

Supporting information for

[4]Cyclo-*N*-alkyl-2,7-carbazole: Influence of the alkyl chain length on the structural, electronic and charge transport properties

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1 General information

Synthesis

All manipulations of oxygen and moisture-sensitive materials were conducted with a standard Schlenk technique. All glassware was kept in an oven at 80°C. Argon atmosphere was generated by three repetitive cycles of vacuum/Argon using a schlenck ramp. Commercially available reagents and solvents were used without further purification other than those detailed below. THF and toluene were obtained through a PURE SOLV™ solvent purification system. Light petroleum refers to the fraction with bp 40-60°C. Analytical thin layer chromatography was carried out using aluminum backed plates coated with Merck Kieselgel 60 GF254 and visualized under UV light (at 254 and 360 nm). Flash chromatography was carried out using Teledyne Isco CombiFlash® Rf 400 (UV detection 200-360nm), over standard silica cartridges (Redisep® Isco or Puriflash® columns Interchim). In order to be purified through a recycling size exclusion chromatography apparatus, the compounds were solubilized in HPLC grade chloroform (stabilized with ethanol). Prior to injection, the solution was filtered through a 0.45 µm PTFE filter. Purification was performed on a LC-9160 II NEXT system from the Japan Analytical Industry Co., Ltd. (JAI) equipped with coupled UV-vis 4Ch NEXT through a set of two JAIGEL-2H columns at an elution rate of 10 mL.min⁻¹ (CHCl₃). ¹H and ¹³C NMR spectra were recorded using Bruker 300 MHz instruments (¹H frequency, corresponding ¹³C frequency: 75 MHz); chemical shifts were recorded in ppm and J values in Hz. The residual signals for the NMR solvents used are 5.32 ppm (proton) and 54.00 ppm (carbon) for CD₂Cl₂, 7.26 ppm (proton) and 77.16 ppm (carbon) for CDCl₃ and 77.16 ppm (carbon), 2.090 ppm (proton) for toluene-d₈. In the ¹³C NMR spectra, signals corresponding to C, CH, CH₂ or CH₃ groups, assigned from DEPT experiment, are noted. The following abbreviations have been used for the NMR assignment: s for singlet, d for doublet, t for triplet, q for quadruplet and m for multiplet. High resolution mass spectra were recorded at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO-Rennes) on a Thermo Fisher Q-Exactive instrument or a Bruker MaXis 4G or a Bruker Ultraflex III.

X-ray

Crystals were picked up with a cryoloop and then frozen at 150 K under a stream of dry N₂. Data were collected on a D8 VENTURE Bruker AXS diffractometer with Mo-Kα radiation (λ = 0.71073 Å).

Structures were solved by direct methods (SIR92)¹ and refined (SHELXL-2014/7)² by full-matrix least-squares methods as implemented in the WinGX software package.³ An empirical absorption (multi-scan) correction was applied. Hydrogen atoms were introduced at calculated positions (riding model) included in structure factor calculation but not refined. Refinement parameters are summarized in Table S 23, Table S 24 and Table S 25.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication data: [4]C-Et-Cbz (CCDC 1893079), [4]C-Bu-Cbz (CCDC 2055214) and [4]C-Hex-Cbz (CCDC 2055215). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Figures were generated with Mercury software 3.9.

Spectroscopic studies

Cyclohexane (spectroscopic grade, Acros), THF (spectroscopic grade, Acros), dichloromethane (spectroscopic grade, Acros), acetonitrile (spectroscopic grade, Acros), methanol (spectroscopic grade, Acros), 2-MeTHF (spectroscopic grade, sigma aldrich), 1 N solution of

sulfuric acid in water (Standard solution, Alfa Aesar), and quinine sulfate dihydrate (99+%, ACROS organics) were used without further purification.

UV-visible spectra were recorded using an UV-Visible spectrophotometer SHIMADZU UV-1605. Molar extinction coefficients (ϵ) were calculated from the gradients extracted from the plots of absorbance *vs* concentration with five solutions of different concentrations for each sample and at least two mother solutions were prepared.

$$A = \epsilon \times l \times C$$

Above, *l* refers to the path length and *C* to the sample concentration.

Emission spectra were recorded with a HORIBA Scientific Fluoromax-4 equipped with a Xenon lamp.

Quantum yields in solution (ϕ_{sol}) were calculated relative to quinine sulfate ($\phi_{ref} = 0.546$ in H₂SO₄ 1 N). ϕ_{sol} was determined according to the following equation,

$$\phi_{sol} = \phi_{ref} \times \frac{Grad_s}{Grad_r} \times \left(\frac{\eta_s}{\eta_r}\right)^2$$

where subscripts *s* and *r* refer respectively to the sample and reference, *Grad* is the gradient from the plot of integrated fluorescence intensity *vs* absorbance, η is the refracting index of the solvent ($\eta_s = 1.426$ for cyclohexane). Five solutions of different concentration ($A < 0.1$) of the sample and five solutions of the reference (quinine sulfate) were prepared. The integrated area of the fluorescence peak was plotted against the absorbance at the excitation wavelength for both the sample and reference. The gradients of these plots were then injected in the equation to calculate the reported quantum yield value for the sample.

Absolute quantum yields were recorded using a deported HORIBA Scientific Quanta-Phi integrating sphere linked to the Fluoromax-4.

Fluorescent decay measurements were carried out on the HORIBA Scientific Fluoromax-4 equipped with its TCSPC pulsed source interface.

Spin-coated film were prepare form a 1g/mL solution using a Labspins Tournette from Süss Microtec. Evaporated thin films of nanoring were prepared using the procedure described below for the fabrication of OFET devices.

IR spectra were recorded on a Bruker Vertex 70 using a diamond crystal MIRacle ATR (Pike).

Electrochemical studies

Electrochemical experiments were performed under argon atmosphere using a Pt disk electrode (diameter 1 mm). The counter electrode was a vitreous carbon rod. The reference electrode was either a silver wire in a 0.1 M AgNO₃ solution in CH₃CN for the studies in oxidation or a Silver wire coated by a thin film of AgI (silver(I)iodide) in a 0.1 M Bu₄NI solution in DMF for the studies in reduction. Ferrocene was added to the electrolyte solution at the end of a series of experiments. The ferrocene/ferrocenium (Fc/Fc⁺) couple served as internal standard. The three electrodes cell was connected either to a PAR Model 273 potentiostat/galvanostat (PAR, EG&G, USA) monitored with the ECHEM Software or to a potentiostat/galvanostat (Autolab/PGSTAT101) monitored with the Nova 2.1 Software. Activated Al₂O₃ was added in the electrolytic solution to remove excess moisture. For a further comparison of the electrochemical and optical properties, all potentials are referred to the SCE electrode that was calibrated at - 0.405 V *vs*. Fc/Fc⁺ system. Following the work of Jenekhe,⁴ we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO

level was calculated from: LUMO (eV) = $-[E_{\text{onset}}^{\text{red}} (\text{vs SCE}) + 4.4]$. Similarly the HOMO level was calculated from: HOMO (eV) = $-[E_{\text{onset}}^{\text{ox}} (\text{vs SCE}) + 4.4]$, based on a SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from: $\Delta E^{\text{el}} = |\text{HOMO} - \text{LUMO}|$ (in eV).

Theoretical modelling

a) Absorption spectrum simulation

Full geometry optimization of the ground state and vibrational frequency calculation were performed with Density Functional Theory (DFT)⁵⁻⁶ using the hybrid Becke-3 parameter exchange functional⁷⁻⁹ and the Lee-Yang-Parr non-local correlation functional¹⁰ (B3LYP) implemented in the Gaussian 16 program suite,¹¹ using the 6-31G(d) basis set and the default convergence criterion implemented in the program. To overcome the issue of the many possible conformation of the alkyl chains in the cyclocarbazoles, geometry optimization was performed starting from the X-ray diffraction crystal structure geometry. All stationary points were characterized as minima by analytical frequency calculations.

