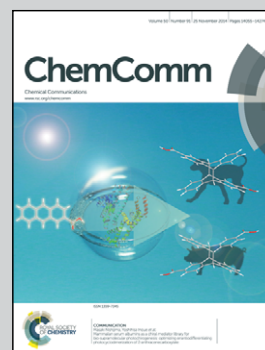


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Biaxial aromatics with face-on/edge-on stacking adaptability: an STM/STS study of 1D nanowires assembled *via* rotatable ethynyls

The dual roles of face-on and edge-on orientations in one molecule are tailored by incorporating rotatable ethynyl linkers to the benzene core. The face-on moieties stabilise the monolayer *via* conformal contact with the substrate while the edge-on biphenyls furnish π - π stacking with neighbouring molecules and build an extended conjugated array.

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Biaxial aromatics with face-on/edge-on stacking adaptability: an STM/STS study of 1D nanowires assembled *via* rotatable ethynyls†

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Scanning tunnelling microscopy/spectroscopy reveals significant electronic communications between edge-on biphenyl moieties of a benzene core derivatised biaxially with four ethynyl-biphenyls. The key to the successful assembly of conjugated 1D nanowires is the rotatable features of ethynyls, which allow dual adaptability of edge-on and face-on orientations for the aromatic rings.

In the past decade, there has been burgeoning interest in exploring the versatile electron-transfer behaviour of organic semiconductors, largely composed of conjugated polyaromatics.^{1–5} One of the goals is the development of efficient electronic devices. The orientation of molecular stacking, particularly for polyaromatics in devices, plays an important role in the charge-transport processes.⁶ Face-on and edge-on orientations are two distinct arrangements in an assembly where the columnar axes are parallel and perpendicular to the plane of a substrate, respectively.⁶ It is proposed that the face-to-face molecular orientation in a column-type packing parallel to a pair of measurement electrodes may enable coherent electronic transport *via* their vertically overlapped π -orbitals.^{5–7} Molecules with large π -conjugated, planar and rigid structures are thus ideal in this regard. However, such molecules usually exhibit strong molecule–substrate attractions, thereby resulting in adsorption on a surface with a lying-down orientation perpendicular to the pair of measurement electrodes.^{8–11} This hampers charge transport in devices, for instance, field-effect transistors (FETs).⁵

The aforementioned obstruction can be overcome by the utilisation of molecular alignment techniques.^{12,13} We previously

demonstrated that a facile flow treatment can easily align a variety of π -conjugated polyaromatics, which would otherwise adopt a face-on orientation, to pack in an edge-on fashion on HOPG (highly oriented pyrolytic graphite).¹⁴ Besides the spontaneous assembly, rationally designed molecules can also self-assemble with edge-on orientation on surfaces. For example, unsubstituted dibenzo[*g,p*]chrysene¹⁵ and amide-substituted tetrathiafulvalene¹⁶ can stack on HOPG with tilted orientation *via* strong intermolecular interactions. STS (scanning tunnelling spectroscopy) can reveal the interactions arising from π -electron coupling between molecules in the assemblies.^{16–18} While rare in examples, it is also possible to visualise intra- or intermolecular interactions by SPM (scanning probe microscopy). For instance, images of hydrogen bonds in an 8-hydroxyquinoline molecule were captured by AFM (atomic force microscopy).¹⁹ Lateral intermolecular electronic coupling was also found by STM (scanning tunnelling microscopy) in a PTCDI (3,4,9,10-perylene-tetracarboxylic diimide) layer after annealing.²⁰

Examples of intermolecular electronic coupling arising from rotation of the molecular skeleton in an assembly remain virtually unexplored. Only very recently, by utilising STM *dI/dV* mapping Simon *et al.* demonstrated that self-assembly of conjugated oligomers of 2,5-dialkoxy-phenylene-thiénylenes can generate 1D charge-transport pathways achieved mainly *via* the head-to-tail stacking of the neighbouring terminal thiophene rings.²¹

Herein, with a molecular building block of a benzene core biaxially derivatised with four ethynyl-biphenyls (**1**, in Scheme 1),²² we report a novel assembly by taking advantage of the rotating feature of the ethynyl linkers which allow the biphenyls to adopt both face-on and edge-on orientations. Stable assemblies form spontaneously on HOPG because the central portion of **1** adopts a face-on orientation that yields strong molecule–substrate interactions. In addition, the edge-on configurations develop electronic coupling between the π -stacked biphenyls. The electrons can effectively communicate between biphenyl moieties and thus delocalise within an array of one-dimensional (1D) nanowires.

