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Synthesis and Solid-State Investigations of Oligo-Phenylene–Ethynylene **Structures with Halide End-Groups**

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In the field of material science functionalization of substrate surfaces (e.g. metal, graphite) with organic molecules is of increasing interest. Desirable targets are molecules with functional groups providing for two-dimensional assembly and three-dimensional crystal growth. We have synthesized a series of halogen-end-capped oligo-phenylene-ethynylenes (OPEs) to study the interactions at the solid/liquid interface and in crystal structures. Organohalides can be involved in a wide variety of intermolecular interactions such as C-X···H, C–X···X–C and C–X··· π -orbitals. The range of halogenbased interactions and the diversity of intermolecular forces along different crystal axes makes the investigation of such

Introduction

In the field of material science the functionalization of metal and graphite surfaces with organic molecules is of increasing interest. Being able to control the electrochemical and physical properties of surfaces such as conductivity, resistance and hydrophilic or hydrophobic properties has made many new applications possible.^[1,2] To alter the properties of an entire surface homogenously the molecules must be arranged in a periodic manner. The easiest way to achieve this is by solution deposition of molecules able to control their orientation with respect to their neighbors. This self-assembly process depends on intermolecular interactions including hydrogen bonding,^[3] hydrogen-halogen or halogen---halogen interactions,[4] Van-der-Waals interactions^[5] and dipole---dipole (molecule---substrate) interac-

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structures particular interesting and challenging. Here we probe the interplay of halide end-groups and the backbone of an OPE to investigate the intermolecular interactions in both solution depositions (2D) and X-ray crystal structures (3D). The STM images and the crystal structures of each OPE reveal striking packing similarities. For each molecule, a plane in the crystal structure with an arrangement of molecules resembling its two-dimensional packing on a flat surface was found. These results support the hypothesis of sheet-by-sheet crystal growth and suggest that flat surfaces would be ideal interfaces to promote crystal growth for halide-end-capped OPEs.

tions.^[6] The self-assembly of organic molecules at the solid/ liquid interface leads to large organized molecular patterns on surfaces. These laterally controlled supramolecular architectures can provide surface properties useful for bottom-up synthetic strategies.^[7] Of particular interest are selfassembled systems yielding porous networks that provide well-defined two-dimensional patterns as templates for functional guests.^[8-13] We previously reported on the selfassembly of fluorinated rods^[14] and branched fluorinated stars^[15] where the fluorine-hydrogen as well as moleculesubstrate interactions dictated the assembly of a lateral network. Inspired by these large-area self-assembled patterns we became interested in the organizing power of halide…hydrogen interactions. To explore the influence of various halides for lateral self-assembly on a flat substrate and for three-dimensional arrangement in single crystals, we designed molecular rods 1-3 (Figure 1). These rods consist of flat and rigid OPE backbones that favor molecule ... substrate interactions.[14,16] Terminal halides groups (Cl, Br and I) are expected to direct the lateral assembly by a wide variety of intermolecular interactions^[4,17,18] such as C-X···H, C-X···X-C and C-X···π-orbital. The differences in electrostatic potentials and size of the halides are expected to vary the strength of the intermolecular interactions and might be reflected in the resulting self-assembled structures. Because halides have both positive and negative electrostatic potentials, they can be attracted by other negative halides (or π -orbitals) or electro-





Figure 1. The model compounds were assembled at the solid/liquid interface and crystallized. The lateral arrangement of the molecules at the surface and in "sheets" in the solid-state structure were investigated.

positive hydrogen atoms.^[4,17,19] Two hexyl substituents on the central phenyl units of the OPE rods enable the processability of the molecular building blocks. These alkyl substituents are expected to reduce the molecular density of the rod on the substrate but should be small enough to allow tight molecular packing directed by the terminal halogens. The spontaneous formation of laterally ordered flat sheets of densely packed molecules is of particular interest as a potential motif for a tightly packed 3D molecular assembly. The stacking of such sheets might result in a crystal-like 3D order providing a perfect interface between a flat substrate material and the molecules' crystalline state.

In the field of crystal engineering various intermolecular interactions have been studied extensively.^[20] Strong and directional hydrogen bonds (e.g. O-H···O or N-H···O) have been investigated in detail.^[21] Of particular interest are halogen bonds because of the two-fold role of the halogen atom. On one hand the halide substituent can interact with a lone-pair provided by a heteroatom in proximity and act as the hydrogen does in a hydrogen bond;^[22] and on the other hand the halide can provide lone-pairs for electron deficient atoms of neighboring molecules. Consequently, various interactions (e.g. C-X···X-C and C-X···Y-C) can be observed with halogen substituents.^[23,24,25] This diversity of possible interactions increases the complexity in controlling the crystal growth by the molecules' design. In a crystal engineering approach the strength of intermolecular interactions is tuned by controlling the spatial arrangement of various substituents by the molecules' backbone structure.^[26,27] A major design challenge in engineering crystals comprising exclusively organic molecules is that molecules with functional groups pointing in all three dimensions are required.^[28] Variation of modular functionalities along one axis and, at the same time, maintaining equally weak intermolecular interactions in all three directions in the crystal is a very difficult task. Alternative organic building blocks are aromatic structures.^[29,30] Two-dimensional structural control is easily achieved in the planes of the aromatic rings whereas the packing of the sheets in the third dimension is less controlled. The aromatic rings impart some interactions of their own (π ··· π , C–H···O) which may contribute to ordered staples. However, such crystals differ considerably in the strength of the interactions of molecules within and between the sheets. The combination of the diversities of halogen-based interactions and of the intermolecular forces along different crystal axes makes crystal engineering with such structures particular interesting and challenging.

Here we systematically investigate halide-based interactions by comparing the self-assembly of terminally halogensubstituted OPE rods 1–3 at the solid-liquid interface (2D) and in a single crystal (3D), and examine the extent of similarity of the patterns obtained by intermolecular interactions.