The energy strain was performed as described in the literature using the B3LYP functionals and the 6-311+G(d,p) basis set.¹²

Optical transition diagrams were obtained through TD-DFT calculations performed using the B3LYP functionals and the 6-311+G(d,p) basis set from the geometry of S_0 .

Calculations were carried out on the OCCIGEN calculator of the Centre Informatique National de l'Enseignement Supérieur (CINES (Montpellier) under project N°2020-A0080805032).

Figures were generated with GaussView 6.0 and GaussSum 3.0.

b) Transfer integral calculation

Experimentally resolved crystal structures were used to estimate electronic couplings in the equilibrium structure but also to build the 3X3X3 supercells on which we performed MD calculations. From the latter, we are able to compute the distribution of the electronic couplings induced by thermal motion at ambient temperature in each structure. This reveals by how much their value is spread by the activation of intermolecular vibrational modes. All the electronic couplings were computed at the Density Functional Theory level within a fragment approach¹³ using the B3LYP function and a DZ basis set, as implemented in the ADF (Amsterdam Density Functional) package. The first step of our analysis consisted in determining the most probable pathways for holes to move along and the dimensionality of the charge transport. To achieve this, we extended the experimental cell into a 3X3X3 supercell and computed the electronic couplings for all close neighbors of all molecules localized in the pristine unit cell; in practice, dimers are considered when the closest atoms are within a 0-5 Å range.

Molecular Dynamics simulations were performed with the Dreiding force field, as implemented in the Material Studio package. For all four investigated systems, we started by computing the charge distribution in the molecule using the Qeq method¹⁴⁻¹⁵. All default values were chosen in the force field except for the hydrogen van der Waals radius (changed from 3.195 to 2.83 Å) and the treatment of electrostatic interactions from the shielded to pure coulombic (1/r) regime. The output of this relaxation was used as input for a dynamic run in the NVT ensemble with the Nose thermostat. Once all MD runs were validated by ensuring that the lattice fluctuations occur around the equilibrium geometry, we extracted around 150 snapshots through the whole simulation, and computed couplings for inequivalent molecules in the crystal structure.

An important fact is to take into consideration when looking at the following distributions. What matters, in the scope of the hopping model is the absolute value of the electronic coupling. This is why some mean values of the Gaussian fits do not match the actual distributions. They were computed on the basis of data sets compounded solely by absolute values. We preferred to keep

the histograms and fits appearance close to the raw data in order to emphasize the Gaussian character of these distributions

Thermal analysis

Thermal Gravimetric Analysis (TGA) was carried out by using a Q50 apparatus from TA instruments. TGA curves were measured at 5°C/min under air.

Differential Scanning Calorimetry (DSC) was carried out by using a DSC Q1000 from TA instrument. DSC traces were measured at 5°C/min, 3 heating/cooling cycles were successively carried out under air.

The S/WAXS patterns were obtained with a transmission Guinier-like geometry. A linear focalized monochromatic Cu K α 1 beam ($\lambda = 1.5405 \text{ \AA}$) was obtained using a sealed-tube generator (600 W) equipped with a bent quartz monochromator. The samples were filled in home-made sealed cells of 1 mm path. The sample temperature was controlled within $\pm 0.01 \text{ }^\circ\text{C}$, and exposure times were varied from 4 to 24 h. The patterns were recorded with a curved Inel CPS120 counter gas-filled detector (periodicities up to 90 \AA) and on image plates scanned by Amersham Typhoon IP with 25 μm resolution (periodicities up to 120 \AA). I(2 θ) profiles were obtained from images, by using home-developed software.

Organic field effect transistors fabrication

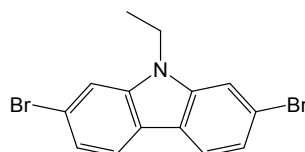
The fabrication process is described as follows: 150 nm thick aluminium layer was evaporated and patterned by conventional photolithography on a 5 \times 5 cm² rigid glass substrate. Then, SU-8 2000.5 Photoresist from Microchem¹⁶ was then spin-coated in order to obtain a 400 nm thick layer. 50 nm thick gold layer was then thermally evaporated and patterned by photolithography. Finally, the OSCs were deposited by evaporation under vacuum as a 40 nm thick layer.

2 Synthetic procedures

General procedure for alkylation of 2,7-dibromo-9H-carbazole

2,7-Dibromo-9H-carbazole (1.0 eq), KOH (3.0 eq) and tetrabutylammonium hydrogen sulfate (0.1 eq) were charged in a round bottom flask. Then the corresponding brominated alkyl (2.5 eq) and dry DMF (0.30 M) were added. The resulting mixture was stirred at 80°C overnight. After cooling to RT, a saturated solution of ammonium chloride was added. The organic layer was extracted with CH₂Cl₂. The organic layer was then washed with water, brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude was purified with flash chromatography on silica gel.

2,7-dibromo-N-ethyl-carbazole



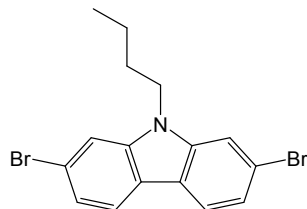
The *title compound* was synthesized using the general procedure for alkylation of 2,7-dibromo-9H-carbazole.

2,7-Dibromo-9H-carbazole (2.00 g, 6.15 mmol, 1.0 eq), KOH (1.04 g, 18.50 mmol, 3.0 eq), tetrabutylammonium hydrogen sulfate (209 mg, 0.62 mmol, 0.1 eq), 1-bromoethane (1.14 mL, 15.40 mmol, 2.5 eq) and dry DMF (20 mL).

After purification flash chromatography on silica gel [column condition: silica cartridge (40 g); solid deposit on Celite®; λ detection: (254 nm, 280 nm); CH₂Cl₂/light petroleum (5:95) at 40 mL/min], the *title compound* was obtained as a white solid (2.10 g, 5.95 mmol); yield 97%; ¹H NMR (300 MHz, CDCl₃) δ 7.89 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 1.7 Hz, 2H), 7.34 (dd, J = 8.3,

1.7 Hz, 2H), 4.28 (q, $J = 7.2$ Hz, 2H), 1.43 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 141.1 (2C), 122.7 (2CH), 121.7 (2CH), 121.6 (2C), 119.9 (2C), 112.0 (2CH), 38.0 (CH_2), 13.9 (CH_3) ppm. IR (ATR platinum) 2971, 2932, 1869, 1621, 1584, 1485, 1471, 1449, 1424, 1404, 1377, 1347, 1339, 1326, 1315, 1268, 1231, 1223, 1132, 1084, 1055, 1024, 997, 941, 919, 890, 851, 841, 802, 794, 786, 750, 721, 667, 603, 590, 558, 435 cm^{-1} . HRMS (ASAP, 80°C): $[\text{M}+\text{H}]^+$ found 351.9336 for $\text{C}_{14}\text{H}_{12}\text{NBr}_2$ required 351.9331. m.p.: 133°C .

2,7-dibromo-*N*-butyl-carbazole

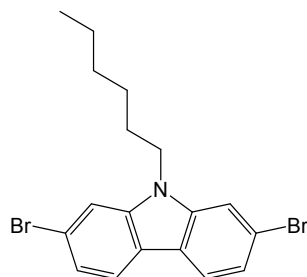


The *title compound* was synthesized using the general procedure for alkylation of 2,7-dibromo-9H-carbazole.

