Supplementary Material (ESI) for Chemical Communications

Supplementary Information

On the route to mimic natural movements: Synthesis and photophysical properties of a molecular arachnoid

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1. Synthesis

General. NMR spectra were obtained on a Varian Gemini 200 spectrometer (200 MHz ^{1}H-NMR and 50 MHz ^{13}C-NMR) and on a Jeol JNM-EX400 (400 MHz ^{1}H-NMR). Chemical shifts are reported in ppm using the solvent residual signal as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_3OD: δ_H = 3.31 ppm, δ_C = 49.00 ppm; C_5D_5N: δ_H = 7.19, 7.55, 8.71 ppm, δ_C = 123.5, 135.5, 149.5 ppm; $(CD_3)_2SO$: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Coupling constants (*J*) are given in Hz. The resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *dd* (doublet of doublets), *m* (multiplet), *br* (broad signal). IR spectra (KBr) were recorded on a Perkin Elmer 2000 spectometer by Mr. Paolo de Baseggio. Mass spectrometry measurements: Electrospray Ionization (ESI) performed on a Perkin-Elmer API1 at 5600 eV and Electron Impact (EI) performed on a Ion trap GCQ Finnigan Thermoquest at 70 eV were recorded at Università degli Studi di Trieste by Dr. Fabio Holland. Melting Points (m.p.) were measured on a *Büchi* SMP-20. Chemicals were purchased from, *Aldrich*, *Fluka* and *Riedel* and used as received.

Solvents were purchased from *JTBaker* and *Aldrich*, and deuterated solvents from *Cambridge Isotope Laboratories*. The solutions were degassed following the "freeze-pump-thaw" cycles methodology. Solvents such as CH_2Cl_2, toluene, THF, and NEt_3 were distilled from Na/benzophenone, and CaH_2 respectively. Synthesis of 1,3,6,8-tetrabromopyrene and 1,3,6,8-tetraethynylpyrene were prepared according to literature procedures.

Molecular Arachnoid **1**. To a degassed solution of dry THF (1 mL) and *i*Pr_2NH (1 ml), tetrabromopyrene **9** (0.040 g, 0.08 mmol), $[Pd(PPh_3)_2]Cl_2$ (0.006 g, 0.008 mmol), CuI (0.002 g, 0.008 mmol), PPh_3 (0.004 g, 0.016 mmol) and compound **8** (0.230 g, 0.47 mmol) were added and the solution degassed. The reaction mixture was allowed to react at room temperature under Ar atmosphere for 20 h. The residue was then filtered through celite and the solvent evaporated. Purification of the crude by CC (cyclohexane/CH_2Cl_2, 7:3) yielded **1** (0.02 g, 12%). UV/Vis (CH_2Cl_2): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) = 313 (102796), 329 (101075), 370 (97742), 414 (110430), 490 nm (155914 $м^{-1}$ cm^{-1}). ν_{max}/cm^{-1} 3039, 2923 and 2853 (C–H), 2200 (C≡C), 1607, 1590 and 1519 (C=C), 1367 (CH_3), 1128 (C=C), 847 and 811 (C–H). δ_H(500 MHz; $CDCl_3$; Me_4Si) 8.06 (4 H, dt, Pyrene), 7.88 (2 H, dt, *J* 8.5, Pyrene), 7.78 (16 H, dt, *J* 7, Ph), 7.63 (8 H, dt, *J* 7.5, Ph), 7.55 (8 H, dt, *J* 7.5, Ph), 7.43 (8 H, dt, *J* 8.5, Ph), 6.57 (8 H, dt, *J* 8, Ph), 3.27 (16 H, t, N(8×CH_2)), 1.59 (16 H, m, 8×CH_2), 1.34 (48 H, s, 24×CH_2), 0.93 (24 H, t, 8×CH_3). HR-MALDI-TOF-MS (Matrix : DCTB) calcd for $C_{152}H_{158}N_{12}^+$ (M^+) 2151.2732, found 2151.2788.

