional 1,3,5-tris(4-carboxyphenyl)benzene self-assembly at the 1-phenyloctane/graphite interface revisited *J. Phys. Chem. C* **116** 10029–32
- [19] Viciana-Chumillas M, Hieulle J, Mallah T and Silly F 2012 Compact hydrogen-bonded self-assembly of ni(ii)-salen derivative investigated using scanning tunneling microscopy *J. Phys. Chem. C* **116** 23404–7
- [20] Silly F, Kervella Y and Jousselme B 2015 Engineering porous and compact two-dimensional nanoarchitectures on surfaces taking advantage of bisterpyridine-derivatives self-assembly *RSC Adv.* **5** 101740–4
- [21] Mura M and Silly F 2015 Experimental and theoretical analysis of hydrogen bonding in two-dimensional chiral 4,4-(1,4-phenylene)bis(2,2:6,2-terpyridine) self-assembled nanoarchitecture *J. Phys. Chem. C* **119** 27125–30
- [22] Haq S, Liu N, Humblot V, Jansen A P J and Raval R 2009 Drastic symmetry breaking in supramolecular organization of enantiomerically unbalanced monolayers at surfaces *Nat. Chem.* **1** 409–14
- [23] De Cat I, Guo Z, George S J, Meijer E W, Schenning A P H J and De Feyter S 2012 Induction of chirality in an achiral monolayer at the liquid/solid interface by a supramolecular chiral auxiliary *J. Am. Chem. Soc.* **134** 3171–7
- [24] Prins L J, Jong F D, Timmerman P and Reinhoudt D N 2000 An enantiomerically pure hydrogen-bonded assembly *Nature* **408** 181–4
- [25] Karan S, Wang Y, Robles R, Lorente N and Berndt R 2013 Surface-supported supramolecular pentamers *J. Am. Chem. Soc.* **135** 14004–7
- [26] Silly F 2013 Selecting two-dimensional halogen-halogen bonded self-assembled 1,3,5-tris(4-iodophenyl)benzene porous nanoarchitectures at the solid-liquid interface *J. Phys. Chem. C* **117** 20244–9
- [27] Guo Z *et al* 2011 Nucleoside-assisted self-assembly of oligo(*p*-phenylenevinylene)s at liquid/solid interface: Chirality and nanostructures *J. Am. Chem. Soc.* **133** 17764–71
- [28] Shchyrba A *et al* 2013 Chirality transfer in 1d self-assemblies: Influence of H-bonding versus metal coordination between dicyano[7]helicene enantiomers *J. Am. Chem. Soc.* **135** 15270–3
- [29] Qian P, Nanjo H, Yokoyama T, Suzuki T M, Akasaka K and Orhui H 2000 Chiral molecular patterns of self-assembled ion pairs composed of (r, s), (s)-16-methyloctadecanoic acid and 4,4-bipyridine *Chem. Commun.* **2000** 2021–2
- [30] Zeng X, Chang S, Deng K, Zhang J, Sun H, Zeng Q and Xie J 2015 Synthesis and Molecular Structures of BINOL Complexes: An STM Investigation of 2d Self-Assembly *Cryst. Growth Des.* **15** 3096–100
- [31] Böhringer M, Schneider W-D and Berndt R 2000 Real space observation of a chiral phase transition in a two-dimensional organic layer *Angew. Chem. Int. Ed.* **39** 792–5
- [32] Yang B, Wang Y, Cun H, Du S, Xu M, Wang Y, Ernst K-H and Gao H-J 2010 Direct observation of enantiospecific substitution in a two-dimensional chiral phase transition *J. Am. Chem. Soc.* **132** 10440–4
- [33] Silly F 2009 A robust method for processing scanning probe microscopy images and determining nanoobject position and dimensions *J. Microsc-Oxford* **236** 211–8
- [34] Schmidt M U *et al* 2011 The thermodynamically stable form of solid barbituric acid: The enol tautomer *Angew. Chem. Int. Ed.* **50** 7924–6