2,7-Dibromo-9H-carbazole (2.50 g, 7.69 mmol, 1.0 eq), KOH (1.29 g, 23.1 mmol, 3.0 eq), tetrabutylammonium hydrogen sulfate (0.261 mg, 0.769 mmol, 0.1 eq), 1-bromobutane (1.79 mL, 19.2 mmol, 2.5 eq) and dry DMF (30 mL).

After purification flash chromatography on silica gel [column condition: silica cartridge (40 g); solid deposit on Celite®; λ detection: (254 nm, 280 nm); CH_2Cl_2 /light petroleum (5/95) at 40 mL/min], the *title compound* was obtained as a white solid (2.85 g, 7.46 mmol); yield 97%; ^1H NMR (300 MHz, CDCl_3) δ 7.89 (d, $J = 8.2$ Hz, 2H), 7.53 (d, $J = 1.7$ Hz, 2H), 7.34 (dd, $J = 8.3, 1.7$ Hz, 2H), 4.21 (t, $J = 7.2$ Hz, 2H), 1.84 (tt, $J = 9.5, 6.8$ Hz, 2H), 1.48 – 1.33 (m, 2H), 0.97 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 141.5 (2C), 122.7 (2CH), 121.6 (2CH), 121.4 (2C), 119.8 (2C), 112.1 (2CH), 43.3 (CH_2), 31.1 (CH_2), 20.7 (CH_2), 14.0 (CH_3) ppm. IR (ATR platinum) 2958, 2926, 2874, 2858, 1621, 1585, 1565, 1483, 1467, 1452, 1441, 1424, 1406, 1382, 1371, 1341, 1327, 1316, 1266, 1241, 1225, 1212, 1203, 1133, 1117, 1054, 997, 976, 957, 938, 899, 878, 852, 835, 815, 793, 771, 750, 733, 721, 665, 649, 592, 558, 436, 422 cm^{-1} . HRMS (ASAP, 130°C): Found $[\text{M}+\text{H}]^+$, 379.9648, $\text{C}_{16}\text{H}_{16}\text{NBr}_2$ required 379.9644. m.p.: 118°C .

2,7-dibromo-*N*-hexyl-carbazole



The *title compound* was synthesized using the general procedure for alkylation of 2,7-dibromo-9H-carbazole.

2,7-Dibromo-9H-carbazole (3.00 g, 9.23 mmol, 1.0 eq), KOH (1.55 g, 27.7 mmol, 3.0 eq), tetrabutylammonium hydrogen sulfate (0.313 mg, 0.923 mmol, 0.1 eq), 1-bromohexane (3.23 mL, 23.1 mmol, 2.5 eq) and dry DMF (30 mL).

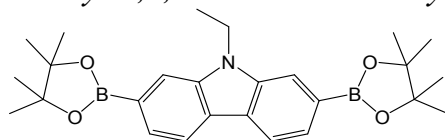
After purification flash chromatography on silica gel [column condition: silica cartridge (40 g); solid deposit on Celite®; λ detection: (254 nm, 280 nm); CH_2Cl_2 /light petroleum (5/95) at 40 mL/min], the *title compound* was obtained as a white solid (3.53 g, 8.35 mmol); yield 90%; ^1H NMR (300 MHz, CDCl_3): δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 1.7$ Hz, 2H), 7.34 (dd, $J = 8.3, 1.7$ Hz, 2H), 4.19 (t, $J = 7.4$ Hz, 2H), 1.84 (m, $J = 7.3$ Hz, 2H), 1.46 – 1.22 (m, 6H), 0.90 (t, 3H)

ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 141.5 (2C), 122.7 (2CH), 121.6 (2CH), 121.4 (2C), 119.8 (2C), 112.2 (2CH), 43.5 (CH_2), 31.6 (CH_2), 28.9 (CH_2), 27.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (ATR platinum) 2964, 2946, 2922, 2866, 2851, 1623, 1587, 1570, 1484, 1466, 1447, 1422, 1409, 1367, 1347, 1340, 1327, 1312, 1300, 1276, 1268, 1252, 1234, 1223, 1193, 1129, 1053, 1043, 1026, 997, 922, 904, 873, 866, 833, 817, 793, 770, 750, 740, 722, 665, 650, 593, 558, 443, 425 cm^{-1} . HRMS (ASAP, 90°C): M^+ -Found 406.9878 for $\text{C}_{18}\text{H}_{19}\text{N}^{79}\text{Br}_2$ required 406.98787. m.p.: 74°C .

General procedure for the synthesis of bis(pinacolato) diboron carbazole derivatives

The corresponding alkylated dibromocarbazole (1.0 eq) was dissolved in anhydrous THF (0.03 M) under an argon atmosphere. The reaction mixture was cooled to -78°C . A 2.5 M in hexanes solution of *n*-BuLi (3.3 eq) was then added dropwise to the solution at -78°C . The solution was stirred at this temperature for one hour and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.5 eq) was added to the mixture and stirred at -78°C for 15 minutes. The reaction mixture was allowed to warm up to room temperature overnight under stirring. The reaction mixture was quenched with few drops of absolute ethanol and concentrated under reduced pressure. The crude product was dissolved in CH_2Cl_2 . The organic layer was washed with water, brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude was purified with flash chromatography on silica gel.

N-ethyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole **EtCbzBpin₂**

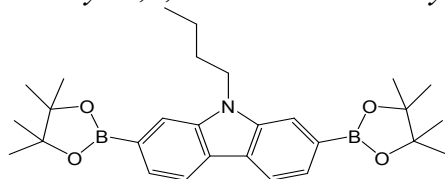


The *title compound* was synthesized using the general procedure for the synthesis of diboronic acid pinacol ester derivatives.

2,7-Dibromo-*N*-ethyl-carbazole (2.00 g, 5.66 mmol, 1.0 eq), THF (120 mL), *n*-BuLi (7.47 mL, 18.68 mmol, 3.3 eq) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.04 mL, 19.81 mmol, 3.5 eq).

After flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λ detection: (254 nm, 280 nm); CH_2Cl_2 /light petroleum (3/7) at 40 mL/min], the *title compound* was obtained as a white solid (2.04 g, 4.56 mmol); yield 81%; ^1H NMR (300 MHz, CDCl_3) δ 8.15 (dd, $J = 7.8, 0.8$ Hz, 2H), 7.92 (s, 2H), 7.71 (dd, $J = 7.8, 0.9$ Hz, 2H), 4.49 (q, $J = 7.2$ Hz, 2H), 1.48 (t, $J = 7.2$ Hz, 3H), 1.43 (s, 24H). ^{13}C NMR (75 MHz, CDCl_3) δ 140.1 (2C), 125.3 (4C), 125.0 (2CH), 120.2 (2CH), 115.2 (2CH), 84.0 (4C), 37.6 (CH_2), 25.1 (8 CH_3), 14.4 (CH_3) ppm. IR (ATR platinum): 2991, 2977, 1560, 1501, 1483, 1453, 1436, 1390, 1381, 1370, 1357, 1338, 1316, 1261, 1233, 1211, 1167, 1142, 1132, 1111, 1076, 1058, 1000, 965, 949, 937, 876, 854, 836, 818, 776, 757, 736, 706, 688, 671, 646, 595, 579, 559, 421 cm^{-1} . HRMS (ASAP, 240°C): Found $[\text{M}+\text{H}]^+$, 448.2832, $\text{C}_{26}\text{H}_{36}\text{NO}_4^{11}\text{B}_2$ required 448.28249. m.p.: 342°C .