Bis-azobenezene **12**. This compound is obtained as a side product from the reaction between tetra-bromopyrene and ethynylazobenzene **8**. UV/Vis (CH_2Cl_2): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) = 315 (40306), 391 (43367), 473 nm (50510 $м^{-1}$ cm^{-1}). ν_{max}/cm^{-1} 2925 and 2854 (C–H), 2202 (C≡C), 1606, 1590 and 1519 (C=C), 1369 (CH_3), 1129

(C=C), 854 and 813 (C–H). δ_H(500 MHz; $CDCl_3$; Me_4Si) 7.91 (8 H, dt, *J* 6, Ph), 7.65 (8 H, dd, *J* 7.5 and 8, Ph), 7.39 (4 H, dt, *J* 8, Ph), 6.59 (4 H, dt, *J* 7.5, Ph), 3.29 (8 H, t, *J* 7.5, N(2×CH_2)), 1.59 (8 H, m, 4×CH_2), 1.33 (24 H, s, 12×CH_2), 0.91 (12 H, t, 4×CH_3). HR-MALDI-TOF-MS (Matrix : DCTB) calcd for $C_{68}H_{76}N_6^+$ (M^+) 976.6131, found 976.6125.

Tetrasubstituted pyrene molecule **11**. To a degassed solution of dry THF (2 mL) and Et_3N (6 mL), 4-iodo-N,N-dihexylaniline **94** (0.240 g, 0.85 mmol), [$PdCl_2(PPh_3)_2$] (40 mg, 0.034 mmol), and CuI (13 mg, 0.068 mmol) were added and the resulting mixture degassed a second time. 1,3,6,8-Tetraethynylpyrene **10** (0.05 g, 0.17 mmol) was added, the solution degassed one last time, and stirred overnight at 45 °C under Ar. Notably, already after a few minutes the reaction color changed to red. The resulting red mixture was filtered over celite and filter washed with CH_2Cl_2. Removal of the solvents under vacuum and purification of the crude by CC (cyclohexane/CH_2Cl_2 2:1) yielded **11** (0.082 g, 37%) as a dark red solid. m.p.: 101-104 ºC. ν_{max}/cm^{-1} 3434.8, 2924.5, 2853.8, 2364.6, 2189.9, 1605.9, 1591.8, 1519.3, 1466.2, 1404.1, 1369.7, 1292.9, 1253.1, 1184.0, 1138.7, 1065.5, 809.3. δ_H(200 MHz; $CDCl_3$) 8.69 (4H, s, Pyrene), 8.32 (2H, s, Pyrene), 7.55 (8H, d, *J* 8.7, Ph), 6.64 (8H, d, *J* 8.7, Ph), 3.31 (16H, t, N(8×CH_2)), 1.57 (16H, m, 8×CH_2), 1.33 (48H, s, 24×CH_2), 0.91 (24H, t, 8×CH_3). δ_C (50 MHz; $CDCl_3$) 148.18, 133.16, 131.07, 128.55, 126.45, 124.57, 119.58, 111.4, 108.94, 97.55, 86.25, 51.17, 31.90, 27.41, 27.01, 22.89, 14.26; MS (5600 eV, ESI): calcd for $C_{96}H_{126}N_4$ 1336.05, found 1337 $(M)^+$.