Panel a of Fig. 1 displays a typical STM image of **1** assembled in hexadecane (0.32 mM **1**). The bright and relatively dim features are attributed, respectively, to the conjugated moieties

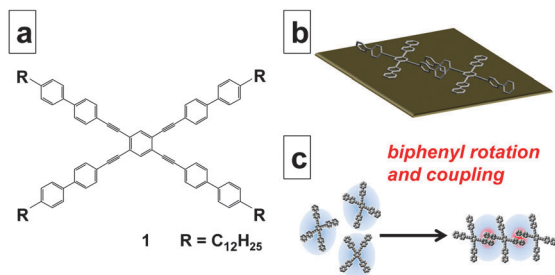
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† Electronic supplementary information (ESI) available: Synthesis of **1**, experimental details, and additional images. See DOI: 10.1039/c4cc02704c

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Scheme 1 (a) Structure of 1,2,4,5-tetrakis-(4-dodecyl-4'-ethynyl-biphenyl)benzene (**1**) and (b and c) sketches to illustrate the rotatable ethynyls enabling biphenyl stacking in an assembly.

and alkyl chains based on the molecular structure and the expected degree of tunnelling conductance. The bright features are discontinuous along the direction vertical to the image frame, yet appear to be conformally stacked in the other molecular axis and organise into 1D wires. Note that the concept of tailored assembly is realised because the aromatics in one of the axes adopt the face-on orientation to stabilise the adsorption and the terminal biphenyls of the other axis take the edge-on position. The detailed analysis of the structures and stacking properties are described in the next paragraphs.

To manifest the intermolecular interactions within the linear chains, presented in Fig. 1b a mesh-like assembly is prepared at a 100-fold lower concentration (3.2 μM) which yields inferior contacts between molecules. To be succinct, the structures are henceforth termed linear and mesh. The two polymorphs are very stable at the corresponding concentration. To show the long-range order of the assemblies, images with scan sizes up to 100 nm are shown (Fig. S1, ESI[†]). Fig. 1c and d show high resolution images in which the methylene units are discernible. It is, however, not easy to distinguish hexadecane solvent from dodecyl sidechains of **1** due to their similarity in tunnelling conductance and topographical appearance. Thus, only those that appeared to be “unconnected” to the phenyl termini are referred as solvent molecules, indicated by blue arrows and molecular models in Fig. 1c–f. The linear motif has one coadsorbed solvent molecule per unit area bound by four adjacent **1**, one molecule less than that of the mesh-like assembly. To correlate the lattice vectors of the assembly with respect to those of the underlying HOPG, the latter (white arrows in Fig. 1c and d) are determined by imaging with a smaller bias at a larger tunnelling current. The co-assembled solvent molecules and alkyl chains of **1** are found to be aligned in parallel with one of the main symmetry axes. The commensurate structure maximises the adsorbate–substrate attractions and optimises the assembly. In the mesh motif (right panels), there are two mesh sizes. The larger one contains 2 hexadecane and 4 dodecyl chains which are uniaxially commensurated with the HOPG substrate. Incommensuration is found for the smaller one with 2 hexadecane and 2 dodecyl chains which appear to be less defined than those in larger meshes. The packing density of the linear motif is 0.27 $1/\text{nm}^2$, only slightly denser than that of the mesh (0.23 $1/\text{nm}^2$). The intriguing similarity in packing densities found from concentrations, which differed by two