N-butyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole **BuCbzBpin₂**

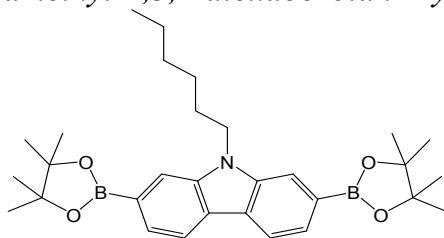


The *title compound* was synthesized using the general procedure for the synthesis of diboronic acid pinacol ester derivatives.

2,7-Dibromo-*N*-butyl-carbazole (2.00 g, 5.25 mmol, 1.0 eq), THF (80 mL), *n*-BuLi (11.5 mL, 17.3 mmol, 3.3 eq) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.75 mL, 18.4 mmol, 3.5 eq).

After flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λ detection: (254 nm, 280 nm); CH₂Cl₂/light petroleum (3/7) at 40 mL/min], the *title compound* was obtained as a white solid (1.85 g, 3.89 mmol); yield 73 %; ¹H NMR (300 MHz, CDCl₃): δ 8.12 (dd, *J* = 7.8, 0.8 Hz, 2H), 7.89 (s, 2H), 7.68 (dd, *J* = 7.8, 0.9 Hz, 2H), 4.39 (t, *J* = 7.3 Hz, 2H), 1.97 – 1.80 (m, 2H), 1.40 (s, 26H), 0.95 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 140.6 (2C), 125.2 (4C), 125.0 (2CH), 120.2 (2CH), 115.4 (2CH), 83.9 (8C), 42.9 (CH₂), 31.6 (CH₂), 25.1 (8CH₃), 20.7 (CH₂), 14.1 (CH₃) ppm. IR (ATR, platinum): 2979, 2956, 2928, 1624, 1558, 1499, 1482, 1466, 1450, 1433, 1391, 1381, 1371, 1354, 1337, 1313, 1266, 1249, 1231, 1213, 1167, 1141, 1113, 1075, 1056, 998, 972, 958, 914, 880, 856, 824, 808, 782, 735, 706, 689, 673, 644, 579, 558, 521, 420 cm⁻¹. HRMS (ASAP, 170 °C): Found [M+H]⁺, 476.3143, C₂₈H₄₀NO₄¹¹B₂ required 476.31379. m.p. : 213°C.

N-hexyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole **HexCbzBpin₂**



The *title compound* was synthesized using the general procedure for the synthesis of diboronic acid pinacol ester derivatives.

2,7-Dibromo-*N*-butyl-carbazole (2.00 g, 4.89 mmol, 1.0 eq), THF (80 mL), *n*-BuLi (6.45 mL, 16.1 mmol, 3.3 eq) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.49 mL, 17.1 mmol, 3.5 eq).

After flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; λ detection: (254 nm, 280 nm); CH₂Cl₂/light petroleum (3/7) at 40 mL/min], giving the *title compound* as a white solid (2.17 g, 4.30 mmol); yield 88 %; ¹H NMR (300 MHz, CDCl₃): δ 8.14 (d, *J* = 7.8 Hz, 2H), 7.91 (s, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 4.41 (t, *J* = 7.3 Hz, 2H), 1.91 (m, *J* = 7.3 Hz, 2H), 1.43 (s, 30H), 0.91 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 140.6 (2C), 125.2 (4C), 125.0 (2CH), 120.2 (2CH), 115.4 (2CH), 83.9 (8C), 43.0 (CH₂), 31.8 (CH₂), 29.3 (CH₂), 27.0 (CH₂), 25.1 (8CH₃), 22.8 (CH₂), 14.2 (CH₃) ppm. IR (ATR platinum): 2994, 2977, 2956, 2926, 2861, 1625, 1599, 1560, 1501, 1484, 1454, 1433, 1392, 1380, 1371, 1355, 1338, 1312, 1267, 1256, 1236, 1213, 1166, 1141, 1113, 1076, 1060, 999, 966, 940, 909, 882, 855, 822, 790, 764, 736, 728, 706, 689, 671, 642, 590, 577, 557, 520, 419 cm⁻¹. HRMS (ESI, CH₃OH/CH₂Cl₂: 90/10): [M+K]⁺ found 542.3010 for C₃₀H₄₃NO₄¹¹B₂K required 542.30098. m.p.: 209°C.

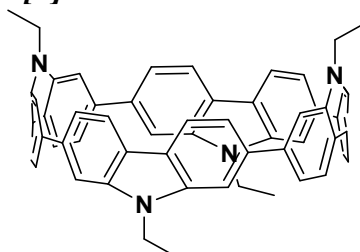
General procedure for nanoring synthesis

Diboronic acid pinacol ester derivative (1.0 eq), cesium fluoride (6.0 eq) and 1,5-cyclooctadieneplatinum (II) dichloride (1.0 eq) were dissolved in solvent A (2.65×10^{-2} mol.L⁻¹) under an argon atmosphere and stirred at 70°C for 24 h. Solvent was then removed under reduced pressure and the crude product was dried under vacuum at 60°C for 24 h. Triphenylphosphine (15 eq) was then added to the crude product and Solvent B (1.77×10^{-2} mol.L⁻¹) was added under an argon atmosphere, see Table S 1. The resulting mixture was stirred for one or half an hour at room temperature and then at the reflux of solvent B for 48 h. Then, solvent was removed under reduced pressure. The crude product was dissolved in CH₂Cl₂. Water was added and the organic layer was extracted with CH₂Cl₂, dried over MgSO₄, filtered and solvent was removed under reduced pressure.

Table S 1 Optimization of solvents system for transmetallation and reductive elimination step in nanorings synthesis.

Nanoring	Transmetallation	reductive elimination		Yield (%)
	Solvent A	Solvent B	Time (h)	
[4]C-Et-Cbz	THF	Toluene	0.5/24	6
[4]C-Et-Cbz	THF	<i>o</i> -DCB	0.5/24	16
[4]C-Et-Cbz	THF	<i>o</i> -DCB	1/48	25
[4]C-Et-Cbz	DCE	<i>o</i> -DCB	1/48	64
[4]C-Bu-Cbz	THF	<i>o</i> -DCB	1/48	25
[4]C-Bu-Cbz	DCE	<i>o</i> -DCB	1/48	60
[4]C-Bu-Cbz	TCE	<i>o</i> -DCB	1/48	< 1
[4]C-Bu-Cbz	CCl ₄	<i>o</i> -DCB	1/48	< 1
[4]C-Bu-Cbz	DMF	<i>o</i> -DCB	1/48	9
[4]C-Bu-Cbz	<i>o</i> -DCB	<i>o</i> -DCB	1/48	< 1
[4]C-Hex-Cbz	THF	<i>o</i> -DCB	1/48	24
[4]C-Hex-Cbz	DCE	<i>o</i> -DCB	1/48	52

[4]cyclo-*N*-ethyl-2,7-carbazole [4]C-Et-Cbz



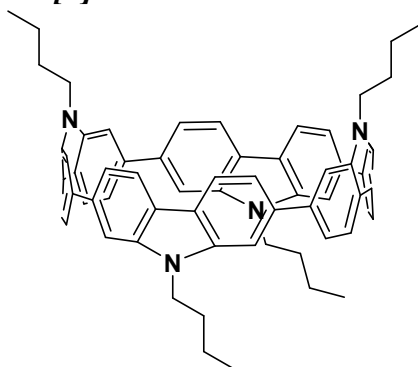
The *title compound* was synthesized using the general procedure for nanoring synthesis.

1st step: **3a** (0.250 g, 0.559 mmol, 1.0 eq), cesium fluoride (0.510 g, 5.35 mmol, 9.6 eq) and 1,5-cyclooctadieneplatinum (II) dichloride (0.209 g, 0.559 mmol, 1.0 eq) in extra dry DCE (21 mL).