Results and Discussion

The OPE target structures consist of a π -conjugated backbone and either chlorine, bromine or iodine endgroups. The target structures were synthesized by either a convergent or divergent approach.^[31] Attempts to synthesize these structures directly failed (Scheme 1) owing to polymerization, homo-coupling and poor solubility of the target structures. Hexyl chains were introduced to the central unit of the OPE structure to increase the solubility and processability of the target structures.

The assembly of dichloro-OPE 1 and dibromo-OPE 2 is shown in Scheme 2. Both rods were assembled by using a

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Scheme 1. One-step synthetic strategy to terminally halogen-functionalized OPE rods.

pseudo-high-dilution strategy profiting from the increased reactivity of aryl iodides in Sonogashira coupling chemistry.^[32] 1,4-Diiodo-2,5-dihexylbenzene (4) was synthesized following a literature procedure.^[33] With building block 4 and the commercially available compounds (4-chlorophenylethynyl)trimethylsilane (5) and (4-bromophenylethynyl)trimethylsilane (6) in hand, assembly of target structures 1 and 2 was achieved through Sonogashira cross-coupling reactions (Scheme 2). An in situ deprotection method^[32] was chosen to minimize the amount of free acetylene in the reaction mixture and prevent homocoupling. 1,8-Diazabi-



Scheme 2. Synthesis of dichloro-OPE 1 and dibromo-OPE 2.

cyclo[5.4.0]undec-7-ene, as a non-nucleophilic base and small traces of water were used to slowly deprotect the TMS-acetylenes **5** and **6**. The low concentration of free acetylene favored its reaction with the Pd-activated aryl iodide and provided the desired rods **1** and **2** in reasonable yields. Dichloro-OPE **1** and dibromo-OPE **2** were isolated in 65 and 73% yield, respectively.

For the synthesis of diiodo-OPE derivative **3** various different strategies were explored (Scheme 3). The strategy described for **1** and **2**, on the basis of increased reactivity of iodine as a leaving group in the Sonogashira cross coupling reaction, $^{[34,35]}$ gave polymeric products instead of desired rod **3**.

Initially a halide exchange reaction was attempted with dibromo-OPE **2** [Scheme 3 (A)].^[36,37] Treatment of **2** with butyllithium and 1,2-diiodoethane led to a mixture of products. The isolation of diiodo-OPE **3** turned out to be challenging owing to very similar polarities of the dibromo-OPE **2** and the corresponding iodo-bromo-OPE. However, the target structure **3** was isolated in a low yield (22%) as an off-white solid by column chromatography.

Masking strategies were considered to improve the yield and purity of the target structure. An ideal masking group would be readily available, stable to a variety of chemical



Scheme 3. Synthesis of diiodo-OPE 3 by using various strategies ranging from halide exchange (A), to functional group interconversion and masking strategies (B–D).



conversions, and conveniently transformed under mild conditions and in a high yield to form the desired aryl iodide.^[31]

An amine is suitable for functional group interconversion. Diamino-OPE **8** was synthesized for subsequent conversion to diiodo-OPE **3**, see Scheme 3 (B).^[38] The idea was to profit from the polarity differences between starting material **8** and product **3**. This strategy was first reported by Sandmeyer^[39] and has been improved over the course of the last century.^[38,40] Compound **8** was synthesized by using a Sonogashira coupling reaction in a yield of 90% with building blocks **4** and **7**.^[41,42] The product was then converted into a diazonium salt by using sulfuric acid and sodium nitrite in acetonitrile at 0 °C. After 24 h the reaction was quenched with sodium iodide to afford diiodo-OPE **3** in an improved yield of 50%.^[40] However, during the reaction considerable amounts of partially dehalogenated OPEs were formed that again made isolation of **3** challenging.

Dimethylpyrroles were proposed as base-stable masking groups for iodines under Sandmeyer-type conditions, see Scheme 3 (C).^[43,40] Building block 10 was obtained by using a literature procedure starting from 4-iodoaniline (9).[44] The second diacetylene, building block 11, was obtained in 90% yield by using standard cross-coupling conditions.^[45] Assembling masked OPE 12 by using a divergent approach gave an overall yield of 58%. The final Sandmeyer-type reaction, undertaken in a water/acetonitrile mixture as solvent, gave the diiodo-OPE 3 in a yield of 72%. Simple filtration through a short silica plug (40:1 hexane:tert-butylmethylether), gave product 3 in an overall yield of 41% as a white crystalline solid. Interestingly, side products with similar polarities were not observed. The increased solubility of the dimethylpyrrole-OPE 12 in the water/acetonitrile mixture, may have improved the formation of the diazonium salt during the Sandmeyer reaction. As in the case of diamino-OPE 8 – see part B of Scheme 3 – the slow formation of the diazonium salt in the heterogeneous dispersion is assumed to be responsible for the large quantity of side products.

Finally, alkylated triazenes were explored as masking groups for iodines [Scheme 3 (D)].^[46,47] Triazenes can be directly substituted with iodine by using methyl iodide in a sealed tube at 120 °C, and alkylated triazenes are stable towards strong bases and high temperatures. Pyrrolidinetriazenes are known for favorable crystallization properties and we hoped this property might improve the isolation of these intermediates. Triazene building block 13 was synthesized following a procedure reported by Godt.^[48] Ditriazene-OPE 14 was synthesized by using a cross-coupling reaction in very poor yield (7%). Even changing the disconnection strategy and putting the acetylenes on the central unit did not improve the yield. Instead diamino-OPE 8 was transformed into ditriazene-OPE 14 and isolated by crystallization in 80% yield. OPE 14 was subsequently transformed into diiodo-OPE 3 in a yield of 75%. Simple filtration through silica (cyclohexane) gave the pure product. The overall yield for the triazene strategy was 54%, which represents a slight increase over the yield for the pyrrole strategy of 41%. However, the considerably increased temperature required during the triazene strategy might be a drawback when additional functional groups are present.