2. Photophysical Characterization

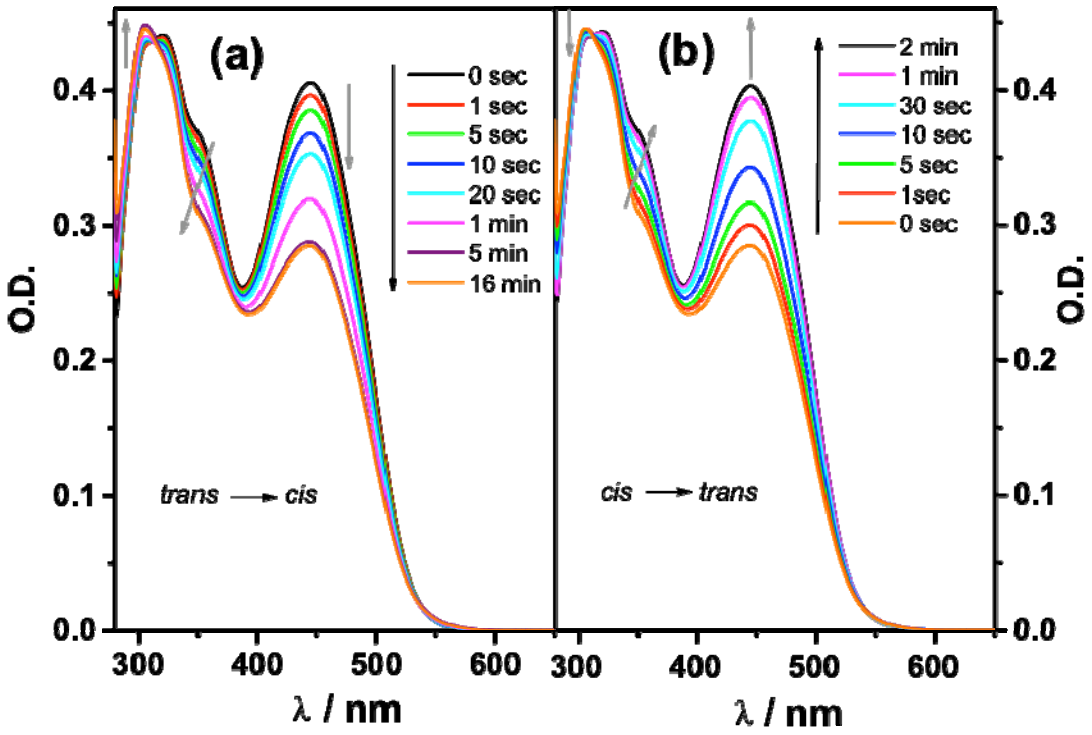


Fig. SI1 (a) Time evolution of the absorption spectra of a 4.0×10^{-6} M solution of *trans*-**12** in toluene under 460 nm irradiation, until the photostationary state is reached. (b) Back reaction observed over time under 313 nm irradiation. As for **1**, the initial *trans*-**12** spectrum is fully recovered showing complete reversibility.

Experimental part

Absorption spectra were recorded with a Perkin-Elmer Lambda 950 UV/Vis/NIR spectrophotometer. Emission spectra were obtained with an Edinburgh FLS920 spectrometer, equipped with either a Peltier-cooled Hamamatsu R-928 (Vis region) or a supercooled (193 K) Hamamatsu R5509-72 PMT detector (NIR region); in the latter configuration, a TM300 emission monochromator with NIR grating blazed at 1000 nm was used. An Edinburgh Xe900 450 W xenon arc lamp was used as light source; the emission calibration curves were supplied by the manufacturer. Irradiation experiments of azobenzene units were carried out using 150 watt argon lamp, the excitation wavelength was selected by means of Andover Corporation optical

bandpass filters (10 ± 2 nm). All measurements were carried out in spectroscopy grade toluene used without further purification, and under ambient atmosphere at room temperature.

3. Molecular Modeling

Method. The stability of nine isomers has been evaluated after optimization of the ground state geometries *in vacuo* by using the PM3 semiempirical quantum mechanical method, as implemented in HYPERCHEM 8.0.8 for Windows program (Hypercube, Inc.) with the built-in parameters. A Polak-Ribiere conjugated gradient minimization algorithm with a termination condition of a RMS gradient < 0.001 Kcal·mol^{-1}·Å^{-1} and a SCF convergence limit of 10^{-5} was used for the geometry optimization.

Discussion. The geometrical structure of nine different isomers was first constructed and then optimized by using the semi-empirical quantum mechanical method PM3 in order to assess the relative stability of the different isomers. The isomers considered were built up starting from the full *trans* configuration and introducing an increasing number of *cis* conformation in the azobenzene part of the four molecular arms. Geometric structures of the nine fully optimized conformations are shown in Fig. SI2, and a selected list of torsion angles, dihedral angles and bond lengths, used to describe the rigidity and rotational range of aza-bonds, are reported in Table SI1. The phenyl-aza-phenyl region in the *trans* configuration is planar, as indicated by the -C-N=N-C- torsion angle close to 180°, and the PM3 method yields a -N=N- bond length of 1.232 Å, in close agreement with the results obtained experimentally by XRD for the unsubstituted azobenzene (1.247 Å) (*J. Phys. Chem. A* **1997**, *101*, 5555-5566). In the case of the *cis* configuration the same torsion angle is between 0.1 – 0.4° and the

calculation show a tendency to decrease the -N=N- bond length by ca. 0.015 Å when passing from the *trans* to the *cis* form. The enthalpy of formation (in Kcal·mol^{-1}) for nine minimized conformer geometries and their relative stability with respect to the full *trans* **tttt** isomer (set at zero) are collected in Table SI2 and compared in Fig. SI3. The PM3 calculations show that the all-*trans* **tttt** isomer is the most stable and that each *cis* configuration of the aza bonds introduced in the different arms of the molecule destabilize the structure by roughly 2.6 Kcal mol^{-1} (Table SI2). Furthermore, isomers with the same number of *cis* and *trans* aza bonds show a similar stability (Figure SI2). Then, it may be concluded that the four arms behave as non-interacting. In fact, the central pyrene core makes them stay apart, so as to avoid any close contact of the pendant arms even in the most gathered all-*cis* conformation (**cccc** isomer).

