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Supporting Information

for

Heteroatom-Doped Perihexacene from a Double Helicene Precursor: On-Surface Synthesis and Properties

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1. General Method

All commercially available chemicals were used without further purification unless otherwise noted. Column chromatography was done with silica gel (particle size 0.063-0.200 mm) and thin layer chromatography (TLC) was performed on silica gel-coated aluminum sheets with F254 indicator. All yields given refer to isolated yields. Nuclear magnetic resonance (NMR) spectra were recorded on an AVANCE 300 MHz Bruker spectrometer. Chemical shifts were reported in ppm. Coupling constants (J values) were reported in Hertz. ^1H NMR chemical shifts were referenced to CHDCl_2 (5.320 ppm) or $\text{C}_2\text{H}_2\text{DCl}_4$ (6.000 ppm). ^{13}C NMR chemical shifts were referenced to CD_2Cl_2 (54.00 ppm). The attached proton test (APT) technique of ^{13}C NMR (J-modulated spin-echo for ^{13}C -nuclei coupled to ^1H -nuclei) was used to distinguish the carbon atoms with even or odd number of attached protons. The quaternary (C) and methylene (CH_2) signals were in the upper phase and the methine (CH) and methyl (CH_3) signals were in the opposite phase. Field desorption mass spectrometry (FD-MS) was carried out on a VG-Instrument ZAB 2-SE-FDP. High-resolution mass spectrometry (HRMS) was performed either on a Q-Tof Ultima 3 (micromass/Waters) by electrospray ionization (ESI) or on a SYNAPT G2 Si high resolution time-of-flight mass spectrometer (Waters Corp., Manchester, UK) by matrix-assisted laser desorption/ionization (MALDI) with tetracyanoquinodimethane (TCNQ) as the matrix. Absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Photoluminescence spectra were recorded on a J&MTIDAS spectrofluorometer. The photoluminescence quantum yield (Φ_{F}) was measured with 9,10-diphenylanthracene as a standard.¹

All surface-assisted experiments were performed in ultrahigh vacuum (UHV) chambers with a base pressure of 10^{-11} mbar. The Au(111) single crystal was cleaned by sputtering (Ar^+ , 1 keV) and annealing up to 750 K. The precursor **2** was thermally evaporated onto the Au(111) surface held at room temperature. The sublimation temperature of precursor **2** is 635 K.

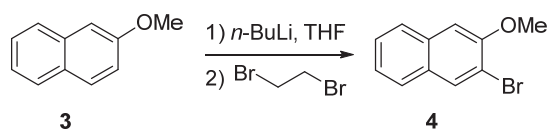
Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) experiments were carried out with a low-temperature scanning probe microscopy

system (LT-SPM, ScientaOmicron, Germany) at a temperature of 4.9 K. Scanning tunneling spectra (dI/dV) were detected with a lock-in amplifier (HF2LI by Zurich Instruments, Switzerland). Commercial Qplus sensors² equipped with tungsten tips (resonance frequency = 22350 Hz, Q-factor = 11000; tunneling current separated, ScientaOmicron) were used for non-contact AFM (nc-AFM) measurements. Repeated indentation to the substrate was used to shape the apex of the tip prior to the pick-up of a CO molecule from the sample.³ Frequency-shift images at constant height with the CO-sensitized tip were performed with an amplitude of 100 pm.

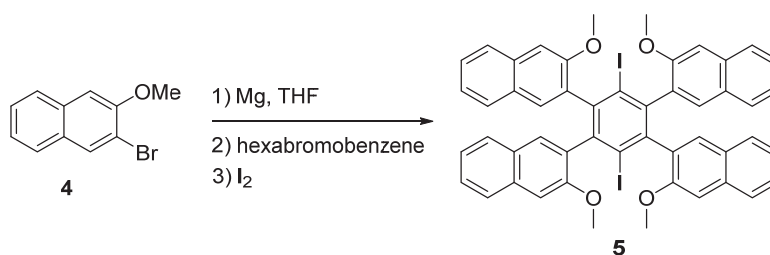
X-ray photoelectron spectroscopy (XPS) measurements were performed on the PEARL beamline of the SLS synchrotron radiation facility (Villigen, Switzerland), using linearly polarized radiation with photon energy of 425 eV.⁴ After deposition at room temperature, the sample was then transferred into the analysis chamber where the fast-XPS map was recorded during the in-situ annealing of the sample. High-resolution XPS (HR-XPS) spectra were recorded before and after the temperature ramp. XPS spectra were obtained in normal emission geometry, using a hemispherical electron analyzer equipped with a multichannel plate (MCP) detector. HR-XPS spectra were recorded in “sweep” mode with 20 eV pass energy, while the fast-XPS measurement was performed using the “fix” mode (snapshots of the C 1s level) acquiring one spectrum every 5 s with 50 eV pass energy.

Raman spectroscopy was performed in a Bruker Senterra Raman Microscope using a 532 nm laser (corresponding to 2.33 eV excitation energy). The Raman spectra of the perihexacene analogue **1** were acquired using three scans of 60 seconds adopting 2 mW laser irradiation power; the Raman spectra of the precursor **2** were acquired using a single scan of 10 seconds adopting 0.2 mW laser irradiation power. In both cases a 50× objective lens was used, which results in a 1-2 μm spot size. The Raman spectrum of **1** was measured on the Au(111) surface, while the Raman spectrum of **2** was measured on the powder sample.

2. Procedures of Solution Synthesis

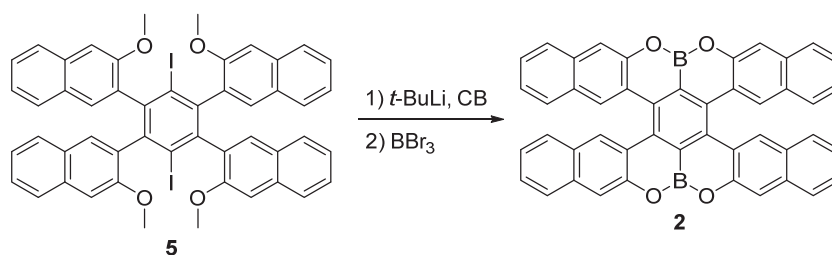


2-Bromo-3-methoxynaphthalene (4).⁵ To a solution of 2-methoxynaphthalene (15.8 g, 100 mmol) in dry THF (120 mL) was added n -BuLi (1.60 M in hexane, 66.0 mL, 106 mmol) at -78 °C under argon. After the mixture was stirred at room temperature for 1 h, 1,2-dibromoethane (20.7 g, 110 mmol) was added at -78 °C. The resulting mixture was then stirred at room temperature for 24 h before quenching by an aqueous NH₄Cl solution. The mixture was extracted with ether (30 mL \times 3) and the combined organic layers were washed with brine and water and dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by recrystallization from hexane to give 17.5 g of compound **4** (74%) as a white solid. ¹H NMR (300 MHz, CD₂Cl₂, 298 K, ppm) δ 8.07 (s, 1H), 7.75 (dd, J = 8.3, 1.4 Hz, 1H), 7.71 (dd, J = 8.1, 1.4 Hz, 1H), 7.47 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.37 (ddd, J = 8.1, 6.9, 1.4 Hz, 1H), 7.20 (s, 1H), 3.99 (s, 3H). ¹³C NMR (75 MHz, CD₂Cl₂, 298 K, ppm) δ 154.16, 134.20, 132.74, 129.96, 127.30, 127.21, 127.14, 125.04, 113.82, 107.27, 56.76. FD-MS (8 kV) m/z : Calcd for C₁₁H₉BrO: 236.0; Found: 235.9 (100%) [M]⁺.



1,4-Diiodo-2,3,5,6-tetra(3-methoxynaphthalen-2-yl)benzene (5). To a Schlenk flask containing activated Mg (480 mg, 20.0 mmol) and 5 mL of dry THF was slowly added a solution of 2-bromo-3-methoxynaphthalene (**4**) (3.79 g, 16.0 mmol) in 20 mL of dry THF. After the mixture was stirred at 60 °C for 2 h, the generated Grignard reagent was transferred into a Schlenk tube charged with hexabromobenzene (1.10 g,

2.00 mmol) under argon and the resulting mixture was stirred at 80 °C for 24 h. Iodine (3.05 g, 12.0 mmol) was added at 0 °C and the reaction mixture was stirred at room temperature for 2 h. After quenching with water, the mixture was extracted with chloroform for three times. The combined organic layers were washed with brine and water and dried over MgSO₄. After removal of the solvents under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: hexane/CH₂Cl₂ = 1 : 1), and then sonicated in 3 mL of toluene, filtrated, and washed with hexane to give 496 mg (26%) of compound **5** as a white solid. ¹H NMR (300 MHz, C₂D₂Cl₄, 298 K, ppm) δ 8.04 – 6.25 (m, 24H, aromatic signals of stereoisomers), 4.20 – 3.45 (m, 12H, methyl signals of stereoisomers). HRMS (ESI) *m/z*: Calcd for C₅₀H₃₇O₄I₂: 955.0781; Found: 955.0767 [M + H]⁺.