2nd step: Triphenylphosphine (2.20 g, 8.39 mmol, 15 eq) was then added to the crude product in 1,2-dichlorobenzene (32 mL).

The residue was purified first with flash chromatography on silica gel [column conditions: silica cartridge (80 g); solid deposit on Celite®; λ detection (254 nm, 280 nm); gradient dichloromethane/light petroleum 20 % to 50 % for 60 min at 40 mL/min] and second with recycling size exclusion chromatography (CHCl₃) giving the *title compound* as a yellow solid (69 mg; 8.93×10^{-2} mmol) yield 64 %; ¹H NMR (300 MHz, CDCl₃) δ 7.95 (d, *J* = 8.3 Hz, 8H), 7.51 (dd, *J* = 8.3, 1.4 Hz, 8H), 6.53 (d, *J* = 1.4 Hz, 8H), 3.71 (q, *J* = 7.2 Hz, 8H), 1.19 (t, *J* = 7.2 Hz, 12H); ¹³C NMR (75 MHz, CD₂Cl₂) δ 143.95 (8C), 141.93 (16C), 122.69 (8CH), 117.03 (8CH), 115.88 (8CH), 37.37 (4CH₂), 14.39 (4CH₃) ppm. IR (ATR platinum): 3049, 2968, 2931, 1610, 1588, 1560, 1474, 1447, 1415, 1380, 1326, 1318, 1259, 1241, 1226, 1175, 1129, 1074, 1060, 1014, 994, 939, 937, 868, 849; 824, 792, 753, 735, 654, 628, 584, 552, 480, 458 cm⁻¹; HRMS (ESI⁺, CH₂Cl₂): Found ([M]⁺, 772.3556; C₅₆H₄₄N₄ required 772.35605; m.p. >350°C

[4]cyclo-N-butyl-2,7-carbazole [4]C-Bu-Cbz



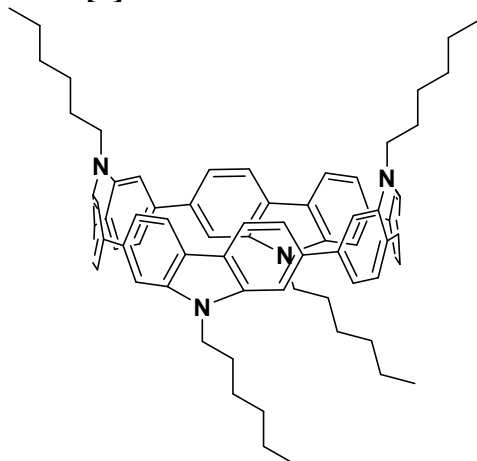
The *title compound* was synthesized using the general procedure for nanoring synthesis.

1st step : **3b** (0.250 g, 0.526 mmol, 1.0 eq), cesium fluoride (0.479 g, 3.16 mmol, 6.0 eq) and 1,5-cyclooctadieneplatinum (II) dichloride (0.197 g, 0.526 mmol, 1.0 eq) in extra dry DCE (20 mL).

2nd step: Triphenylphosphine (2.07 g, 7.89 mmol, 15 eq) was then added to the crude product in 1,2-dichlorobenzene (30 mL).

The residue was purified first with flash chromatography on silica gel [column conditions: silica cartridge (80 g); solid deposit on Celite®; λ detection (254 nm, 280 nm); gradient dichloromethane/light petroleum 20 % to 50 % for 60 min at 40 mL/min] and second with recycling size exclusion chromatography (CHCl₃) to give the *title compound* as a yellow solid (0.070 g, 7.91×10^{-2} mmol); yield 60 %; ¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 8.3 Hz, 8H), 7.49 (d, *J* = 8.3 Hz, 8H), 6.49 (s, 8H), 3.55 (t, *J* = 6.9 Hz, 8H), 1.68 (m, *J* = 7.1 Hz, 8H), 1.31 (m, *J* = 7.3 Hz, 8H), 0.89 (t, *J* = 7.3 Hz, 12H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 143.8 (8C), 142.0 (16C), 122.3 (8CH), 116.7 (8CH), 115.7 (8CH), 41.8 (4CH₂), 31.4 (4CH₂), 20.3 (4CH₂), 13.9 (4CH₃) ppm. IR(ATR platinum) 2957, 2929, 2899, 2869, 1610, 1587, 1560, 1542, 1475, 1450, 1414, 1356, 1320, 1302, 1257, 1244, 1217, 1192, 1131, 1110, 1066, 1030, 995, 926, 863, 845, 831, 812, 792, 755, 741, 725, 715, 702, 667, 654, 627, 604, 593, 575, 552, 502, 465, 452, 441, 424 cm⁻¹. HRMS (MALDI, DCTB): M⁺ found 884.482 for C₆₄H₆₀N₄ required 884.48125. m.p. > 350°C.

[4]cyclo-N-hexyl-2,7-carbazole [4]C-Hex-Cbz



The *title compound* was synthesized using the general procedure for nanoring synthesis.

1st step: **3c** (0.250 g, 0.497 mmol, 1.0 eq), cesium fluoride (0.453 g, 2.98 mmol, 6.0 eq) and 1,5-cyclooctadieneplatinum (II) dichloride (0.186 g, 0.497 mmol, 1.0 eq) in extra dry DCE (19 mL).

2nd step: Triphenylphosphine (1.95 g, 7.45 mmol, 15 eq) was then added to the crude product in 1,2-dichlorobenzene (28 mL).

The residue was purified first with flash chromatography on silica gel [column conditions: silica cartridge (80 g); solid deposit on Celite®; λ detection (254 nm, 280 nm); gradient dichloromethane/light petroleum 20 % to 50 % for 60 min at 40 mL/min] and second with recycling size exclusion chromatography (CHCl₃) giving the *title compound* as a yellow solid (0.064 g, 6.42×10^{-2} mmol); yield 52 %; ¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, $J = 8.3$ Hz, 8H), 7.49 (d, $J = 8.3$ Hz, 8H), 6.49 (s, 8H), 3.54 (t, $J = 7.0$ Hz, 6H), 1.64 (q, $J = 6.9$ Hz, 6H), 1.31 – 1.17 (m, 24H), 0.86 (t, $J = 5.5$ Hz, 12H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 143.8 (8C), 142.0 (16C), 122.3 (8CH), 116.6 (8CH), 115.7 (8CH), 42.1 (4CH₂), 31.5 (4CH₂), 29.1 (4CH₂), 26.7 (4CH₂), 22.6 (4CH₂), 14.2 (4CH₃) ppm. IR (ATR platinum) : 2955, 2922, 2854, 1610, 1587, 1562, 1550, 1476, 1450, 1414, 1376, 1353, 1319, 1302, 1258, 1244, 1219, 1179, 1130, 1063, 1028, 995, 863, 847, 822, 798, 758, 745, 725, 654, 625, 552, 458 cm⁻¹. HRMS (ASAP, 330 °C): Found [M⁺], 996.6061, C₇₂H₇₆N₄ required 996.60645. m.p. > 350°C.