All target structures and intermediates were characterized by ¹H and ¹³C NMR spectroscopy and mass spectrometry, and by elemental analysis where applicable. In the case of the target structures, the identity was corroborated by X-ray analysis.

Crystal Structures and Surface Images

The crystals for X-ray analysis were either grown by slow cooling of a saturated cyclohexane solution to 4 °C or by slow evaporation of cyclohexane at room temperature. All three compounds crystallize in the centro-symmetric space group $P\overline{1}$. The unit cells of OPEs 1 and 2 each contain one molecule, whereas that of 3 contains two molecules and a cyclohexane molecule. In all three structures the molecules are located on an inversion center of the space group $P\overline{1}$. Thus, in the case of 1 and 2 the molecules are arranged parallel to each other. In the case of 3 the two molecules and the solvent molecule are located on different inversion centers of the space group $P\overline{1}$ permitting the formation of a fishbone-like arrangement in the direction I···I of the two different orientations forming an angle of about 90°.

All the STM measurements were taken with a Nanoscope IIIa Scanning tunneling microscope, and the STM tip was prepared by mechanically cutting Pt/Ir wire (90:10). The molecules were dissolved in 1-phenyloctane to make saturated solutions. The solution was subsequently dropped on a freshly cleaved highly oriented pyrolytic graphite (HOPG) surface. The HOPG/1-phenyloctane interface was investigated by STM. All STM images were performed in constant current mode.

Dichloro-OPE 1 and Dibromo-OPE 2

The crystal structures of both OPEs **1** and **2** show a parallel arrangement of the rods (see parts a in Figures 2 and 3) forming several layers shifted by 5.2 and 5.7 Å, respectively. By looking at a planar cut through the crystal structures similar Cl···Cl (Figure 2, b, 5.0 and 4.8 Å) and Br···Br (Figure 3, b, 4.8 and 5.1 Å) distances were observed. Cl···H as well as Br···H interactions could be observed where the terminal halogen interacted with two hydrogen atoms coming from two different rods. The area of the unit cell (in a plane) comprising a single OPE molecule is about 1.84 nm² for dichloro-OPE **1** and about 1.93 nm² for dibromo-OPE **2** (see Supporting Information).

Parts c in Figures 2 and 3 show the STM images of a monolayer of OPEs 1 and 2 on a HOPG surface. A lamellar structure, where the rods lie parallel to each other, was observed in each case. The unit cell for dichloro-OPE 1 was determined with $a = (2.0 \pm 0.1)$ nm, $b = (1.0 \pm 0.1)$ nm and $a = (76 \pm 2)^{\circ}$ whereas the unit cell for dibromo-OPE 2 was determined with $a = (2.0 \pm 0.1)$ nm, $b = (1.0 \pm 0.1)$ nm and $a = (75 \pm 4)^{\circ}$. The unit cells, which contain one molecule,



Figure 2. (a) The crystal structure of dichloro-OPE 1 reveals a parallel arrangement of rods. Hexyl chains and hydrogen atoms have been removed for clarity. (b) Planar cut through the crystal structure of 1. The slightly larger distance of 5.0 Å is shown in blue and the slightly shorter distance of 4.8 Å is shown in black. The Cl···H interactions (3.4 Å) are shown in green. (c) STM image of a HOPG surface covered with 1.

have a surface area of about 1.94 nm^2 for **1** and 1.93 nm^2 for **2**.

By comparing the individual molecular arrangements of a planar cut through the crystal structure (see b in Figures 2 and 3) with the molecular arrangements at the solid liquid interface (see c in Figures 2 and 3) an exact match of the parallel crystal arrangement was observed. The same zigzag arrangement of the chlorines and the bromines was found. X...H interactions as well as alkyl-chain interdigitations could be observed on the surface. Eight X...H interactions per molecule were observed (see b in Figure 2 and 3, indicated in green) in the crystal structure and at the solid liquid interface.

Diiodo-OPE 3

The packing order of the crystal structure reveals several layers of molecules (Figure 4, a). Looking at the unit cell, three planar sheets are observed having a total height of 7.3 Å. When looking at that planar cut through the crystal



Figure 3. (a) The crystal structure of dibromo-OPE **2** reveals a parallel arrangement of rods. Hexyl chains and hydrogen atoms have been removed for clarity. (b) Crystal structure of **2** showing the parallel order. The larger distance of 5.1 Å is shown in blue and the shorter distance of 4.8 Å is shown in black. The Br···H interactions (3.3 Å) are shown in green. (c) STM image of a HOPG surface covered with **2**.

(Figure 4, b) a perpendicular arrangement of the rods is observed. This arrangement leads to the formation of two cavities. The distance between the iodines within these cavities is 14.2 and 8.3 Å, respectively. The angles of the perpendicular rods are between 92.3 and 93.7°. The central benzene units of the rods are situated in the corners of the unit cell at a distance of 15.0 and 15.3 Å to one another. The area of the unit cell (in a plane) comprising two molecules and a cyclohexane is about 4.54 nm² (see Supporting Information).

The terminal iodine has a strong positive electrostatic potential along the molecular axis and a negative electrostatic potential off the axis forming a "belt" around the iodine.^[4] Therefore, it can interact with electron donors such as other halogens and π -orbitals as well as electron acceptors including hydrogen atoms.^[17] The perpendicular arrangement of the rods comes from a strong I··· π -orbital interaction where



Figure 4. (a) The crystal structure of diiodo-OPE **3** reveals a perpendicular arrangement of rods forming large and small cavities. Solvent, hexyl chains and hydrogen atoms have been removed for clarity. (b) Planar cut through the crystal structure of **3** showing the square cavities. The larger iodine-iodine distance of 14.2 Å is shown in blue and the shorter iodine-iodine distance of 8.3 Å is shown in black. The I···H (3.2 Å and 3.3 Å) and the I···π-orbital (4.1 Å) interactions are shown in green. (c) STM image of a HOPG surface covered with **3**.

the electropositive potential of the iodine interacts with an electronegative π -orbital of a second rod (Figure 4, a). The central benzene unit undergoes π - π stacking with another rod that is perpendicular. This crystal structure reveals that the functional groups (I, H, C=C) within the molecule dictate the two-dimensional arrangement. The central benzene unit controls the three-dimensional arrangement.