12a,26a-Dibora-12,13,26,27-tetraoxa-benzo[1,2,3-*hi*:4,5,6-*h'i'*]dihexacene (2).** To a solution of compound **5** (0.14 g, 0.15 mmol) in anhydrous chlorobenzene (10 mL) was added *t*-BuLi (1.7 M in hexane, 0.35 mL, 0.60 mmol) at –45 °C under argon. After stirring at 0 °C for 3 h, BBr₃ (1.0 M in heptane, 0.40 mL, 0.40 mmol) was added at –45 °C. The reaction mixture was stirred at 40 °C for 24 h. After quenching with methanol, the precipitate was filtrated and washed thoroughly with methanol, water, acetone, dichloromethane, and hexane, to afford 43 mg (43%) of compound **2** as a yellow solid. The solubility of **2** in CD₂Cl₂, CDCl₃, 1,1,2,2-tetrachloroethane-*d*₄, toluene-*d*₈, DMSO-*d*₆, etc. was extremely low, so that even an ¹H NMR spectrum could not be recorded at high temperatures (up to 140 °C). HRMS (MALDI) *m/z*: Calcd for C₄₆H₂₄B₂O₄: 662.1861; Found: 662.1876 [M]⁺.

3. Photophysical Properties

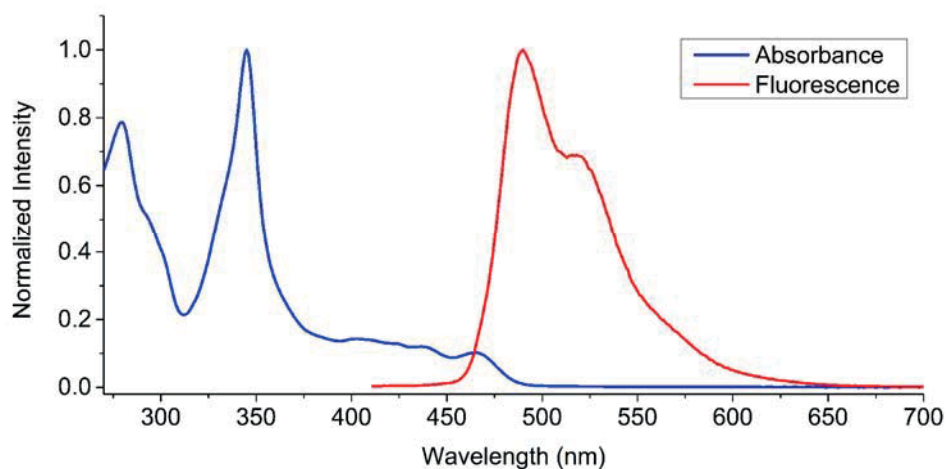


Figure S1. Absorption and emission spectra of **2** in $\text{C}_2\text{H}_2\text{Cl}_4$ solutions. The absorption maximum is at 345 nm (absorption coefficient: $6.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The absorption onset is at 487 nm, corresponding to an optical energy gap of 2.55 eV. According to time-dependent density functional theory (TD-DFT) calculations, the lowest energy absorption is assigned to the HOMO \rightarrow LUMO transition, whereas the absorption maximum is mainly contributed to by the HOMO-5 \rightarrow LUMO transition (Figure S7). A green-yellow fluorescence was observed for compound **2**, with an emission maximum at 490 nm and a quantum yield of 3%.

4. Scanning Tunneling Microscopy

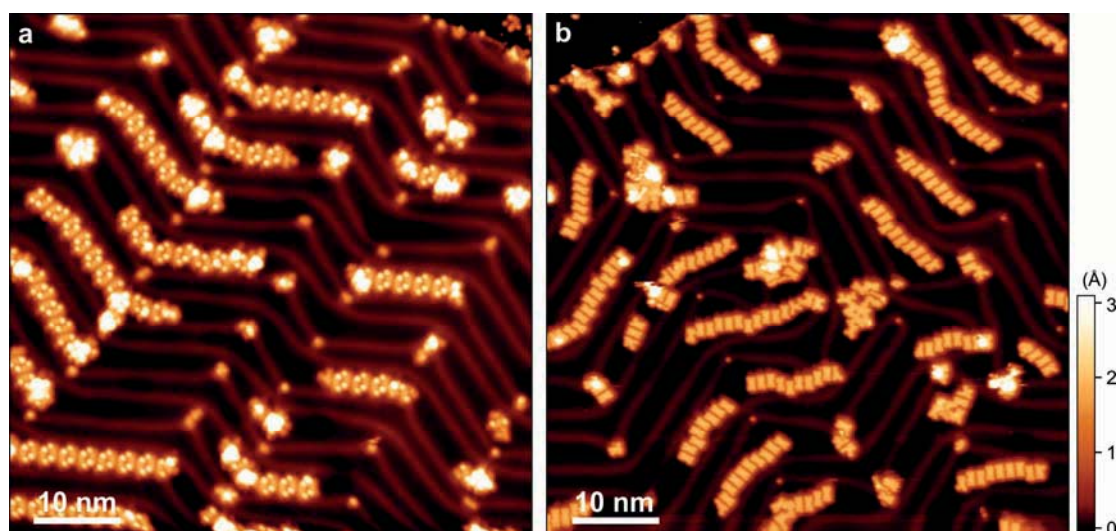


Figure S2. (a) STM image of precursor **2** deposited on Au(111) held at room temperature (tunneling parameters: -2.0 V , 100 pA). (b) STM image of product **1** after annealing to $380 \text{ }^\circ\text{C}$ (tunneling parameters: 0.6 V , 20 pA).

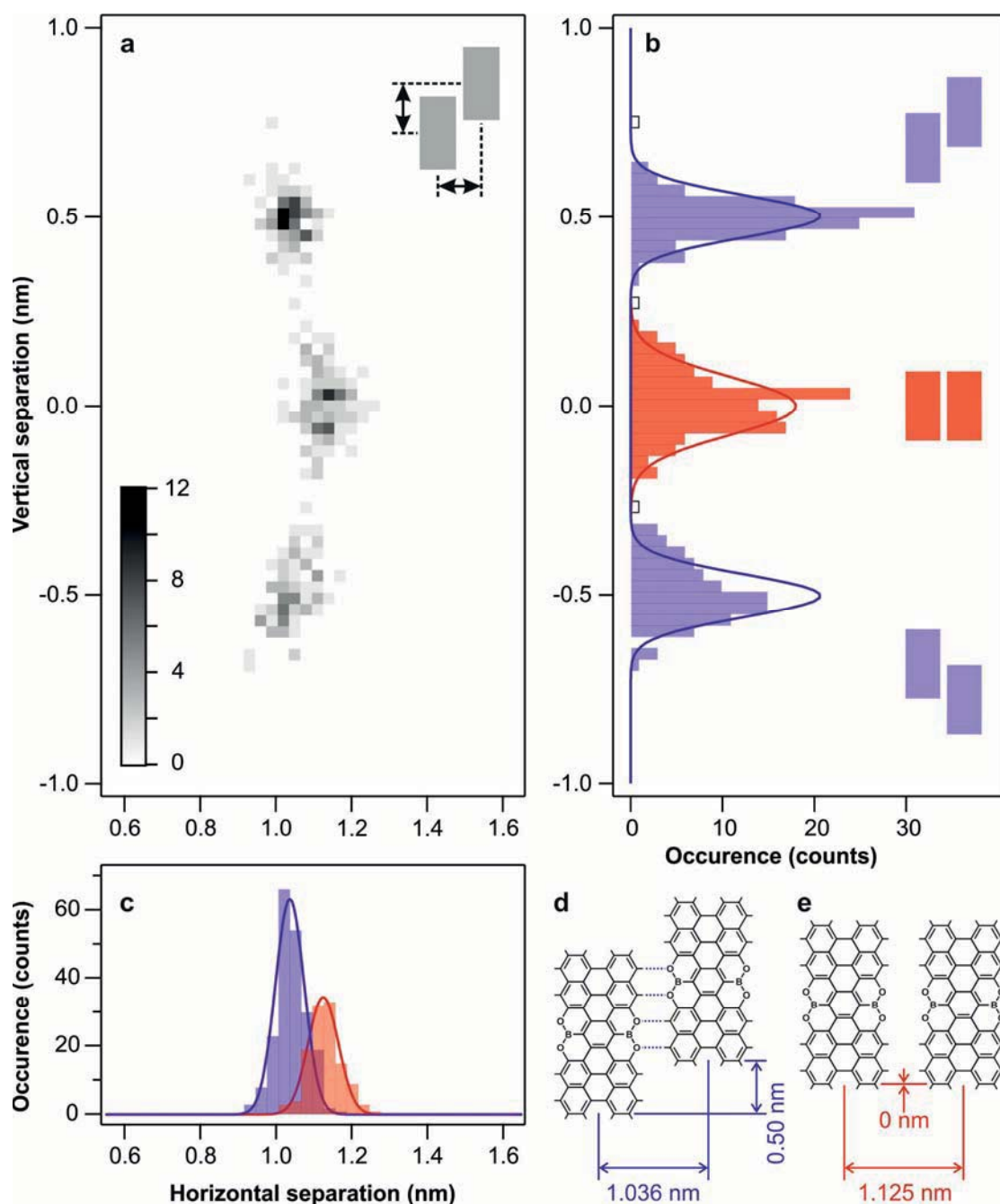


Figure S3. Separation analysis for neighboring perihexacene analogue 1 on Au(111). (a) Distribution map for 326 molecule pairs. (b) Histogram of the vertical separation, with highlighted areas for “abreast” (red) and “stepped” arrangement (blue). (c) Horizontal distribution of molecules in the two regions highlighted in (b) with the corresponding Gauss fits (stepped assembly in blue, abreast assembly in red). Molecular models of (d) the stepped arrangement and (e) the abreast arrangement with vertical and horizontal separation distances. The peripheral short bonds indicate C–H bonds where the hydrogen atoms are omitted for clarity.