3 2D COSY and NOESY NMR Spectra

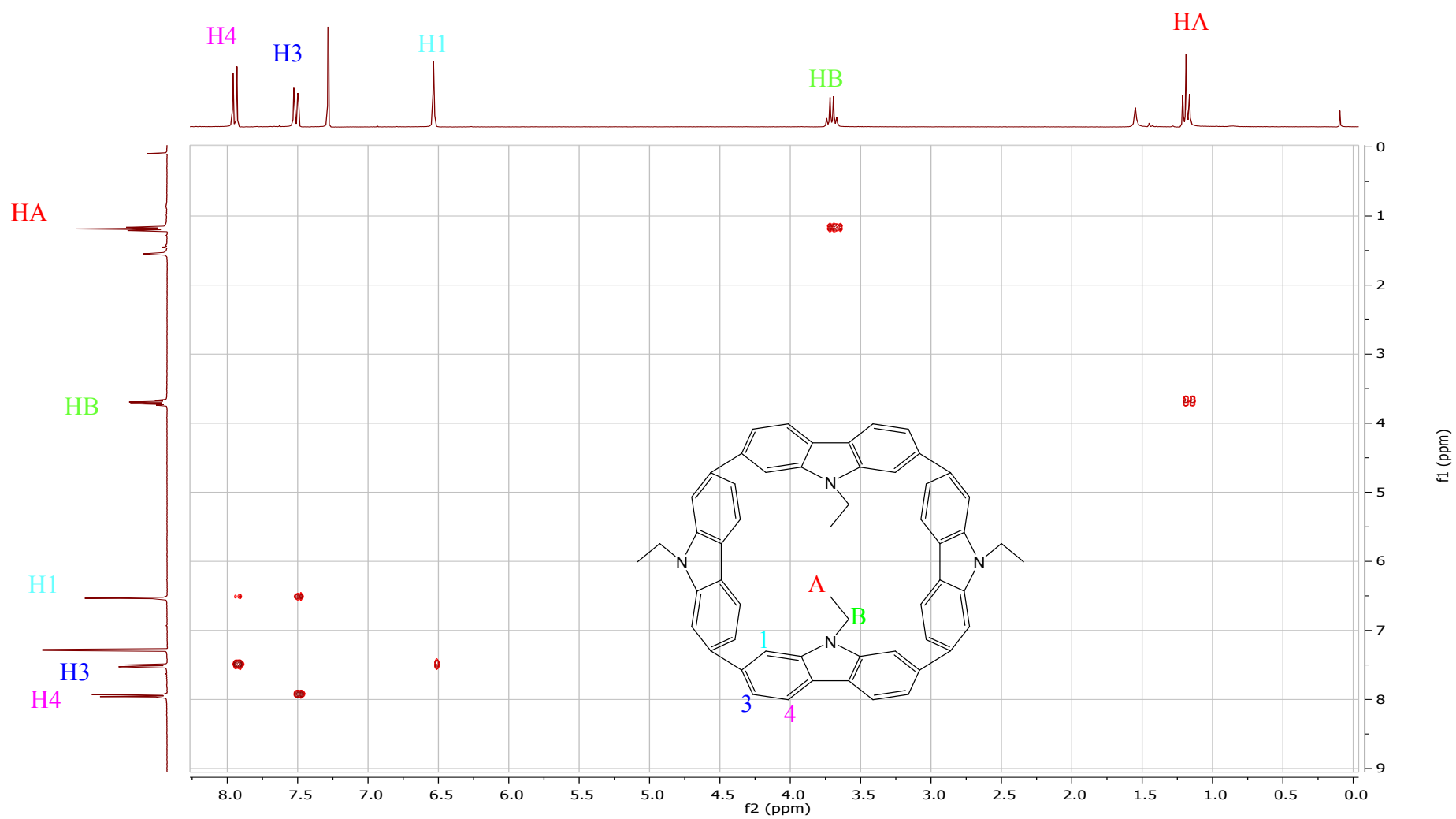


Figure S1 [4]C-Et-Cbz – COSY – CDCl₃

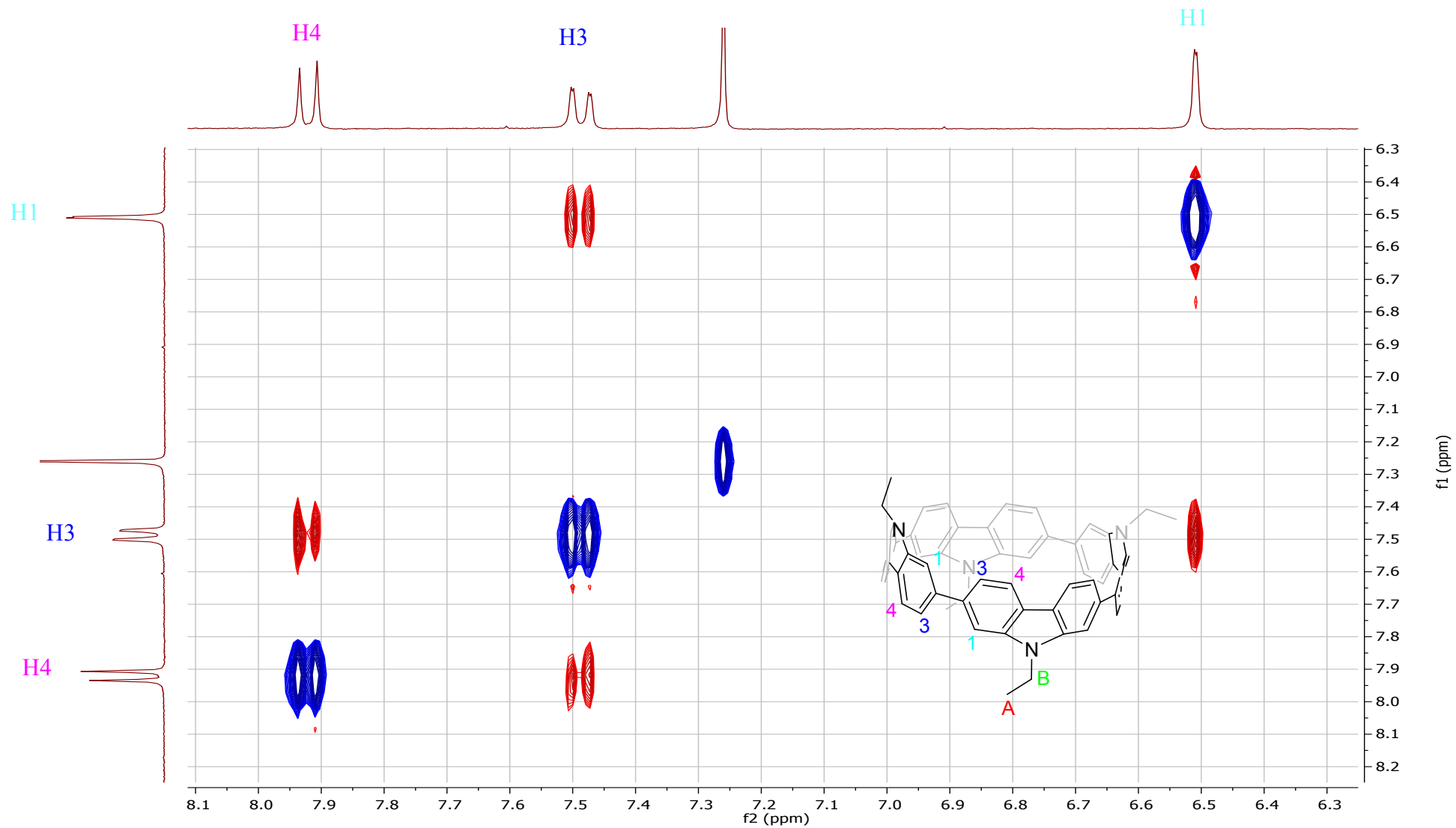


Figure S2 [4]C-Et-Cbz – NOESY – CDCl₃