Table SI1. Geometrical parameters around the azobenzene group for the nine geometrically optimised configurational isomers.

Isomer	*Bond length (Å)*			*Bond angle (°)*		*Dihedral angle (°)*
	C_1-N_1	N_1=N_2	N_2-C_2	C_1-N_1=N_2	N_1=N_2-C_2	C_1-N_1=N_2-C_2
tttt	1.4469	1.2321	1.4461	119.97	120.03	179.94
cttt	1.4522	1.2166	1.4522	126.92	126.83	0.15
tctt	1.4465	1.2318	1.4457	119.87	119.83	179.48
cctt	1.4520	1.2168	1.4517	127.16	127.09	0.23
ctct	1.4523	1.2170	1.4521	126.93	126.80	0.14
cttc	1.4524	1.2167	1.4524	126.87	126.90	0.01
ccct	1.4526	1.2168	1.4522	127.05	126.96	0.10
cctc	1.4522	1.2164	1.4518	127.08	126.85	0.18
cccc	1.4523	1.2167	1.4520	127.04	127.02	0.39

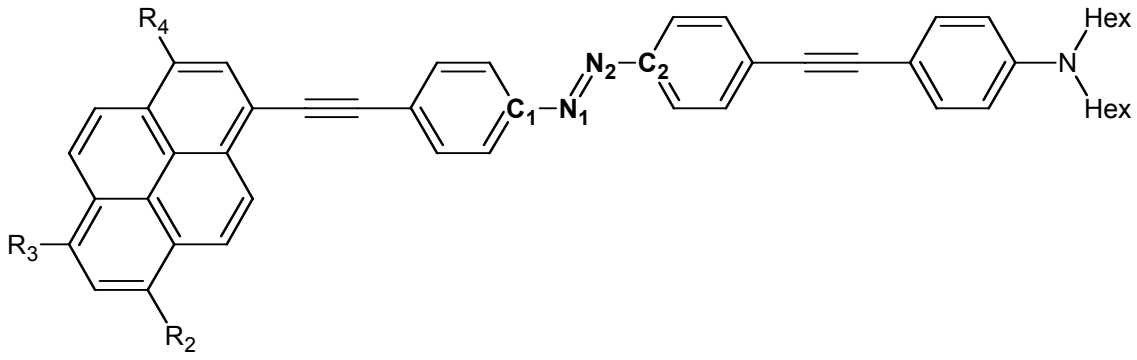
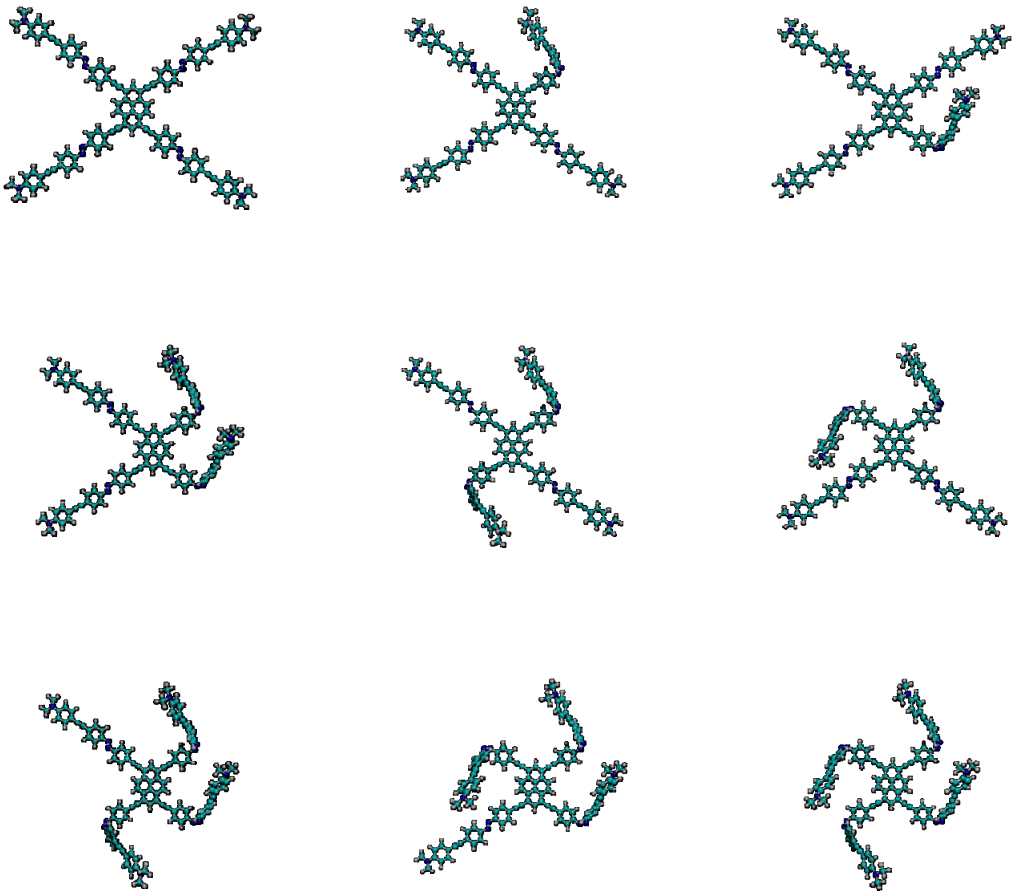