Both species, precursor **2** and perihexacene analogue **1**, assemble into chains on the Au(111) surface (Figure S2). In the case of the latter the arrangement along each chain occurs in two different fashions, namely the “stepped” and the “abreast” arrangement. To investigate the differences for the two packing schemes in more detail, we measured the distances within all chains in an STM image of $120 \times 120 \text{ nm}^2$ (containing 73 chains, *i.e.*, dimers to oligomers, incorporating 326 separations). Figure S3a shows the distribution map of the horizontal separation (along the chain) and the vertical separation (perpendicular to the chain) between neighboring molecules. Three distinct areas can be observed. Integrating the number of molecules with the same vertical separation reveals three clear maxima assignable to the abreast and the stepped arrangements, highlighted in red and blue, respectively (Figure S3b). A Gauss fit to the latter reveals an average separation of 0.5 nm, corresponding to an upshift of approximately two zigzag cusps, which can be associated with the formation of four $\text{O}\cdots\text{H}$ hydrogen bonds (up and down shifts are equivalent in case of the symmetric molecule). Next, the distances of the two species are analyzed for their horizontal separation. Figure S3c shows the two histograms and the corresponding fits to the data points, revealing a separation of 1.036 nm for the stepped and 1.125 nm for the abreast arranged molecules. With this information the bond length of the $\text{O}\cdots\text{H}$ hydrogen bonds present in the stepped case can be determined to be 0.19 nm and the $\text{O}\cdots\text{O}$ distance in the abreast case 0.40 nm. The latter translates into a O-Au distance of 0.235 nm for the coordinating Au adatom, which is well within the range expected for metal coordination.

5. Scanning Tunneling Spectroscopy

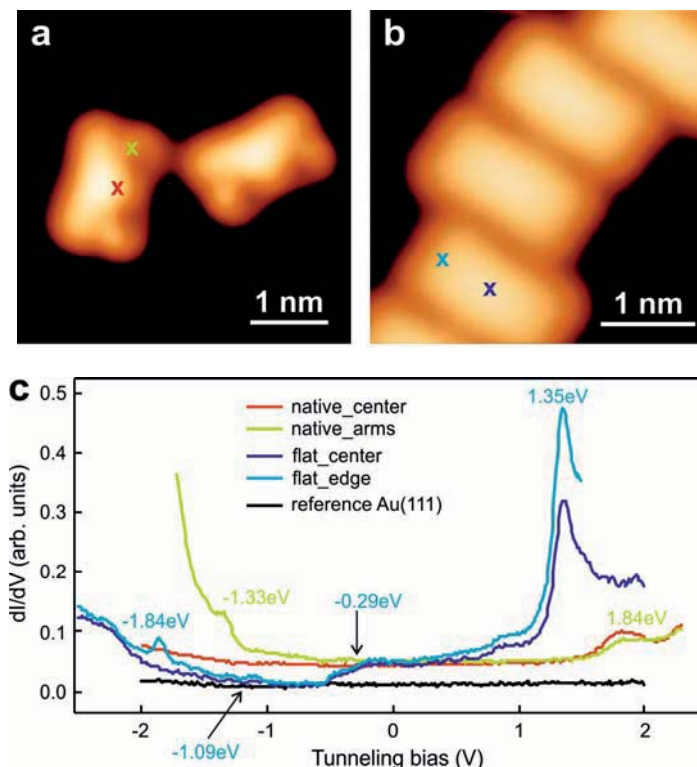


Figure S4. Differential conductance (dI/dV) spectra (c) of precursor **2** and perihexacene analogue **1** with the corresponding positions indicated in the STM images (a,b). Tunneling parameters: (a) 300 mV, 100 pA; (b) 100 mV, 30 pA.

6. Fast XPS Mapping

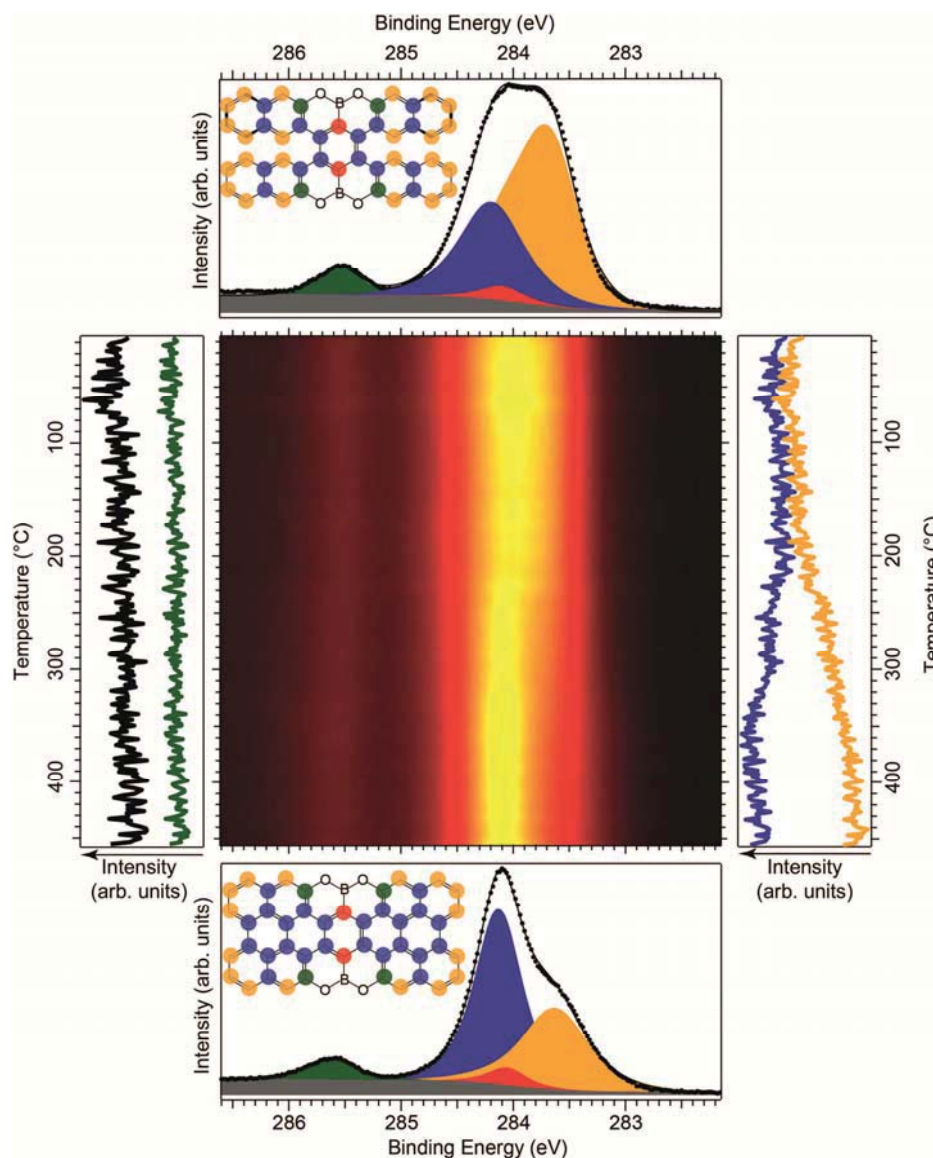


Figure S5. Fast XPS mapping for the C 1s level of **2** deposited on Au(111) and annealed with a heating rate of $0.2\text{ }^{\circ}\text{C s}^{-1}$ (central panel, pass energy = 50 eV). High-resolution C 1s spectra (pass energy = 20 eV) acquired before and after the heating ramp (top and bottom panels) together with representative schemes of the molecule in the two phases. Vertical profiles representing the change of the C–C and C–H components (blue and orange, respectively) are reported in the right panel. The C–O component (green) and the total area of each spectrum (black) are not significantly changing during the annealing, as shown by the curves reported in the left panel.

7. Theoretical Simulations

7.1 Gas-phase quantum chemistry calculations. The geometries were optimized in the gas phase at the B3LYP/6-311G(d,p) level of theory using the Gaussian 09 software package.⁶ Frequencies were calculated for each geometry to confirm the local energy minimum or the transition state. The rate constant (k) at room temperature (298.15 K) was estimated using the Eyring equation⁷

$$k = \kappa(k_B T/h) \exp(-\Delta G^\ddagger/RT)$$

where k is the rate constant; κ is the transmission coefficient which is taken to be unity; k_B is the Boltzmann constant; T is the temperature; h is the Planck constant; ΔG^\ddagger is the Gibbs energy of activation; R is the gas constant.

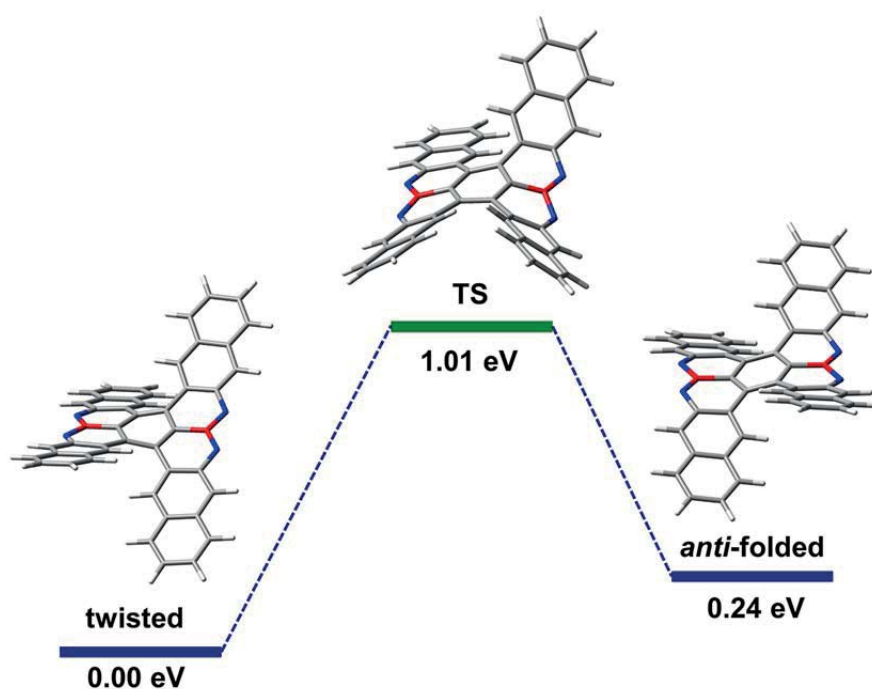


Figure S6. Isomerization process of compound **2** from the twisted to the *anti*-folded conformation. The relative Gibbs free energies were calculated at the B3LYP/6-311G(d,p) level. As estimated from the Eyring equation, the rate constants for the forward isomerization (k_f , from twisted-**2** to *anti*-**2**) and the backward reaction (k_b , from *anti*-**2** to twisted-**2**) are $4.7 \times 10^{-5} \text{ s}^{-1}$ and $5.8 \times 10^{-1} \text{ s}^{-1}$, respectively. Therefore, the thermodynamic equilibrium constant $K (= k_f/k_b)$ of the forward reaction is 8.1×10^{-5} , indicating that compound **2** dominantly adopts the twisted conformation at the equilibrium state at room temperature.