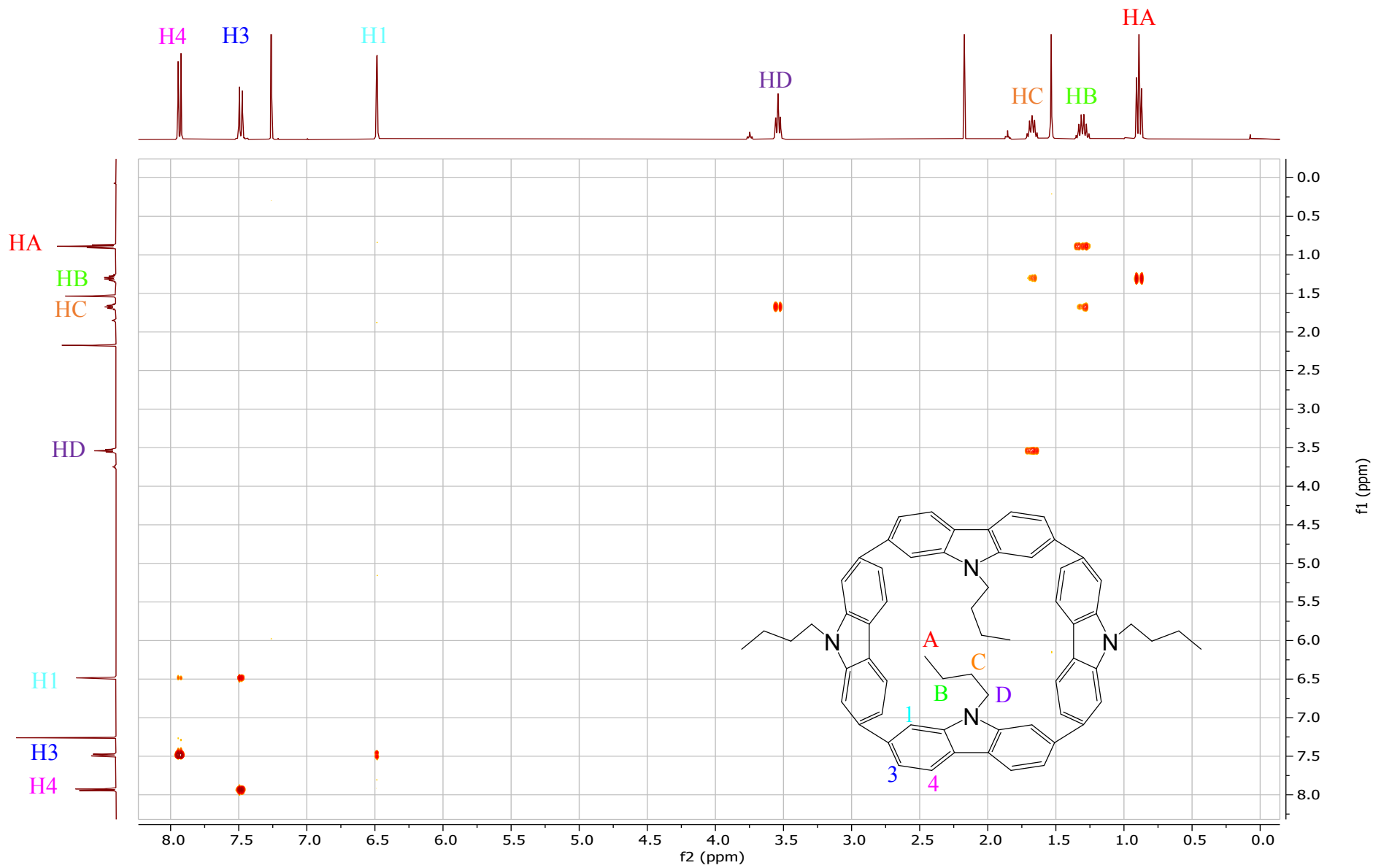


Figure S 3 [4]C-Bu-Cbz – COSY – CDCl₃

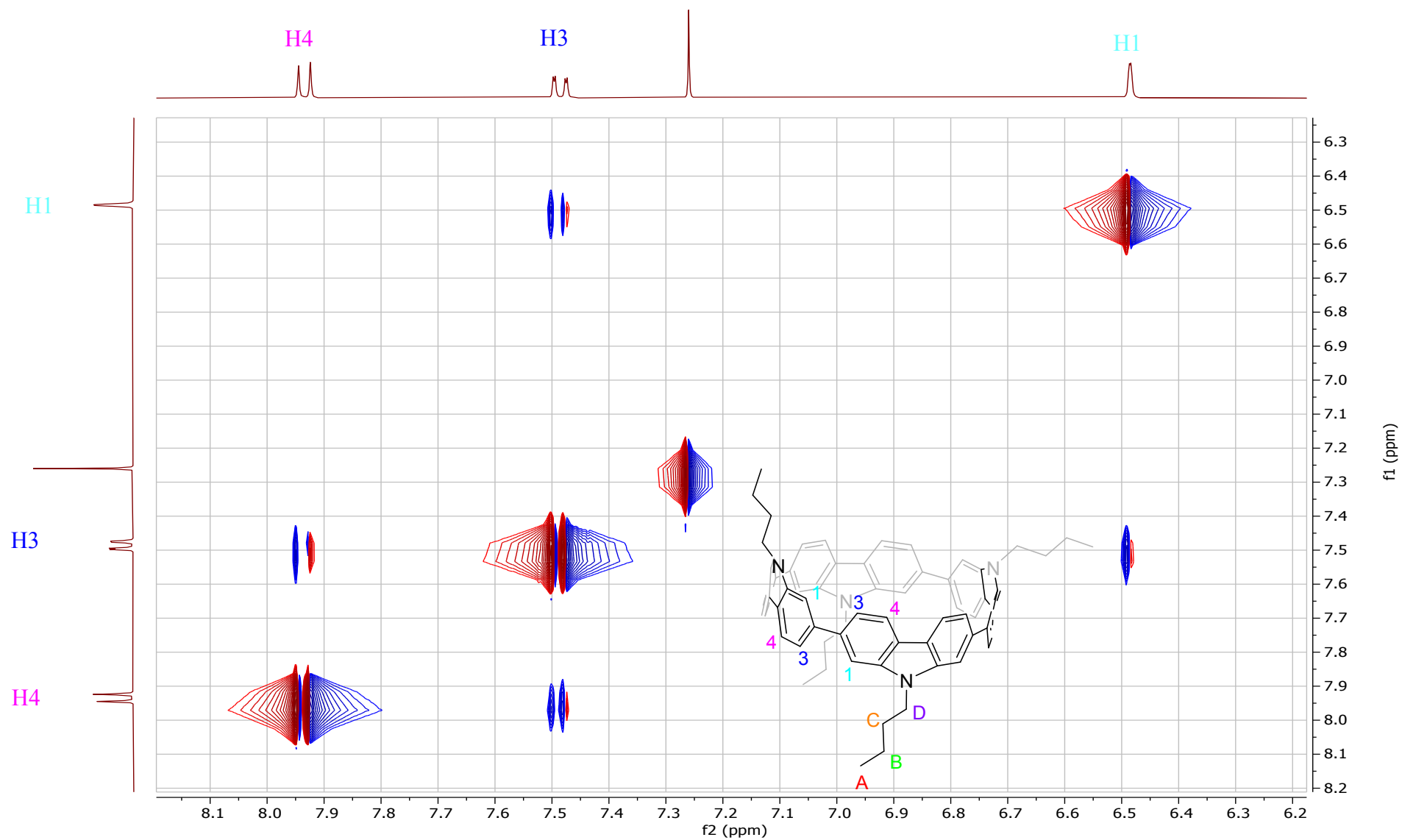


Figure S 4 [4]C-Bu-Cbz – NOESY – CDCl₃

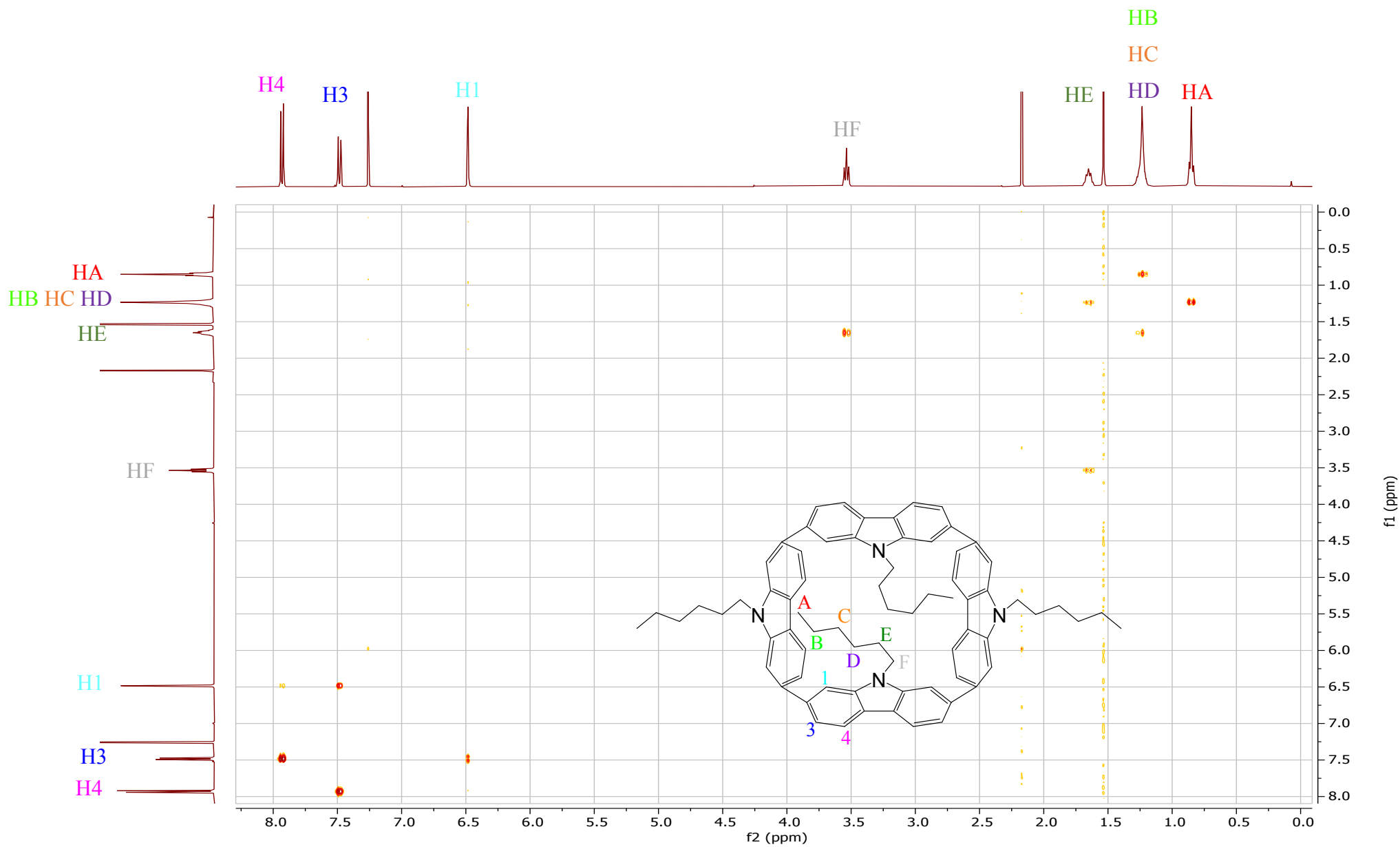