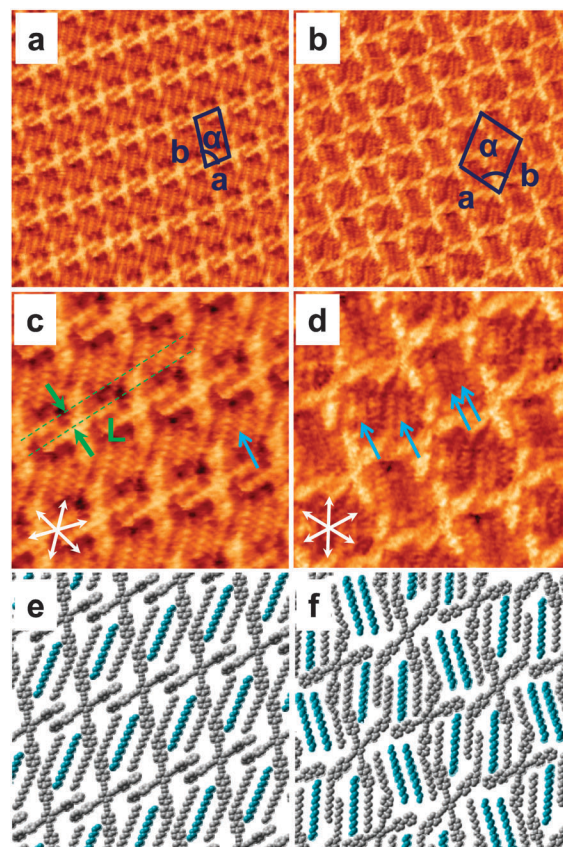


Fig. 1 STM images and proposed packing models for (left panel) linear and (right panel) mesh-like assemblies of **1** at the respective concentrations of 0.32 mM and 3.2 μM in hexadecane. Panels e and f show illustration to facilitate the visualisation of **1** in the images. Solvent molecules are pointed by the blue arrows in the images and are blue-coloured in the illustrations. The green marks in (c) define L of 0.44 (± 0.03) nm for the neighbouring spacing of the edge-on biphenyls. A tilt angle of 37° from the surface normal will render an ideal π - π stacking distance of 0.35 nm between the planes of benzene rings. Imaging conditions: E_{bias} , -0.85 V; $i_{\text{tunnelling}}$, 50 pA; frame size: (a,b), 16×16 nm^2 ; (c,d), 6.7×6.7 nm^2 . Unit cell parameters of $|\vec{a}|$, $|\vec{b}|$, and α : (a) linear, 1.5 (± 0.2) nm, 2.5 (± 0.3) nm, 87° ($\pm 2^\circ$); (b) mesh, 2.7 (± 0.2) nm, 3.3 (± 0.2) nm, 83° ($\pm 2^\circ$). White arrows: the 3-fold symmetry of the underlying HOPG.

orders of magnitude is ascribed to the participation of the co-adsorbed solvent molecules.

For alkyl derivatised aromatics, it is often reported that some of the alkyl side arms float in solution.^{23–26} The same is true for **1** although all derivatised alkyls adsorbed on the substrate would presumably gain the most of the adsorbate–substrate interactions.²⁷ Furthermore, an interesting correlation is noticed that biphenyls of **1** likely lie on the surface if the tagged alkyl arms adsorb on the surface while the biphenyls develop the edge-on configuration for those with terminal alkyls unobserved in STM images. To confirm this finding, section-profile analyses are employed. Fig. 2a presents a cutaway view corresponding to the red line in the image. The profile unveils an apparent height difference of *ca.* 0.20 nm between the edge-on and face-on biphenyls of **1**. The discrepancy is attributable to biphenyl rotations, suggesting that the interactions between edge-on biphenyls are more favourable and thus stronger than that of