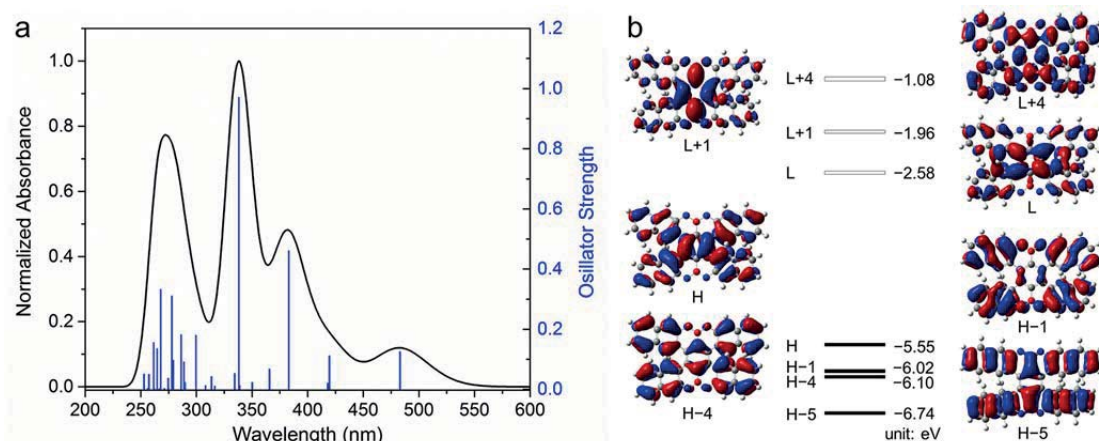


Figure S7. (a) The simulated absorption spectrum of compound **2** (Gaussian line shape, half-width: 0.15 eV) and the oscillator strengths (blue bars) by TDDFT calculations at the B3LYP/6-311G(d,p) level. The twisted conformation was used since it dominantly exists at the equilibrium state. (b) Selected molecular orbitals and energy levels of **2** calculated at the B3LYP/6-311G(d,p) level. H: HOMO; L: LUMO.

Table S1. Selected electronic transitions of **2** calculated by TDDFT method.

Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Configuration
1	2.57	483	0.1258	HOMO→LUMO (0.70534)
2	2.96	420	0.1121	HOMO-1→LUMO (0.69904)
3	3.24	383	0.4612	HOMO-5→LUMO (-0.14374) HOMO-4→LUMO (0.47269) HOMO→LUMO+1 (0.48195)
4	3.67	338	0.9707	HOMO-5→LUMO (0.59951) HOMO-1→LUMO+1 (0.24188) HOMO→LUMO+1 (0.14698) HOMO→LUMO+4 (-0.11746)

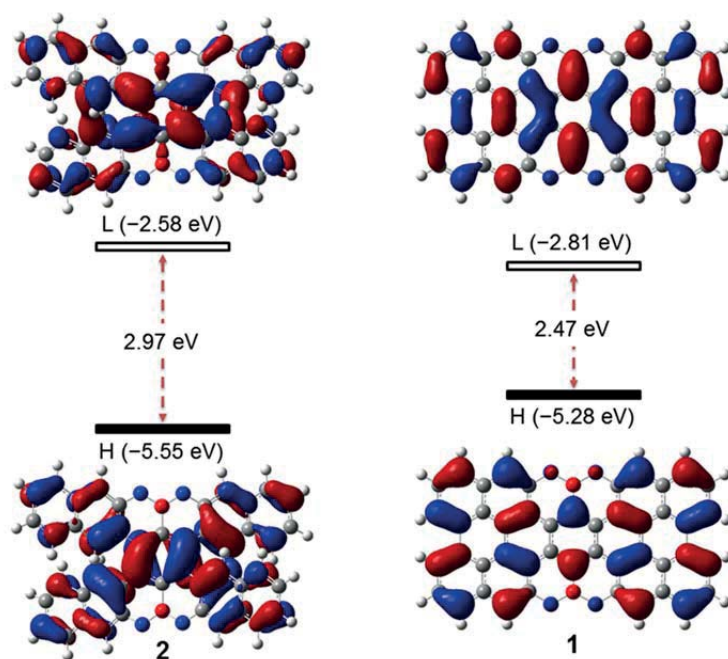


Figure S8. Frontier molecular orbitals of compounds **2** and **1** and associated energy levels according to DFT calculations at the B3LYP/6-311G(d,p) level, showing that **1** has a lower HOMO-LUMO gap than **2**.

7.2 On-Surface Simulations. DFT calculations were performed using the Vienna Ab initio simulation package (VASP)⁸ using the projector augmented wave (PAW) method⁹ and the optB86b-vdW functional, which includes long-range van der Waals (vdW) interactions.¹⁰ Considering the large size of the supercells, the k -point sampling was restricted to the Γ point. A plane-wave cutoff of 400 eV was used. The vacuum regions in all the calculations were larger than 10 Å. We used a four layer thick rectangular 8×5 Au(111) slab in the calculations involving isolated molecules while a four layer thick rectangular 8×4 Au(111) slab was used in the calculations involving hydrogen bonded chains of precursor **2**. The smallest distance between any two atoms in a molecule and its periodic image was larger than 4.5 Å, ensuring minimal interaction.

The energy barriers for the isomerization process of precursor **2** from the twisted to the *anti*-folded conformation were calculated using the climbing-image nudged elastic band (NEB) method.¹¹ We used 16 intermediate structures in our NEB calculations. The bottom two layers in the Au slab were fixed throughout the NEB

calculations while remainder of the atomic coordinates were relaxed using a conjugate-gradient algorithm until all forces were smaller in magnitude than 0.05 eV/Å.

Table S2. Energetics of precursor 2 as single molecules.^a

	Total energy (eV)		Binding energy (eV)
	Gas phase	Substrate-supported	
T	-482.73	-659.79	3.75
A	-482.55	-659.82	3.96

^a T: twisted conformation of **2**; A: *anti*-folded conformation of **2**.

Table S3. Energetics of hydrogen bonded chains of precursor 2.^a

	Total energy (eV)		Binding energy (eV)
	Gas phase	Substrate-supported	
TT	-966.12	-1065.59	7.31
TA	-965.85	-1065.95	7.94
AA	-965.52	-1065.88	8.20

^a The chains are labeled as TT, TA, and AA depending on the conformations of the monomers in the smallest repeating units. The energies shown in this table are for the repeating units, that is, the dimers TT, TA, and AA.

Table S4. Binding energies of hydrogen-bonds in chains of precursor 2.^a

	Gas phase	Substrate-supported
TT	0.71	0.70
TA	0.69	0.83
AA	0.61	0.75

^a The chains are labeled as TT, TA, and AA depending on the conformations of the monomers in the smallest repeating units.

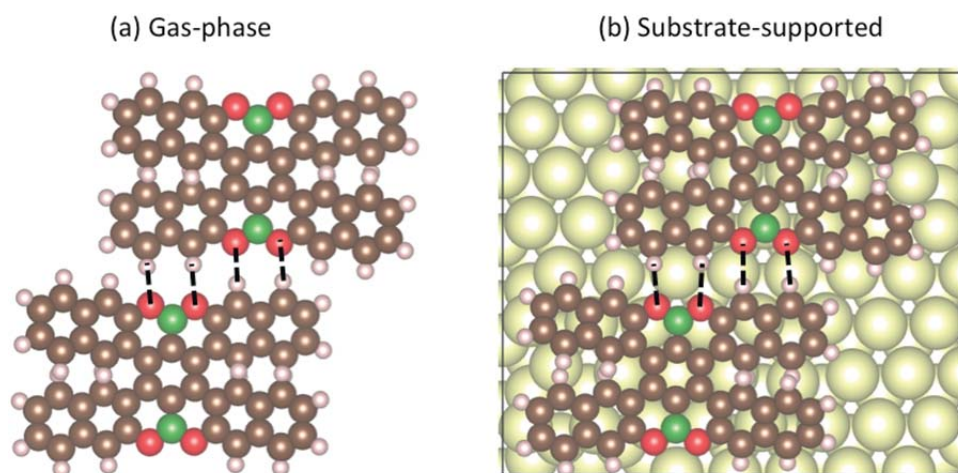


Figure S9. Atomistic schematics of the hydrogen-bonded chains of precursor **2** in the (a) gas-phase and (b) substrate-supported configurations. Hydrogen bonds are depicted by black dashed lines.