Figure 4 (c) shows the STM image of a monolayer of diiodo-OPE **3** at the solid/liquid interface. The molecules form a highly ordered network with large and small pores. The unit cell was determined with $a = (2.1 \pm 0.1)$ nm, $b = (2.0 \pm 0.1)$ nm and $a = (90 \pm 4)^{\circ}$. The unit cell contains two molecules with a surface area of about 4.2 nm². By looking at the molecular arrangement on the surface the rods lie



perpendicular to each other forming large and small cavities.

The molecular arrangement observed in a planar cut through the crystal (Figure 4, b) and the arrangement at the solid/liquid interface (Figure 4, c) match almost perfectly. The area of two molecules in the crystal structure is about 4.5 nm^2 , which is similar to the surface coverage at the solid/liquid interface of 4.2 nm^2 . The same interactions where a terminal iodine interacts with a π -orbital and two hydrogen atoms were identified. These interactions clearly dictate the two-dimensional assembly in both the crystal structure and at the solid-liquid interface, whereas alkyl chain interdigitation^[16] plays a smaller part. This situation could be due to the eight I···H and four I··· π -orbital interactions per molecule.

Remarkable similarity between a planar cut through the crystal structure and the assembly at the solid-liquid interface was found for OPEs 1-3. However, each OPE shows considerable variation in their arrangement induced by the terminal halide. Similar arrangements were found for dichloro-OPE 1 and dibromo-OPE 2. The halides show a zigzag line coming from X···H interactions and alkyl chain interdigitations (Figures 2 and 3). It seems that these are the only interactions to control molecular arrangement. We were able to measure that dichloro-OPE rods 1 were not commensurable with the graphite sheet and therefore we can assume that the assembly was mainly controlled by intermolecular interactions. Monolayers of dibromo-OPE 2 and diiodo-OPE 3 were not stable enough to determine their commensurability. This indicates that intermolecular interactions dominate their assembly.

For diiodo-OPE **3** a quite different arrangement was observed. The halides interact with electropositive hydrogen atoms from neighboring rods and also with an electronegative π -orbital, leading to a perpendicular arrangement (Figure 4). Presumably the larger size of the iodine together with the larger electropositive potential is responsible for this change in molecular packing. In particular, the latter is assumed to form an interaction with the acetylene π -system resulting in the perpendicular arrangement of the molecular rods.

Differences on the molecular packing of the three structures suggest X···H bonds are the dominating intermolecular interactions which becomes weaker with increasing size and decreasing electronegativity of the halogen atom (Cl > Br > I).^[49] In the case of **3** the X···H bonds are weak enough that the X··· π -system interaction begins to compete.

Conclusions

A series of halide-end-functionalized OPEs were synthesized to investigate their packing properties in single crystals and on atomically flat graphite substrates. In spite of their structural simplicity and similarity, the synthesis of target structures 1-3 was more challenging than expected. OPEs 1 and 2 were synthesized in good yields through an in situ deprotection method to prevent the formation of side products. Various synthetic strategies for OPE **3** were investigated. Functional group interconversion was superior for yield and isolation properties of the target structure and efficient syntheses were developed. Although the triazene masking strategy gave the highest overall yield and a very pure product, the dimethylpyrrole masking-group worked considerably better than the free amine functional group interconversion and requires lower reaction temperatures.

The STM images and the crystal structures for OPEs 1–3 revealed a structural similarity for each rod. In their crystal structures a slice plane with a molecular arrangement resembling their two-dimensional packing on a flat surface was found for each compound. These results support the hypothesis of slice-by-slice crystal growth and suggest flat surfaces as ideal interfaces to promote crystal growth. Of particular interest was the arrangement of diiodo-OPE 3. The STM image and the crystal structure revealed a porous network of alternating pore sizes. This assembly can be rationalized by I···H and I··· π -orbital interactions. This perpendicular arrangement might pave the way to porous crystals grown on flat substrates.

In summary, halides have a large influence on the packing of OPE rods. This is rationalized by their differences in electrostatic potentials. Understanding these interactions will enable controlled surface functionalization and open the door to controlled crystal growth on flat substrates.

Experimental Section

General Remarks: All purchased chemicals were used as received without further purification. Dry solvents and compounds 5, 6 and 7 were purchased from Sigma-Aldrich. All oxygen-sensitive reactions were performed under an argon atmosphere. Glassware was heated to 120 °C and cooled under a flow of argon. Silica gel (60 µm) was purchased from Sigma-Aldrich. TLC plates (silica gel 60 F_{254}) were purchased from Merck. All ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-NMR (400 MHz/100.6 MHz) or on a Bruker DRX-500 (500 MHz/125 MHz) spectrometer. Chemical shifts are given in ppm relative to residual solvent or trimethylsilane as internal standards. NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The measurements were recorded at room temperature. All protons were assigned by using COSY and NOESY experiments. All carbons were assigned by using DEPT, HMQC and HMBC experiments. Mass spectra were recorded on a Bruker esquire 3000 plus for ESI, a Finnigan MAT 95Q for EI or a finnigan MAT 8400 for FAB. HRMS (ESI) spectra were recorded with a LTQ Orbitrap XL (Thermo Fisher Scientific) by using a nanoelectrospray ion source. Elemental analyses were measured with a Perkin-Elmer Analysator 240.