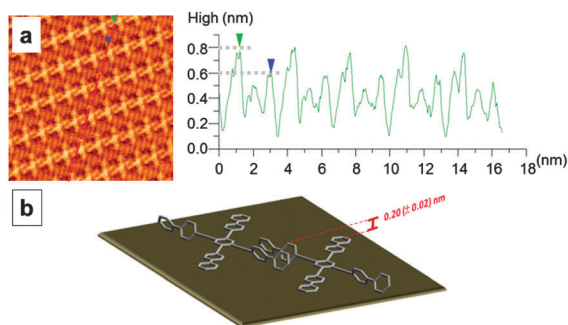


Fig. 2 Section-profile analyses of the topography of the linear motif of **1**. (a) An STM image of the linear structure and its cutaway view of the red line. The apparent height of the edge-on configuration (green triangle) appears ca. 0.20 nm higher than that of the face-on biphenyls (blue triangle). (b) Illustration of the apparent height difference between the edge-on and face-on biphenyls.

conformal contact of the phenyls on HOPG. In contrast, the mesh-like structure exhibits no significant difference in height between biphenyls (Fig. S2, ESI[†]), consistent with the proposed model of uniform face-on biphenyls.

In general, face-on molecules exhibit a tunnelling efficiency superior to those with the edge-on orientation because the former adopts conformal contact with the substrate and yields a stronger electron coupling.²⁸ The opposite is true for the assemblies of **1**. Therefore, the interactions between the stacked biphenyls are further looked into. STS, among very limited methods that can unravel the effect of the electronic coupling between stacked aromatics at the molecular level, is applied to study the edge-on configuration of the biphenyls. Raw and averaged data of STS spectra are provided, respectively, in Fig. S3 (ESI[†]) and Fig. 3 where panels a and b show the molecules from which the spectra were acquired. The *I*-*V* traces for both structures are asymmetric. The current and thus the tunnelling conductance are larger at the negative bias, suggesting that electron tunnelling through the HOMO of **1** is more facile than through the LUMO.^{18,29} Most importantly, the asymmetric feature is more significant for the linear motif (red curve) than the mesh one (blue), resulting in a larger tunnelling current and a smaller turn-on voltage for the former. This is consistent with the model of Davydov splitting³⁰ in which the degenerate energy levels of crystalline or aggregated molecules split such that the HOMO/LUMO gap becomes narrower. The split energy levels develop a pronounced shift of the HOMO edge toward the Fermi level of

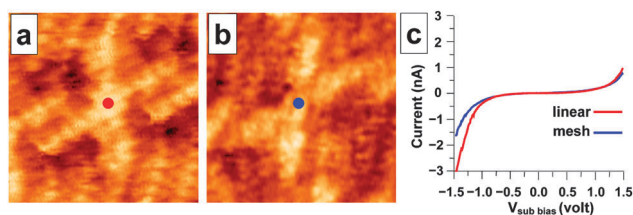


Fig. 3 STM images of the (a) linear and (b) mesh-like assemblies and (c) the corresponding STS spectra. The spectra were averaged from 3 sets of experiments acquired over the positions of red and blue dots indicated in panels a and b. Imaging conditions for (a and b): $E_{\text{bias}} = -0.75$ V; $i_{\text{tunnelling}} = 100$ pA; imaging size, 2.8×2.8 nm².

electrodes and, therefore, lower the turn-on voltage of the *I*-*V* curve.³¹ Note that, for the effect of Davydov splitting to take place, substantial interactions between the edge-on biphenyls is required. Thus, the edge-on stacked biphenyls provide a pathway for electron delocalisation along the linear assembly.

In conclusion, this study demonstrates that the incorporation of rotatable ethynyl linkers allows the aromatic moieties of conjugated molecules to adopt both face-on and edge-on orientations. For the model compound **1**, the tactic of molecular self-assembly yields stable arrays of 1D nanowires. The face-on conformation maximises the adsorbate-substrate interactions and stabilises the assembly. STM shows that the edge-on arrangement offers opportunities to develop building blocks for extended 1D assemblies. A significant finding unveiled by STS is that efficient communications between edge-on configured aromatics can be conveyed by moieties as small as biphenyls. With strong intermolecular interactions, the electron transport pathway within such structures involves “through space” π - π interactions and through covalent bonding, suggesting that the fabrication of conductive wires for future molecular electronics could be realised *via* the approach of molecular self-assembly.

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