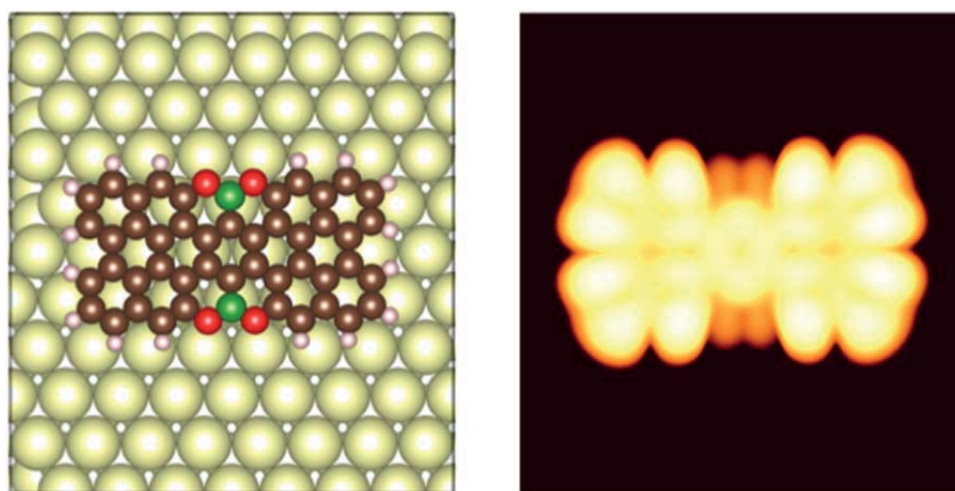


Figure S10. Atomistic schematic of perihexacene analogue **1** (left) and its DFT-simulated STM image (right).

7.3 Assignment of the Main Raman Transitions. The DFT calculations of the Raman spectra of **1** and **2** reported in the main text have been carried out at the B3LYP/6-31G(d,p) level in pre-resonance conditions by using the Gaussian 09 program⁶ and by adopting the excitation wavelengths of 520 nm (**1**) and 530 nm (**2**). These wavelengths were selected because they best reproduced the experimental

observation after systematic inspection of the results of the simulations carried out over a wide range of excitation wavelengths (400–560 nm). The selected wavelengths are both close to the excitation wavelength adopted in the experiments (532 nm). The slight difference between the excitation wavelength selected for **1** vs. **2** (*i.e.*, 520 vs. 530 nm) can be ascribed to the different experimental conditions adopted for recording the spectra of the two molecules (**1** adsorbed on gold vs. **2** as powder). As customary, wavenumbers in all simulated spectra have been uniformly scaled by 0.98 to ease the comparison with experiments. The twisted conformation of **2** was used for these simulations since this is the expected structure of the molecule in the measured powder samples.

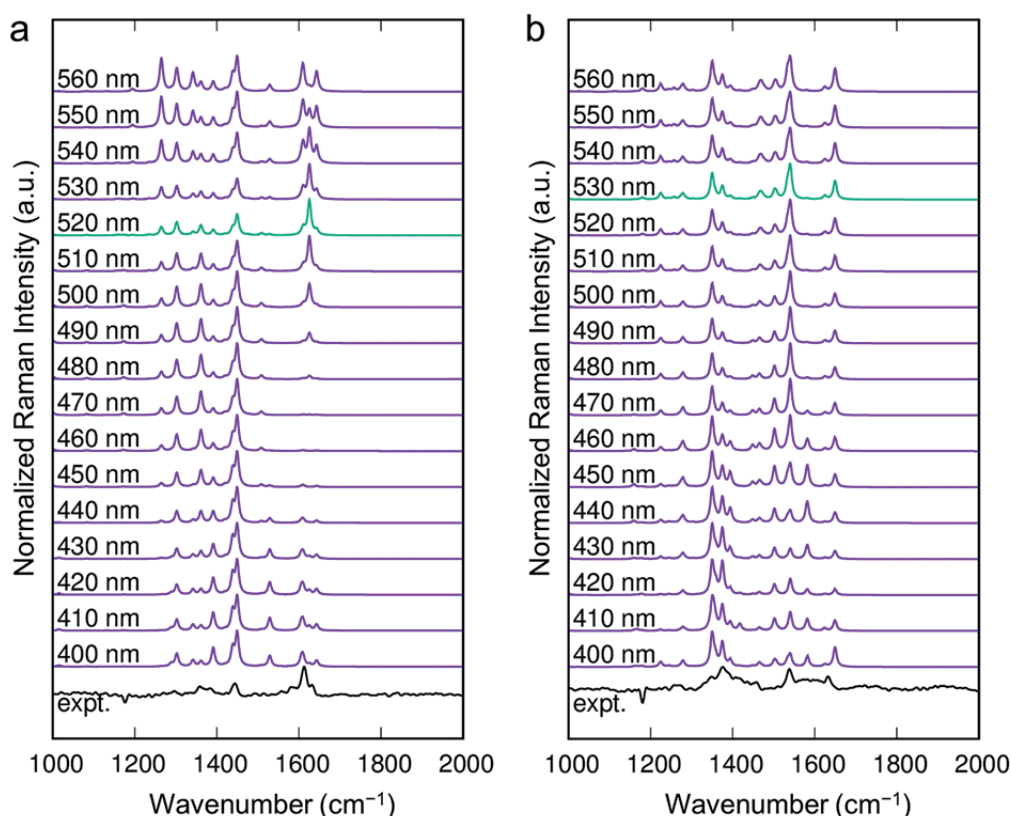


Figure S11. Simulated Raman spectra of (a) **1** and (b) **2** as a function of the excitation wavelength. The spectra selected for Figure 3 in the main text are drawn with green lines. The observed line shape of the G band of **1** (panel a) is the result of an excitation located around 520-530 nm: a weak G signal is obtained for excitations below 500 nm, and above 530 nm the line shape of the G band significantly deviates from the experimental observation. In contrast, the relative intensities of the simulated spectra of **2** are less affected by the choice of the excitation wavelength around 530 nm.

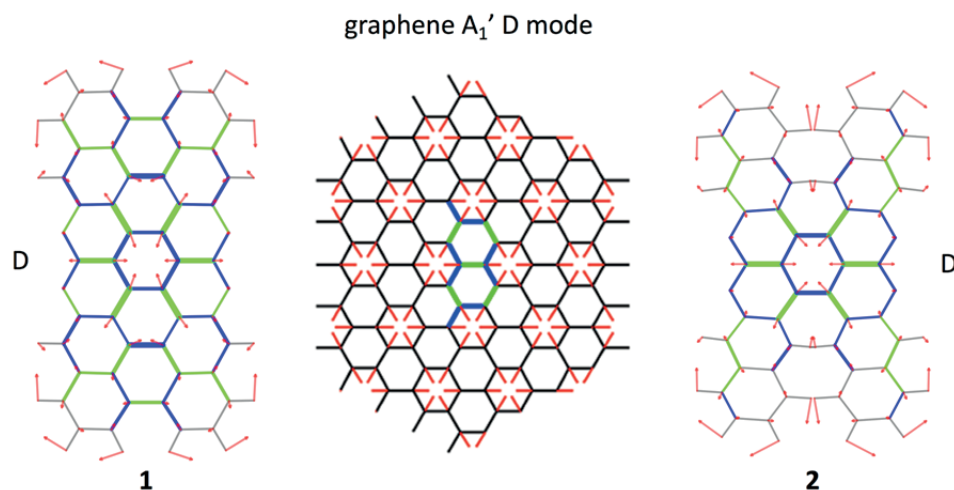


Figure S12. Assignment of the D modes of **1** and **2** based on the nuclear displacements computed for graphene (adapted from the literature¹²). Red arrows (or sticks) represent displacement vectors; CC bonds are represented as green (blue) lines of different thickness according to their relative stretching (shrinking).

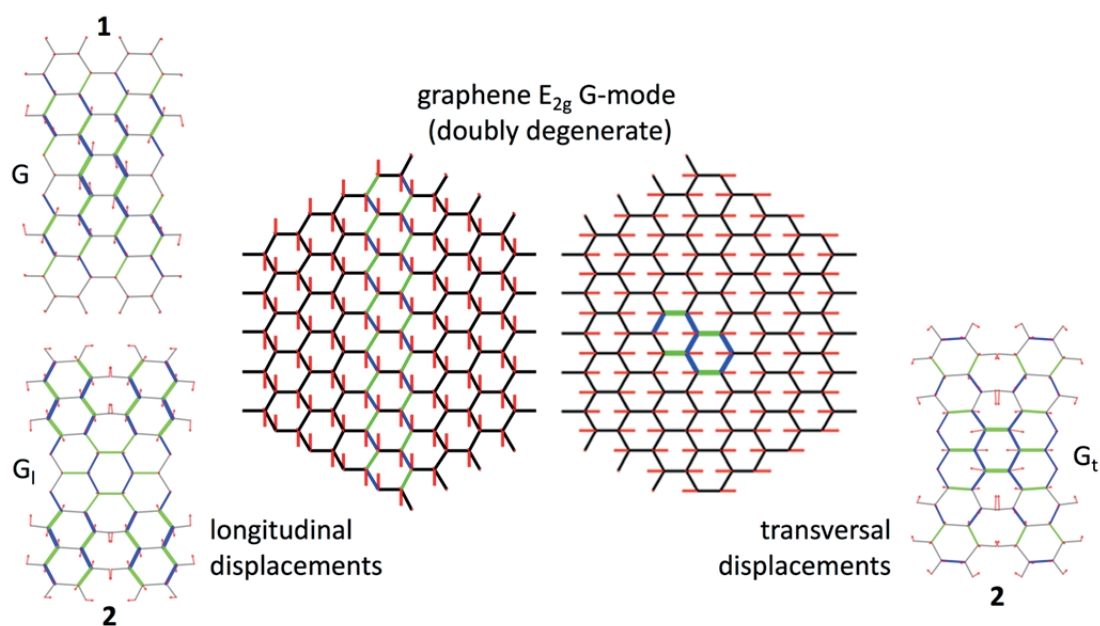


Figure S13. Assignment of the G modes of **1** and **2** based on the nuclear displacements computed for graphene (adapted from the literature¹²). Red arrows (or sticks) represent displacement vectors; CC bonds are represented as green (blue) lines of different thickness according to their relative stretching (shrinking).