1,4-Bis[2-(4-chlorophenyl)ethynyl]-2,5-dihexylbenzene (1): A Schlenk tube was purged with argon, charged with $Pd(PPh_3)_2Cl_2$ (21.3 mg, 0.03 mmol, 0.06 equiv.), CuI (19 mg, 0.1 mmol, 0.2 equiv.) and [(4-chlorohenyl)ethynyl]trimethylsilane (5, 221 mg, 1.02 mmol, 2.05 equiv.), and purged again. Dry benzene (5 mL) and triethylamine (0.84 mL) were added. The brown suspension was degassed for 10 min. 1,4-dihexyl-2,5-diiodobenzene^[33] (4, 249 mg, 0.5 mmol, 1 equiv.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.0 mL, 12 mmol, 24 equiv.) were added to the solution. Deionized

water (0.0115 mL) was added and the reaction mixture was stirred at room temperature for 48 h. The mixture was concentrated under reduced pressure and the residue was dissolved in CH₂Cl₂ and washed with water $(2 \times 20 \text{ mL})$. The organic layer was dried with MgSO₄, filtered and concentrated under reduced pressure to afford the crude product as yellow oil. The oil was purified by column chromatography (cyclohexane) to afford 1 (158 mg, 61.3%) as a white solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.45$ (dt, ³J_{H,H} = 8.8, ${}^{4}J_{H,H}$ = 2 Hz, 4 H), 7.35 (s, 2 H); 7.34 (dt, ${}^{3}J_{H,H}$ = 8.8, ${}^{4}J_{H,H}$ = 2 Hz, 4 H), 2.78 (t, ${}^{3}J_{H,H}$ = 8 Hz, 4 H), 1.70–1.66 (m, 4 H), 1.39–1.30 (m, 12 H), 0.88 (t, ${}^{3}J_{H,H}$ = 6.8 Hz, 6 H) ppm. ${}^{13}C$ NMR (100 MHz, CDCl₃): δ = 142.5 (2 C, C_q), 134.4 (2 C, C_q), 132.8 (4 C, C_t), 132.5 (2 C, C_t), 128.9 (4 C, C_t), 122.5 (2 C, C_a), 122.1 (2 C, C_q), 93.0 (2 C, C_q), 89.5 (2 C, C_q), 34.3 (2 C, C_s), 32.9 (2 C, C_s), 30.8 (2 C, C_s), 29.4 (2 C, C_s), 22.8 (2 C, C_s), 14.3 (2 C, C_p) ppm. MS (EI): m/z (%) = 514.2 (100) [M]⁺, 443.2 (12.5) [M - 2Cl]⁺.

1,4-Bis[2-(4-bromophenyl)ethynyl]-2,5-dihexylbenzene (2): Α Schlenk tube was purged with argon, charged with Pd(PPh₃)₂Cl₂ (34.12 mg, 0.048 mmol, 0.06 equiv.), CuI (30.5 mg, 0.16 mmol, 0.2 equiv.) and [(4-bromophenyl)ethynyl]trimethylsilane (6, 405 mg, 1.6 mmol, 2 equiv.), and purged again. Dry benzene (8 mL) and triethylamine (1.35 mL) were added. The suspension was degassed for 10 min. 1,4-dihexyl-2,5-diiodobenzene^[33] (4, 400 mg, 0.8 mmol, 1 equiv.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (2.9 mL. 19.2 mmol, 24 equiv.) were added, and the resulting solution turned green. Deionized water (0.0115 mL) was added and the reaction mixture was stirred at room temperature for 36 h. The mixture was concentrated under reduced pressure and the residue was dissolved in CH_2Cl_2 and washed with water (2 × 20 mL). The organic layer was dried with MgSO₄, filtered and concentrated under reduced pressure to afford the crude product as a dark oil. The oil was purified by column chromatography (hexane) to afford 2 (354 mg, 73.2%) as a white solid. ¹H NMR (250 MHz, CDCl₃): δ = 7.498 (dt, ${}^{3}J_{H,H} = 8.25$, ${}^{4}J_{H,H} = 2.25$ Hz, 4 H), 7.43–7.24 (m, 6 H), 2.78 (t, ${}^{3}J_{H,H}$ = 7.5 Hz, 4 H), 1.73–1.52 (m, 4 H), 1.36–1.28 (m, 12 H) 0.88 (t, ${}^{3}J_{H,H}$ = 6.75 Hz, 6 H) ppm. ${}^{13}C$ NMR (100 MHz, CDCl₃): δ = 142.3 (2 C, C_q), 132.9 (4 C, C_t), 131.8 (4 C, C_t), 122.5 (2 C, C_q), 122.4 (2 C, C_q), 122.3 (2 C, C_q), 92.9 (2 C, C_q), 89.5 (2 C, C_q), 34.1 (2 C, C_s), 31.7 (2 C, C_s), 30.6 (2 C, C_s), 29.2 (2 C, C_s), 22.6 (2 C, C_s), 14.1 (2 C, C_p) ppm. MS (EI): m/z (%) = 604.1 (100) [M]⁺. C34H36Br2 (604.5): calcd. C 67.56, H 6.00; found C 67.4, H 5.95.

1,4-Bis[2-(4-aminophenyl)ethynyl]-2,5-dihexylbenzene (8): A 25 mL Schlenk tube was purged with argon and charged with 1,4-diiodo-2,5-dihexylbenzene^[33] (4, 996 mg, 2 mmol, 1 equiv.), Pd(PPh₃)₂Cl₂ (141 mg, 0.2 mmol, 0.1 equiv.), CuI (39.9 mg, 0.2 mmol, 0.1 equiv.), 4-ethynylaniline (7, 604 mg, 5 mmol, 2.5 equiv.), triethylamine (7 mL) and dry THF (10 mL). The resulting mixture was degassed for 10 min. and stirred for 16 h at room temperature. The mixture was diluted with tert-butylmethyl ether (tBME) and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (cyclohexane/tBME, 1:2) to afford 8 as a brown solid (858 mg, 90%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.308 (dt, ³J_{H,H} = 8.4, ⁴J_{H,H} = 2.4 Hz, 4 H), 7.31 (s, 2 H), 6.65 (dt, ${}^{3}J_{H,H} = 8.4$, ${}^{4}J_{H,H} = 2.4$ Hz, 4 H), 3.94 (s, 4 H), 2.77 (t, ${}^{3}J_{H,H}$ = 7.6 Hz, 4 H), 1.70–1.64 (m, 4 H), 1.36–1.33 (m, 12 H), 0.89 (t, ${}^{3}J_{H,H}$ = 6.8 Hz, 6 H) ppm. ${}^{13}C$ NMR (100 MHz, CD_2Cl_2): $\delta = 147.5$ (2 C, C_q), 143.2 (2 C, C_q), 133.0 (4 C, C_t), 132.2 (2 C, C_t), 122.9 (2 C, C_q), 114.9 (4 C, C_t), 112.8 (2 C, C_q), 94.9 (2 C, C_q), 86.6 (2 C, C_q), 34.5 (2 C, C_s), 32.2 (2 C, C_s), 31.0 (2 C, C_s), 29.6 (2 C, C_s), 23.0 (2 C, C_s), 14.3 (2 C, C_p) ppm. MS (EI): m/z (%) = 476.3 (100) [M]⁺. C₃₄H₄₀N₂ (476.7): calcd. C 85.67, H 8.46, N 5.88; found C 85.39, H 8.38, N 5.91.