Table SI2. Calculated enthalpy of formation and relative energy levels for the nine configurational isomers.

Isomer	ΔH_f *(Kcal mol^{-1})*	ΔE *(Kcal mol^{-1})* [a]
tttt	917.77	0.00
cttt	920.32	2.55
tctt	920.40	2.63
cctt	922.92	5.15
ctct	922.91	5.14
cttc	922.90	5.13
ccct	925.57	7.80
cctc	925.46	7.69
cccc	928.06	10.29

[a] full trans ***tttt*** isomer set at zero.

Figure SI2. The nine optimised configurational isomers.



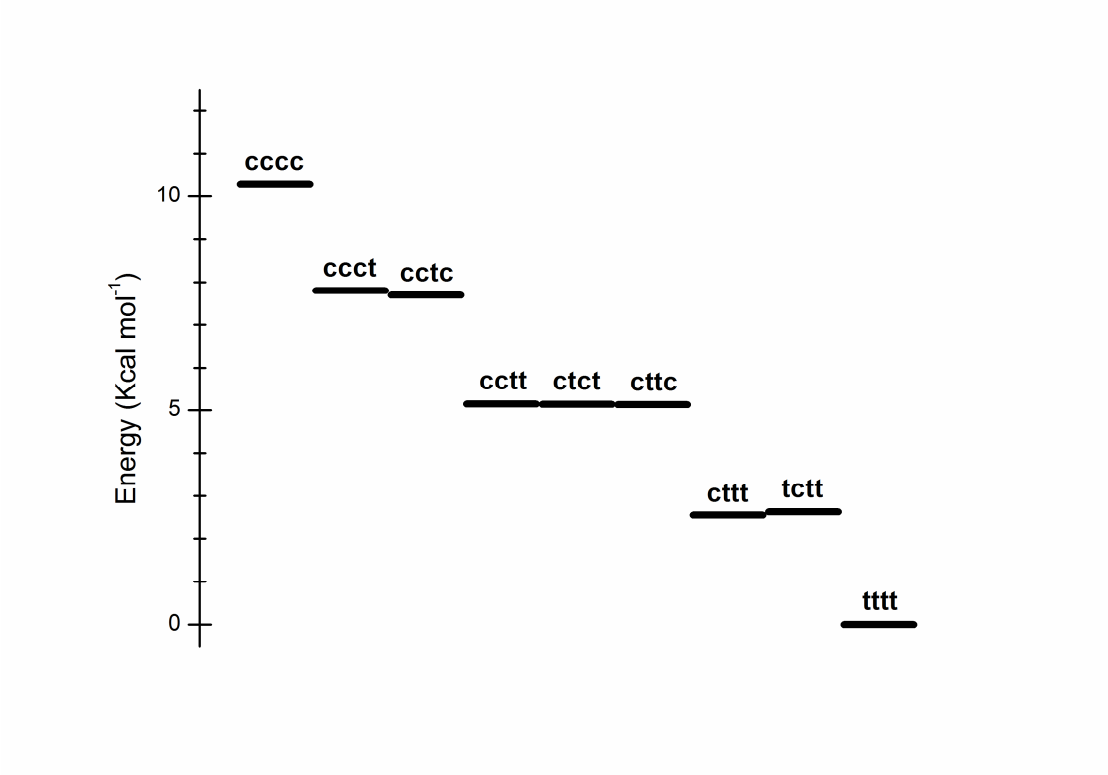
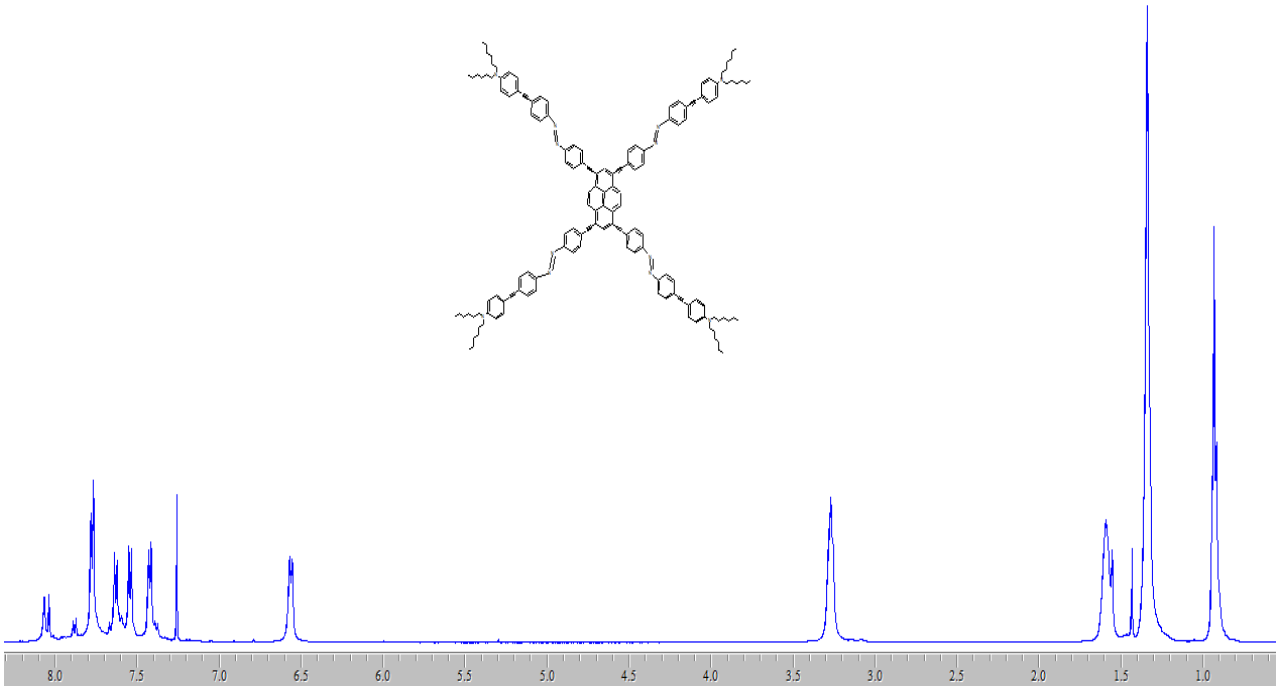
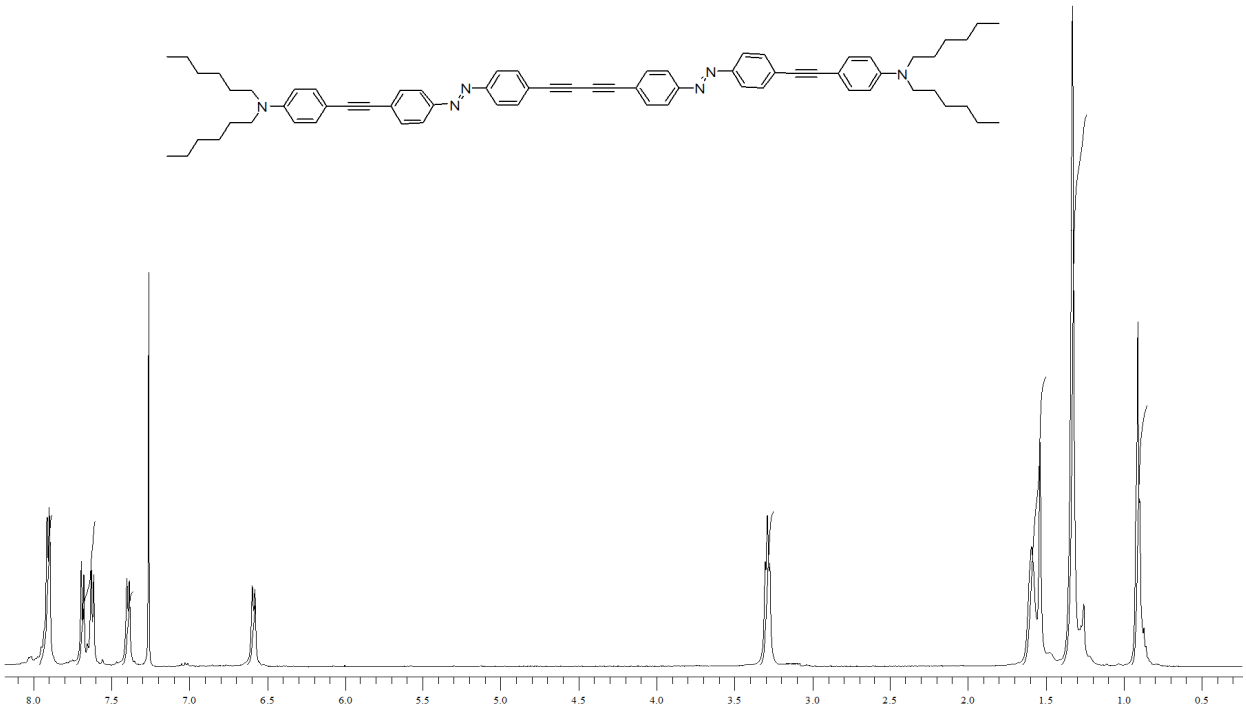
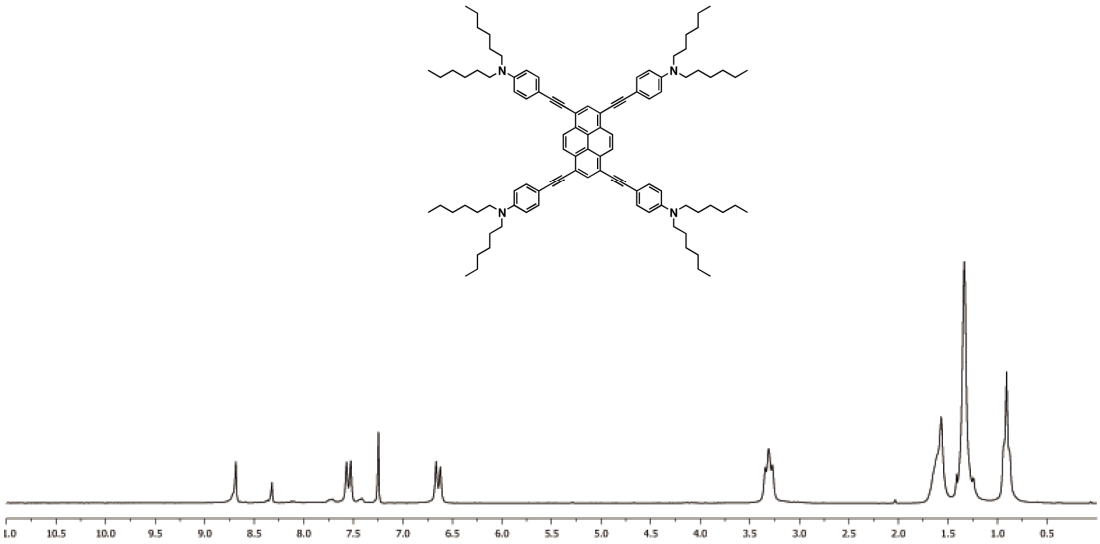