Figure S12 and S13 show the nuclear displacements of the normal modes of **1** and **2** assigned to the relevant observed Raman lines. The D modes of **1** and **2** are

computed respectively at 1479 and 1378 cm^{-1} ; the associated nuclear displacement patterns at the center of the molecule closely match the characteristic D mode of graphene (Figure S12). Interestingly, the Raman spectrum of **2** shows one transversal G mode (G_t , computed at 1572 cm^{-1}) and one longitudinal G mode (G_l , computed at 1683 cm^{-1}). This naming scheme has been adopted after inspecting the direction of the displacements of the π -conjugated carbon atoms with respect to the shape of the molecule (Figure S13). In molecule **1** the observed G peak is longitudinal (computed at 1659 cm^{-1}) and the associated transversal component (computed at 1677 cm^{-1}) is comparatively weak. The latter is predicted and observed as the higher wavenumber shoulder of the G line (see Figure 3 in the main text). Based on DFT calculations, the lower wavenumber shoulder of the G line of **1** is computed at 1643 cm^{-1} and the associated normal mode displays a collective ring stretching pattern not directly related with graphene G mode.

Appendix:

Cartesian coordinates obtained in gas-phase DFT calculations at the B3LYP/6-311G(d,p) level

Optimized twisted 2									
Tag	Symbol	X	Y	Z					
1	C	-1.240631	0.696511	0.146523	18	C	2.275234	2.939918	-0.661506
2	C	-1.240631	-0.696511	-0.146525	19	C	-2.372390	-1.507764	-0.638124
3	C	0.000007	-1.353736	-0.000012	20	C	2.372399	-1.507775	0.638110
4	C	1.240644	-0.696513	0.146513	21	C	2.275235	-2.939918	0.661501
5	C	1.240645	0.696514	-0.146514	22	C	3.299040	-3.728766	1.127544
6	C	0.000007	1.353736	0.000011	23	C	4.475699	-3.157160	1.656348
7	C	-2.372390	1.507763	0.638123	24	C	4.567061	-1.730559	1.723311
8	C	2.372399	1.507775	-0.638111	25	C	3.505950	-0.952855	1.216853
9	C	-2.275227	2.939906	0.661540	26	C	-3.505951	-0.952830	-1.216837
10	C	-3.299037	3.728744	1.127589	27	C	-4.567067	-1.730525	-1.723298
11	C	-4.475701	3.157127	1.656370	28	C	-4.475702	-3.157127	-1.656371
12	C	-4.567064	1.730525	1.723302	29	C	-3.299036	-3.728744	-1.127595
13	C	-3.505948	0.952830	1.216840	30	C	-2.275225	-2.939906	-0.661547
14	C	3.505953	0.952855	-1.216850	31	B	0.000005	2.880034	0.000021
15	C	4.567063	1.730559	-1.723307	32	B	0.000007	-2.880034	-0.000027
16	C	4.475700	3.157160	-1.656349	33	O	-1.140006	3.590827	0.249379
17	C	3.299039	3.728766	-1.127549	34	O	1.140012	3.590832	-0.249334
					35	O	-1.140003	-3.590827	-0.249390
					36	O	1.140015	-3.590832	0.249324

37	C	-5.553233	3.937817	2.152209	2	C	-1.251802	-0.701921	0.103975
38	C	-6.663181	3.335707	2.690902	3	C	0.000001	-1.334466	0.272765
39	C	-6.752729	1.923357	2.764028	4	C	1.251803	-0.701921	0.103975
40	C	-5.729201	1.140860	2.293168	5	C	1.251803	0.701920	-0.103977
41	C	-5.729207	-1.140860	-2.293159	6	C	0.000000	1.334465	-0.272767
42	C	-6.752734	-1.923357	-2.764019	7	C	-2.422582	1.614656	-0.073800
43	C	-6.663184	-3.335707	-2.690898	8	C	2.422582	1.614657	-0.073795
44	C	-5.553234	-3.937817	-2.152209	9	C	-2.338269	2.899367	-0.705748
45	C	5.553226	-3.937860	2.152183	10	C	-3.399065	3.771292	-0.725974
46	C	6.663168	-3.335761	2.690901	11	C	-4.600765	3.467346	-0.050888
47	C	6.752714	-1.923412	2.764057	12	C	-4.675029	2.241460	0.682978
48	C	5.729191	-1.140906	2.293202	13	C	-3.576392	1.356166	0.650551
49	C	5.729196	1.140905	-2.293194	14	C	3.576392	1.356166	0.650556
50	C	6.752719	1.923412	-2.764049	15	C	4.675028	2.241460	0.682986
51	C	6.663171	3.335760	-2.690897	16	C	4.600765	3.467347	-0.050877
52	C	5.553227	3.937859	-2.152183	17	C	3.399066	3.771295	-0.725964
53	H	-3.168290	4.804239	1.108007	18	C	2.338270	2.899369	-0.705740
54	H	-3.591124	-0.123331	1.286069	19	C	-2.422582	-1.614658	0.073797
55	H	3.591128	-0.123305	-1.286102	20	C	2.422582	-1.614658	0.073794
56	H	3.168289	4.804260	-1.107950	21	C	2.338271	-2.899370	0.705740
57	H	3.168292	-4.804261	1.107942	22	C	3.399067	-3.771294	0.725964
58	H	3.591124	0.123305	1.286108	23	C	4.600767	-3.467346	0.050878
59	H	-3.591128	0.123331	-1.286062	24	C	4.675030	-2.241459	-0.682985
60	H	-3.168286	-4.804239	-1.108017	25	C	3.576392	-1.356166	-0.650557
61	H	-5.483753	5.019157	2.101086	26	C	-3.576393	-1.356167	-0.650551
62	H	-7.479659	3.942113	3.066664	27	C	-4.675031	-2.241459	-0.682976
63	H	-7.635847	1.464603	3.193682	28	C	-4.600767	-3.467346	0.050888
64	H	-5.794643	0.059166	2.343221	29	C	-3.399066	-3.771294	0.725971
65	H	-5.794650	-0.059165	-2.343208	30	C	-2.338269	-2.899369	0.705744
66	H	-7.635854	-1.464602	-3.193669	31	B	0.000001	2.722907	-0.920495
67	H	-7.479663	-3.942112	-3.066659	32	B	0.000001	-2.722909	0.920491
68	H	-5.483753	-5.019157	-2.101091	33	O	-1.167845	3.339304	-1.273767
69	H	5.483747	-5.019199	2.101038	34	O	1.167846	3.339308	-1.273758
70	H	7.479642	-3.942173	3.066659	35	O	-1.167844	-3.339309	1.273759
71	H	7.635827	-1.464667	3.193731	36	O	1.167847	-3.339309	1.273757
72	H	5.794632	-0.059212	2.343278	37	C	-5.715786	4.346158	-0.033871
73	H	5.794639	0.059212	-2.343266	38	C	-6.845681	4.028591	0.678634
74	H	7.635833	1.464666	-3.193719	39	C	-6.918678	2.818265	1.411380
75	H	7.479645	3.942173	-3.066655	40	C	-5.858487	1.947297	1.414212
76	H	5.483746	5.019199	-2.101042	41	C	-5.858490	-1.947295	-1.414208
Optimized <i>anti</i> -folded 2					42	C	-6.918682	-2.818261	-1.411375
					43	C	-6.845684	-4.028588	-0.678630
					44	C	-5.715789	-4.346157	0.033872
					45	C	5.715788	-4.346158	0.033860