1,4-Bis{2-[4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl]ethynyl}-2,5-dihexylbenzene (12): A 25 mL Schlenk tube was purged with argon, charged with Pd(PPh₃)₂Cl₂ (42.5 mg, 0.06 mmol, 0.06 equiv.), CuI (38.1 mg, 0.2 mmol, 0.2 equiv.) and TMS-protected acetylene 11^[45] (439 mg, 1.0 mmol, 1 equiv.), and purged again. Dry benzene (10 mL) and triethylamine (1.7 mL) were added. The yellow suspension was degassed for 10 min resulting in a brown solution. Dimethylpyrrole derivative 10[44] (624 mg, 2.1 mmol, 2.1 equiv.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (3.6 mL, 24.0 mmol, 24 equiv.) were added to the solution. Deionized water (0.0144 mL) was added and the reaction mixture was stirred at room temperature for 100 h. The reaction mixture was diluted with tBME and washed with water $(2 \times 20 \text{ mL})$ and brine. The organic layer was dried with MgSO₄, filtered and concentrated under reduced pressure to afford the crude product as a dark oil. The oil was purified by column chromatography (cyclohexane/tBME, 40:1) to afford 12 (367 mg, 58%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.62 (dt, ${}^{3}J_{H,H} = 8.4, {}^{4}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2 H); } 7.22 \text{ (dt, } {}^{3}J_{H,H} = 1.6 \text{ Hz}, 4 \text{ H}), 7.39 \text{ (s, 2$ 8.4, ${}^{4}J_{H,H}$ = 1.6 Hz, 4 H), 5.92 (s, 4 H), 2.83 (t, ${}^{3}J_{H,H}$ = 7.6 Hz, 4 H), 2.06 (s, 12 H), 1.74-1.71 (m, 4 H), 1.43-1.26 (m, 12 H), 0.88 (t, ${}^{3}J_{H,H}$ = 6.8 Hz, 6 H) ppm. ${}^{13}C$ NMR (100 MHz, CDCl₃): δ = 142.6 (2 C, C_q), 132.7 (2 C, C_q), 132.4 (4 C, C_t), 129.3 (2 C, C_t), 129.0 (4 C, C_q), 128.5 (4 C, C_t), 123.0 (2 C, C_q), 122.7 (2 C, C_q), 106.3 (4 C, C_t), 93.4 (2 C, C_q), 89.6 (2 C, C_q), 34.4 (2 C, C_s), 32.0 (2 C, C_s), 30.9 (2 C, C_s), 29.5 (2 C, C_s), 22.9 (2 C, C_s), 14.3 (2 C, C_p), 13.3 (4 C, C_p) ppm. MS (EI): m/z (%) = 632.4 (100) [M]⁺. HRMS (ESI): calcd. for C₄₆H₅₂N₂ [M + H]⁺ 633.4203; found 633.4211.

1,4-Bis{2-[4-(3,3-tetramethylenetriazeno)phenyl]ethynyl}-2,5-dihexylbenzene (14)

Bis(triphenylphosphine)palladium(II) Pathway 1: chloride (42.1 mg, 0.06 mmol, 0.06 equiv.), CuI (47.6 mg, 0.25 mmol, 0.2 equiv.) and 1-(4-trimethylsilylethynylphenyl)-3,3-tetramethylenetriazene^[48] (13, 679 mg, 2.5 mmol, 2.5 equiv.) were added to a 50 mL Schlenk tube and purged with argon. Benzene (12 mL) and triethylamine (1.7 mL) were added. The resulting solution was degassed for 10 min and 1,4-dihexyl-2,5-diiodobenzene^[45] (4, 498 mg, 1,8-diazabicyclo[5.4.0]undec-7-ene 1.0 mmol, 1 equiv.) and (4.48 mL, 30 mmol, 30 equiv.) were added. Water (18 μ L, 1.0 mmol, 1 equiv.) was added and the reaction mixture turned green. The resulting mixture was stirred for 24 h at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in CH₂Cl₂ (60 mL), extracted with water $(2 \times 20 \text{ mL})$ and washed with brine (30 mL). The organic layer was then dried with MgSO₄, filtered and concentrated under reduced pressure to afford a red-brown solid. The residue was purified by column chromatography (hexane/tBME, 2:1 + 3%triethylamine) to afford 14 (45 mg, 7%) as a yellow powder.