Fig. SI3. Relative potential energy levels of the nine isomers (full trans *tttt* isomer set at zero) obtained by the PM3 semi-empirical calculation, in Kcal·mol^{-1}.

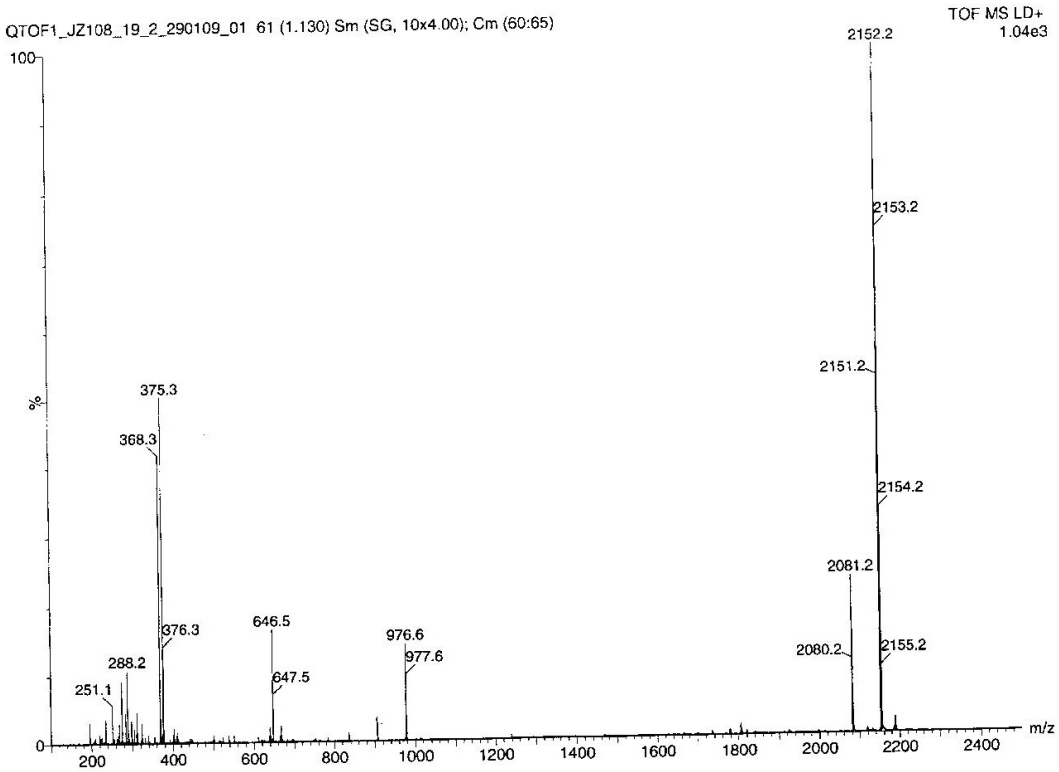
3. Annexes (^{1}H-NMR spectra)

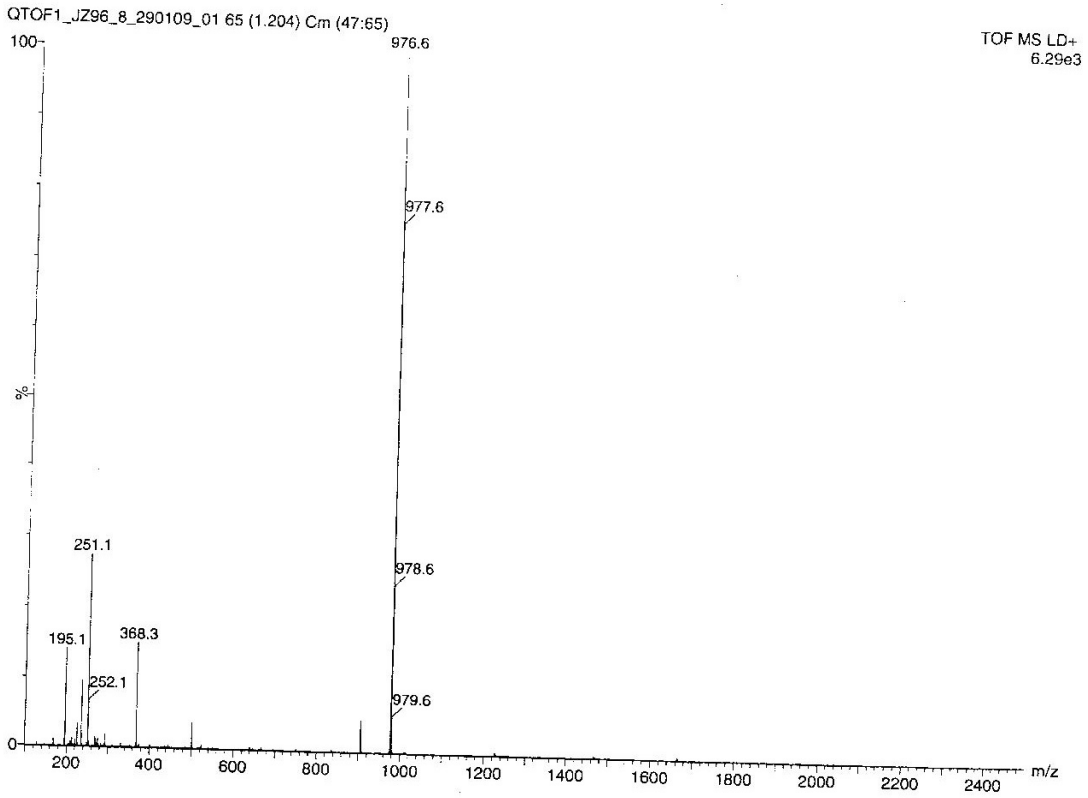






3. Annexes (Mass TOF spectra: Molecules 1 and 12)

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