Tag	Symbol	X	Y	Z
1	C	-1.251802	0.701919	-0.103978

46	C	6.845683	-4.028589	-0.678645	11	C	-4.798896	2.212935	0.972502
47	C	6.918679	-2.818262	-1.411389	12	C	-4.677283	3.558674	0.518875
48	C	5.858487	-1.947295	-1.414219	13	C	-2.371537	-1.586550	-0.349702
49	C	5.858486	1.947296	1.414221	14	C	-3.592141	-1.705980	0.295048
50	C	6.918677	2.818263	1.411391	15	C	-2.132547	-2.611574	-1.342049
51	C	6.845680	4.028591	0.678648	16	C	-4.634626	-2.561748	-0.135327
52	C	5.715786	4.346159	-0.033857	17	C	-3.132029	-3.408197	-1.838947
53	H	-3.274819	4.720997	-1.232674	18	C	-4.430450	-3.378660	-1.286092
54	H	-3.654087	0.437241	1.215132	19	C	2.452525	1.647647	-0.291210
55	H	3.654087	0.437240	1.215136	20	C	2.367231	3.077395	-0.269691
56	H	3.274820	4.721001	-1.232661	21	C	3.670849	1.123059	-0.706930
57	H	3.274822	-4.721000	1.232662	22	C	3.454748	3.886946	-0.495794
58	H	3.654088	-0.437240	-1.215137	23	C	4.803872	1.919340	-0.973391
59	H	-3.654090	-0.437241	-1.215131	24	C	4.708466	3.339125	-0.832624
60	H	-3.274819	-4.720999	1.232670	25	C	2.379663	-1.496193	0.357980
61	H	-5.658871	5.275653	-0.590228	26	C	3.378316	-1.206155	1.271120
62	H	-7.690746	4.707876	0.684758	27	C	2.390915	-2.792515	-0.243420
63	H	-7.817924	2.583494	1.969226	28	C	4.425297	-2.110485	1.555052
64	H	-5.911455	1.017103	1.969786	29	C	3.403148	-3.689068	-0.012332
65	H	-5.911459	-1.017100	-1.969781	30	C	4.451641	-3.374733	0.882712
66	H	-7.817929	-2.583490	-1.969219	31	B	0.011182	2.988235	-0.055784
67	H	-7.690750	-4.707873	-0.684753	32	B	0.169190	-2.521193	-0.953596
68	H	-5.658873	-5.275652	0.590228	33	O	1.169745	3.708514	-0.090243
69	H	5.658874	-5.275653	0.590215	34	O	-1.130118	3.712716	-0.202120
70	H	7.690748	-4.707874	-0.684770	35	O	1.364874	-3.173552	-1.073175
71	H	7.817924	-2.583490	-1.969236	36	O	-0.860483	-2.929434	-1.753297
72	H	5.911455	-1.017099	-1.969792	37	H	-3.224543	5.020151	-0.168952
73	H	5.911454	1.017100	1.969793	38	H	-3.811230	0.376143	1.294072
74	H	7.817922	2.583492	1.969238	39	H	3.311266	4.960075	-0.452698
75	H	7.690745	4.707876	0.684774	40	H	3.780461	0.058062	-0.835561
76	H	5.658871	5.275655	-0.590213	41	H	3.369484	-0.249300	1.779715
					42	H	3.369781	-4.652362	-0.507461
					43	H	-2.873250	-4.129691	-2.604782
					44	H	-3.764330	-1.185462	1.218818
					45	C	5.514181	-4.274869	1.158539
					46	C	6.499801	-3.942527	2.055108
					47	C	6.473290	-2.694073	2.723053
					48	C	5.459759	-1.801454	2.479758
					49	H	5.436978	-0.842883	2.987215
					50	H	5.533680	-5.232786	0.649875
					51	H	7.305717	-4.639098	2.256979
					52	H	7.258842	-2.446934	3.427857
					53	C	6.045586	1.348659	-1.368725
					54	C	7.138828	2.143607	-1.601750

Optimized TS-2

Tag	Symbol	X	Y	Z
1	C	1.241943	-0.588274	0.091458
2	C	0.011388	-1.229358	-0.139474
3	C	-1.261624	-0.618745	-0.048011
4	C	-1.275076	0.804763	0.182985
5	C	-0.009965	1.465077	0.080498
6	C	1.250726	0.823853	0.007101
7	C	-2.443988	1.719345	0.374757
8	C	-2.332148	3.126067	0.070234
9	C	-3.679227	1.355561	0.890616
10	C	-3.403493	3.984995	0.096241

55	H	8.082002	1.699580	-1.898701	20	C	2.431969	-1.433865	0.000106
56	C	7.043300	3.550092	-1.454279	21	C	2.406833	-2.866436	-0.000054
57	H	7.915656	4.166239	-1.641451	22	C	3.586809	-3.558198	-0.000081
58	C	5.858713	4.134302	-1.080796	23	C	4.837807	-2.869294	-0.000028
59	H	5.784870	5.211270	-0.974195	24	C	4.876402	-1.436876	-0.000008
60	H	6.114747	0.271309	-1.475175	25	C	3.646899	-0.724744	0.000073
61	C	-5.884976	-2.618988	0.534616	26	C	-3.646899	-0.724744	0.000074
62	C	-6.896662	-3.420601	0.064950	27	C	-4.876402	-1.436876	-0.000007
63	H	-7.850617	-3.451306	0.578648	28	C	-4.837807	-2.869294	-0.000028
64	C	-6.700275	-4.208381	-1.094058	29	C	-3.586809	-3.558198	-0.000081
65	H	-7.508025	-4.833346	-1.458000	30	C	-2.406833	-2.866436	-0.000053
66	C	-5.494066	-4.192794	-1.752151	31	B	0.000000	2.898955	0.000125
67	H	-5.337671	-4.809539	-2.630628	32	B	0.000000	-2.898955	0.000125
68	H	-6.034547	-2.011874	1.421457	33	O	-1.209225	3.566602	-0.000091
69	C	-5.809700	4.412303	0.571182	34	O	1.209225	3.566602	-0.000092
70	C	-7.006398	3.950652	1.061664	35	O	-1.209225	-3.566602	-0.000091
71	H	-7.867467	4.608563	1.097580	36	O	1.209225	-3.566602	-0.000092
72	C	-7.127483	2.618632	1.527669	37	C	-6.059188	3.576001	-0.000072
73	H	-8.078560	2.271241	1.914547	38	C	-7.258603	2.894146	-0.000096
74	C	-6.048277	1.771670	1.486285	39	C	-7.293138	1.493675	-0.000077
75	H	-6.141398	0.749163	1.836278	40	C	-6.122997	0.737773	-0.000046
76	H	-5.713761	5.434977	0.222642	41	C	-6.122997	-0.737773	-0.000046

Optimized 1

Tag	Symbol	X	Y	Z					
1	C	-1.213412	0.705859	0.000263	45	C	6.122997	0.737773	-0.000046
2	C	-1.213412	-0.705859	0.000264	46	C	7.293137	1.493675	-0.000077
3	C	0.000000	-1.389250	0.000330	47	C	7.258603	2.894146	-0.000096
4	C	1.213412	-0.705859	0.000262	48	C	6.059188	3.576001	-0.000071
5	C	1.213412	0.705859	0.000262	49	C	6.059188	-3.576001	-0.000071
6	C	0.000000	1.389250	0.000329	50	C	7.258603	-2.894146	-0.000096
7	C	-2.431969	1.433865	0.000107	51	C	7.293137	-1.493675	-0.000077
8	C	2.431969	1.433865	0.000106	52	C	6.122997	-0.737773	-0.000046
9	C	-2.406833	2.866436	-0.000053	53	H	-3.569915	4.641503	-0.000143
10	C	-3.586809	3.558198	-0.000081	54	H	3.569915	4.641503	-0.000143
11	C	-4.837807	2.869294	-0.000028	55	H	3.569915	-4.641503	-0.000143
12	C	-4.876402	1.436876	-0.000007	56	H	-3.569915	-4.641503	-0.000143
13	C	-3.646899	0.724744	0.000074	57	H	-6.042574	4.660227	-0.000097
14	C	3.646899	0.724744	0.000073	58	H	-8.192099	3.445611	-0.000130
15	C	4.876402	1.436876	-0.000008	59	H	-8.258680	1.005355	-0.000096
16	C	4.837807	2.869294	-0.000028	60	H	-8.258680	-1.005355	-0.000096
17	C	3.586809	3.558198	-0.000081	61	H	-8.192099	-3.445611	-0.000130
18	C	2.406833	2.866436	-0.000054	62	H	-6.042574	-4.660227	-0.000097
19	C	-2.431969	-1.433865	0.000108	63	H	8.258680	1.005355	-0.000096

64	H	8.192099	3.445611	-0.000129	67	H	8.192099	-3.445611	-0.000129
65	H	6.042574	4.660227	-0.000096	68	H	8.258680	-1.005355	-0.000096
66	H	6.042574	-4.660227	-0.000096					

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9. NMR and MS Spectra

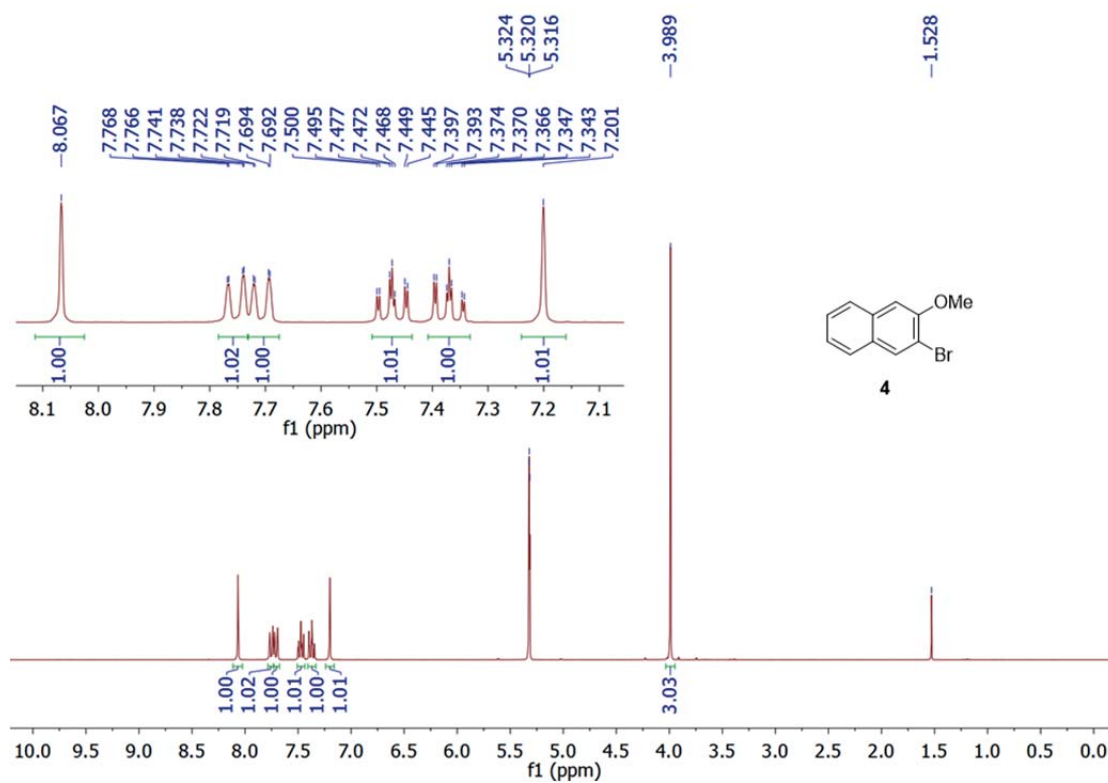


Figure S14. ¹H NMR spectrum of compound 4 (300 MHz, CD₂Cl₂, 298 K).