Pathway 2: A 25 mL two-necked round-bottomed flask was purged with argon and charged with 1,4-bis[2-(4-aminophenyl)ethynyl]-2,5-dihexylbenzene (**8**, 501 mg, 1.05 mmol, 1 equiv.), water (1,5 mL), acetonitrile (1.5 mL) and hydrochloric acid (37%, 0.803 mL, 9.45 mmol, 9 equiv.). The resulting mixture was cooled to 0 °C and stirred for 1 h. A solution of sodium nitrite (145 mg, 2.1 mmol, 2 equiv.) in water (3.5 mL) was added and the mixture was again stirred for 1 h at 0 °C. The mixture was then transferred into another flask containing potassium carbonate (1.466 mg, 10.5 mmol, 10 equiv.), water/acetonitrile, 2:1 (3 mL) and pyrrolidine (0.345 mL, 4.2 mmol, 4 equiv.). The resulting mixture was stirred for 1 h at 0 °C and a further 2 h at room temperature. The mixture was then diluted with CH₂Cl₂ (100 mL). The aqueous phase was separated and washed with CH₂Cl₂ (2 × 50 mL).



organic layers were combined, washed with brine, dried with MgSO₄ and concentrated under reduced pressure to afford the crude product. Ethyl acetate was added and the slurry was put in an ultrasonic bath for 5 min. The mixture was then filtered and the solid product was dried under vacuum to afford 14 (558 mg, 82%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.481 (dt, ³J_{H,H} = 8.8, ${}^{4}J_{H,H}$ = 2 Hz, 4 H), 7.41 (dt, ${}^{3}J_{H,H}$ = 8.8, ${}^{4}J_{H,H}$ = 2 Hz, 4 H), 7.34 (s, 2 H), 3.80 (s, 8 H), 2.80 (t, ${}^{3}J_{H,H} = 7.6$ Hz, 4 H), 2.04 (m, 8 H), 1.72–1.68 (m, 4 H), 1.41–1.31 (m, 12 H), 0.878 (t, ${}^{3}J_{H,H}$ = 7.2 Hz, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 151.4 (2 C, C_q), 142.3 (2 C, C_q), 132.4 (4 C, C_t), 132.3 (2 C, C_t), 122.8 (2 C, C_q), 120.6 (4 C, C_t), 120.0 (2 C, C_q), 94.7 (2 C, C_q), 88.6 (2 C, C_g), 34.4 (C_s, C4), 32.0 (2 C, C_s), 30.0 (2 C, C_s), 29.5 (2 C, C_s), 24.0 (2 C, C_s), 22.9 (4 C, C_s), 14.4 (2 C, C_p) ppm. MS (EI): m/z $(\%) = 640.4 (5.5) [M^+], 543.3 (40.5) [M^+ - C_4H_8N_3], 445.2 (100)$ $[M^+ - C_8 H_{16} N_6]$. HRMS (ESI): calcd. for $C_{42} H_{52} N_6 [M + H]^+$ 641.4326; found 641.4337.

1,4-Bis[2-(4-iodophenyl)ethynyl]-2,5-dihexylbenzene (3)

Halide Exchange: A 25 mL two-necked flask was purged with argon, charged with 1,4-bis[2-(4-bromophenyl)ethynyl]-2,5-dihexylbenzene (2, 100.00 mg, 0.165 mmol, 1 equiv.) and THF (3.00 mL), and the resulting mixture was cooled to -100 °C. nBuLi (0.23 mL, 0.350 mmol, 2.12 equiv., 1.6 M in hexane) was slowly added to the colorless suspension so that the temperature did not exceed -90 °C. The reaction mixture turned green and then yellow. The mixture was then stirred for 45 min before more nBuLi (0.05 mL, 0.080 mmol, 0.5 equiv., 1.6 м in hexane) was added. The reaction mixture was added dropwise with a syringe to a precooled (-78 °C) solution of 1,2-diiodoethane (98.7 mg, 0.350 mmol, 2.12 equiv.) in THF (1.50 mL) and stirred overnight. The dark brown reaction mixture was poured onto an aqueous solution of $Na_2S_2O_3$ (15%) under a layer with diethyl ether. The ether layer was washed twice with an aqueous solution of $Na_2S_2O_3$ (15%). The aqueous layer was extracted with diethyl ether $(3 \times 10 \text{ mL})$. The combined organic extracts were dried with MgSO₄, filtered and concentrated under reduced pressure to gave a yellow residue. The crude product was purified by column chromatography (hexane) to afford 3, (26.02 mg, 22%) as an off-white solid.

Pyrrole Strategy: A 50 mL two-necked round-bottomed flask was purged with argon and charged with 1,4-bis{2-[4-(2,5-dimethyl-1Hpyrrol-1-yl)phenyl]ethynyl}-2,5-dihexylbenzene (12) (100 mg. 0.158 mmol, 1 equiv.), MeCN (4.5 mL) and H₂SO₄ (3.32 mL, 2 м, 6.64 mmol, 42 equiv.). The mixture was cooled to -5 °C. Sodium nitrite (65.4 mg, 0.948 mmol, 6 equiv.) dissolved in water (1 mL) was added dropwise at -5 °C and the mixture was stirred overnight before sodium iodate (189 mg, 1.26 mmol, 8 equiv.) dissolved in water (1 mL) was added. The reaction mixture was then allowed to warm to room temperature over 1 h. The mixture was heated briefly to 60 °C and then stirred at room temperature for 4 h. The mixture was neutralized with a saturated solution of Na2CO3 and then extracted with ethyl acetate (3×40 mL). The combined organic extracts were washed with $Na_2S_2O_3$ (1 N, 2×50 mL) and water (20 mL), dried with MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/tBME, 40:1) to afford 3 (79 mg, 72%) as a white solid.