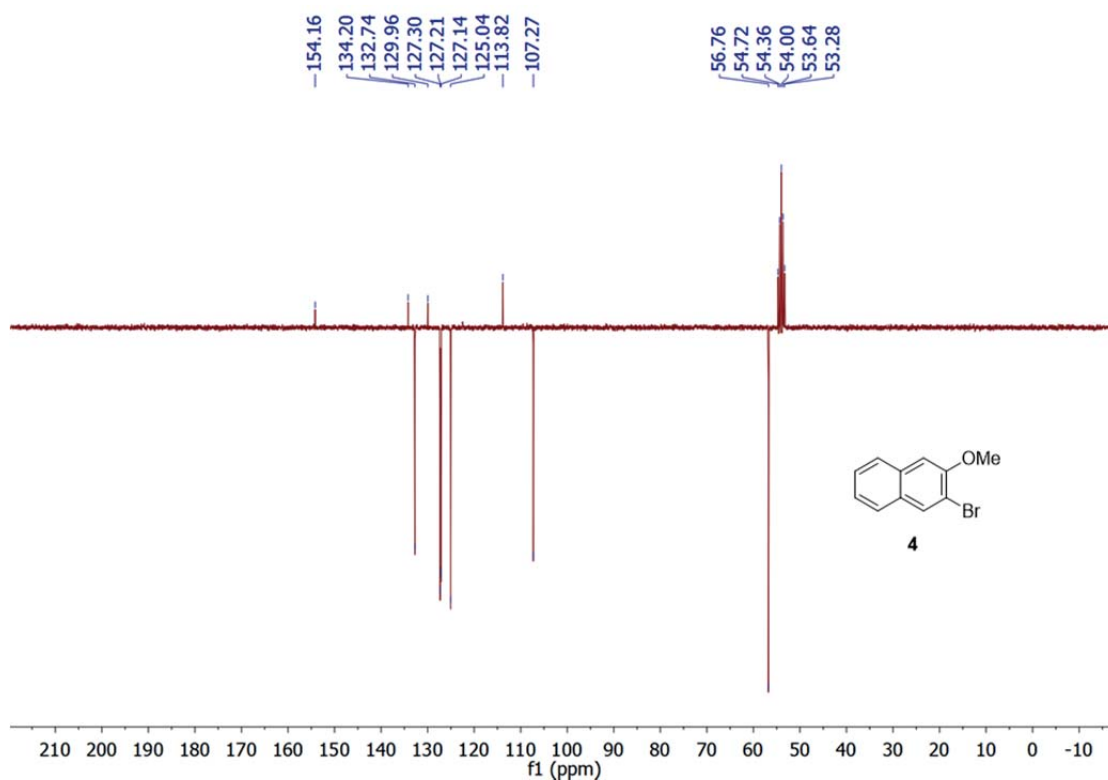


Figure S15. ¹³C NMR (APT) spectrum of compound 4 (75 MHz, CD₂Cl₂, 298 K).

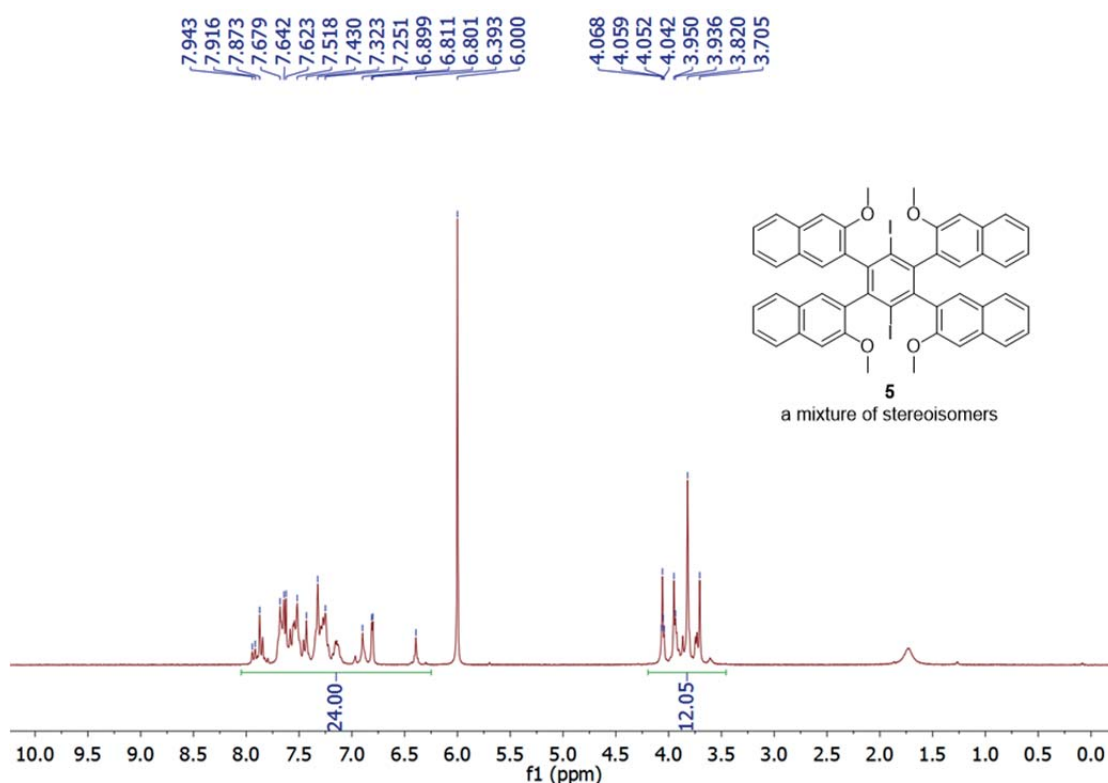


Figure S16. ^1H NMR spectrum of compound **5** (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 298 K).

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 200.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

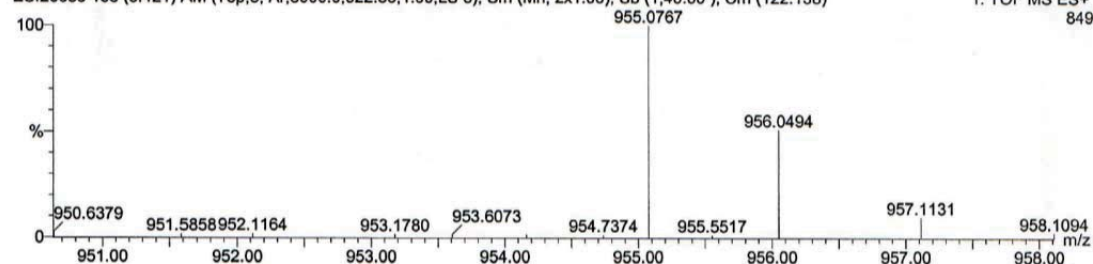
Monoisotopic Mass, Odd and Even Electron Ions

12 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Wang, W181-I, Muellen

ESI26685 138 (3.421) AM (Top,8, Ar,8000.0,922.36,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (122:138)

1: TOF MS ES+
849



Minimum:

Maximum: 200.0 20.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
955.0767	955.0781	-1.4	-1.5	31.5	1	C50 H37 O4 127I2

Figure S17. High-resolution ESI-MS analysis of compound **5**.

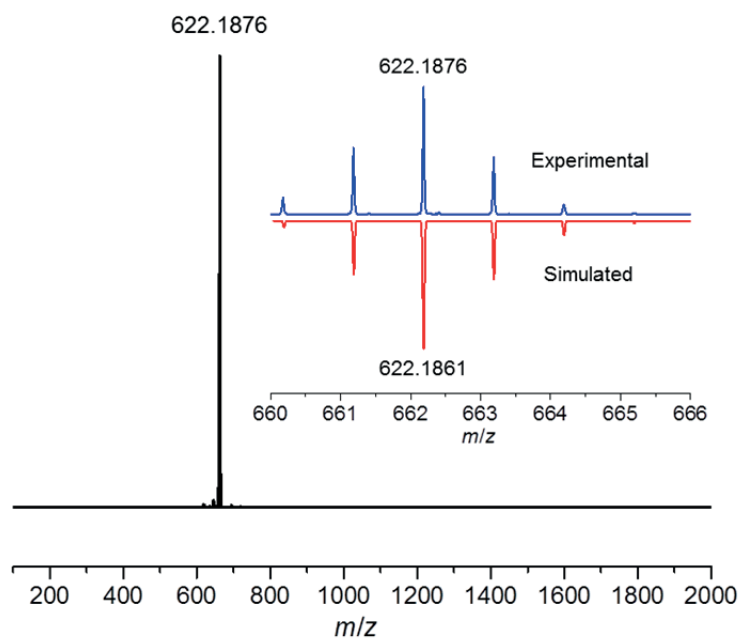


Figure S18. High-resolution MALDI-TOF MS spectrum of compound **2**. Inset: the corresponding experimental and simulated isotopic distributions.