Triazene Strategy: A 10 mL MW-pressure tube was purged with argon and charged with 1,4-bis $2-[4-(3,3-tetramethylenetriazeno)-phenyl]ethynyl}-2,5-dihexylbenzene (14, 60.9 mg, 0.095 mmol, 1 equiv.) and iodomethane (4 mL). The sealed tube was heated to 120 °C and stirred for 12 h. The reaction mixture was then concentrated under reduced pressure. The residue was dissolved in cyclo-$

hexane and filtered through silica to afford 1,4-bis[2-(4-iodophenyl)ethynyl]-2,5-dihexylbenzene (**3**) (52 mg, 78.2%) as a white solid. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.73 (dt, ³J_{H,H} = 8.8, ⁴J_{H,H} = 2 Hz, 4 H), 7.37 (s, 2 H), 7.26 (dt, ³J_{H,H} = 8.8, ⁴J_{H,H} = 2 Hz, 4 H), 2.80 (t, ³J_{H,H} = 7.6 Hz, 4 H), 1.70–4.64 (m, 4 H), 1.42–1.31 (m, 12 H), 0.88 (t, ³J_{H,H} = 6.8 Hz, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 143.0 (2 C, C_q), 138.2 (4 C, C_t), 133.5 (4 C, C_t), 132.9 (2 C, C_t), 123.5 (2 C, C_q), 123.0 (2 C, C_q), 94.6 (2 C, C_q), 93.6 (2 C, C_q), 90.3 (2 C, C_q), 34.6 (2 C, C_s), 32.3 (2 C, C_s), 31.2 (2 C, C_s), 29.8 (2 C, C_s), 23.2 (2 C, C_s), 14.5 (2 C, C_p) ppm. MS (EI): *m*/*z* (%) = 697.9 (100) [M⁺], 572.1 (12.5) [M⁺ – I].

Crystal Data

Dichloro-OPE 1: Crystal data for 1: formula C34H36Cl2, M = 515.57, F(000) = 274, colorless plate, size $0.030 \times 0.070 \times 0.180$ mm³, triclinic, space group $P\bar{1}$, Z = 1, a =5.6220(7) Å, b = 8.0932(11) Å, c = 15.495(2) Å, $a = 86.859(9)^{\circ}$, β = $83.191(9)^{\circ}$, γ = $87.654(9)^{\circ}$, V = 698.59(16) Å³, d_{calcd} = 1.225 Mg·m⁻³. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123 K by using graphite-monochromated Mo- K_{α} radiation with $\lambda = 0.71073$ Å, $\Theta_{\text{max}} = 30.032^{\circ}$. Minimal/ maximal transmission 0.98/0.99, $\mu = 0.253 \text{ mm}^{-1}$. The Apex2 suite has been used for data collection and integration. From a total of 13850 reflections, 4056 were independent (merging r = 0.050). From these, 2222 were considered as observed $[I > 2.0\sigma(I)]$ and were used to refine 163 parameters. The structure was solved by direct methods by using the program Superflip. Least-squares refinement against F was carried out on all non-hydrogen atoms by using the program CRYSTALS. R = 0.0402 (observed data), wR = 0.0823 (all data), GOF = 1.1125. Minimal/maximal residual electron density: -0.26/0.28 eÅ⁻³. Chebychev polynomial weights were used to complete the refinement. Plots were produced by using CAMERON.

Dibromo-OPE 2: Crystal data for **2**: formula C₃₄H₃₆Br₂, M = 604.47, F(000) = 310, colorless needle, size $0.040 \times 0.060 \times 0.270$ mm³, triclinic, space group $P\bar{1}$, Z = 1, a =5.7434(8) Å, b = 8.0996(8) Å, c = 15.4925(16) Å, $a = 86.096(5)^{\circ}$, β = $82.539(5)^\circ$, γ = $87.253(4)^\circ$, V = 712.38(14) Å³, $d_{calcd.}$ = 1.409 Mg· m^{-3} . The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123 K by using graphite-monochromated Mo- K_{α} radiation with $\lambda = 0.71073$ Å, $\Theta_{max} = 37.784^{\circ}$. Minimal/maximal transmission 0.84/0.89, $\mu = 2.866 \text{ mm}^{-1}$. The Apex2 suite has been used for data collection and integration. From a total of 27787 reflections, 7551 were independent (merging r = 0.033). From these, 4999 were considered as observed $[I > 2.0\sigma(I)]$ and were used to refine 163 parameters. The structure was solved by direct methods by using the program Superflip. Least-squares refinement against F was carried out on all non-hydrogen atoms by using the program CRYSTALS. R = 0.0251 (observed data), wR = 0.0471 (all data), GOF = 1.0921. Minimal/maximal residual electron density: -0.35/0.44 eÅ-3. Chebychev polynomial weights were used to complete the refinement. Plots were produced by using CAMERON.

Diiodo-OPE 3: Crystal data for **3**: formula $C_{37}H_{42}I_2$, M = 740.55, F(000) = 740, colorless block, size $0.040 \times 0.130 \times 0.230$ mm³, triclinic, space group $P\bar{1}$, Z = 2, a = 7.2908(9) Å, b = 15.0277(16) Å, c = 15.3177(15) Å, $a = 88.906(6)^{\circ}$, $\beta = 78.977(7)^{\circ}$, $\gamma = 82.784(7)^{\circ}$, V = 1634.2(3) Å³, $d_{calcd.} = 1.505$ Mg·m⁻³. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123 K by using graphite-monochromated Mo- K_{α} radiation with $\lambda = 0.71073$ Å, $\Theta_{max} = 30.242^{\circ}$. Minimal/maximal transmission 0.78/0.93, $\mu = 1.947$ mm⁻¹. The Apex2 suite has been used for data collection and integration. From a total of 32598 reflections, 9576 were independent (merging r = 0.055). From these, 5270 were considered as observed $[I > 2.0\sigma(I)]$ and were used to refine 353 parameters. The structure

was solved by direct methods by using the program Superflip. Least-squares refinement against *F* was carried out on all non-hydrogen atoms by using the program CRYSTALS. R = 0.0558 (observed data), wR = 0.1018 (all data), GOF = 1.0652. Minimal/maximal residual electron density: $-1.41/2.39 \text{ e}\text{Å}^{-3}$. Chebychev polynomial weights were used to complete the refinement. Plots were produced by using CAMERON.

CCDC-849687 (for 1), -849688 (for 2) and -849689 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ¹H and ¹³C NMR spectra of compounds 1–3, 8, 12, and 14; large-area STM images and planar cuts through the crystal structures of compounds 1–3; experimental procedures of compounds 4, 10, 11 and 13.

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