Figure S 5 [4]C-Hex-Cbz – COSY – CDCl₃

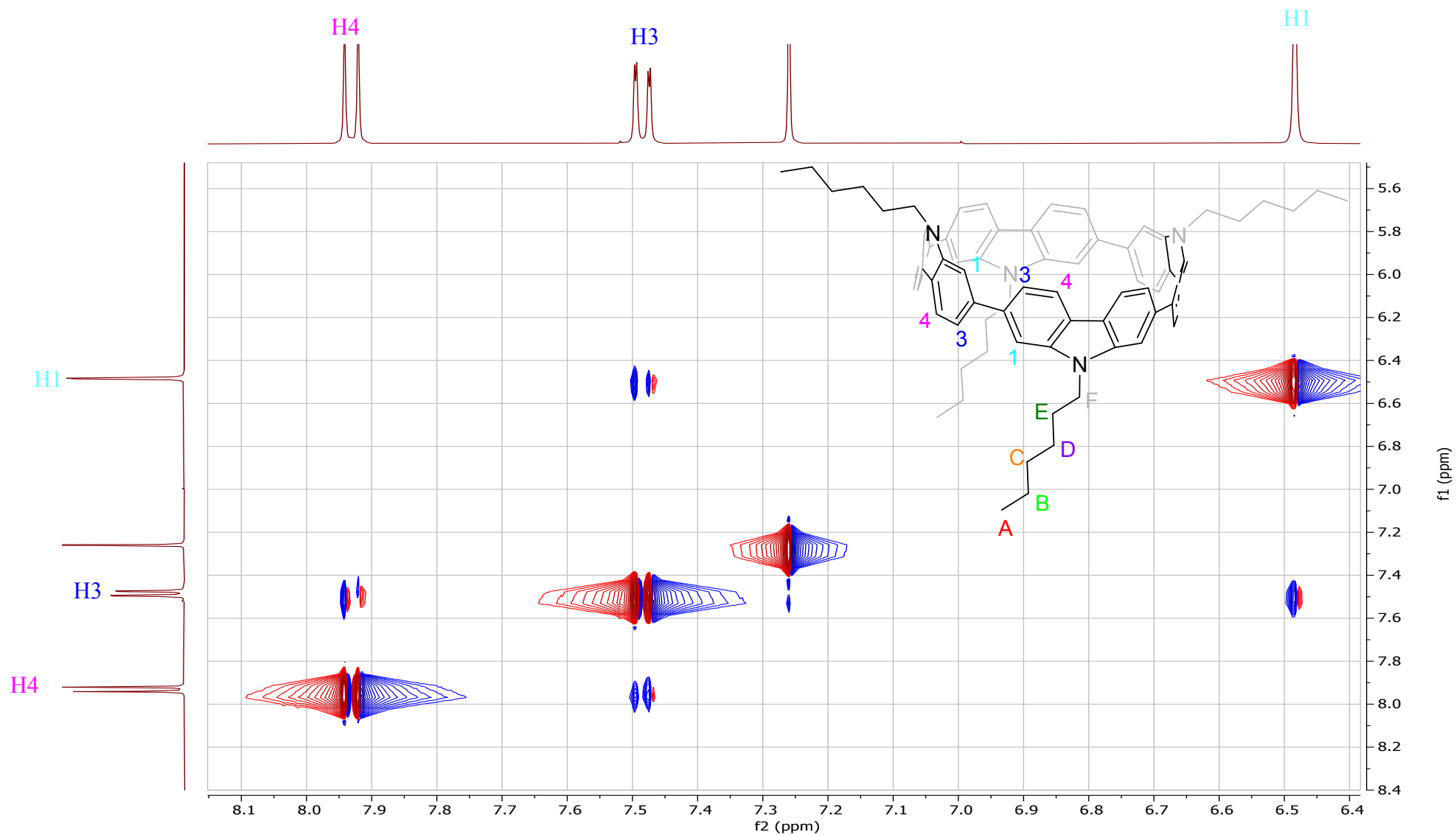


Figure S 6 [4]C-Hex-Cbz – NOESY – CDCl₃

4 Structural and thermal properties

Axes and mean diameter \emptyset

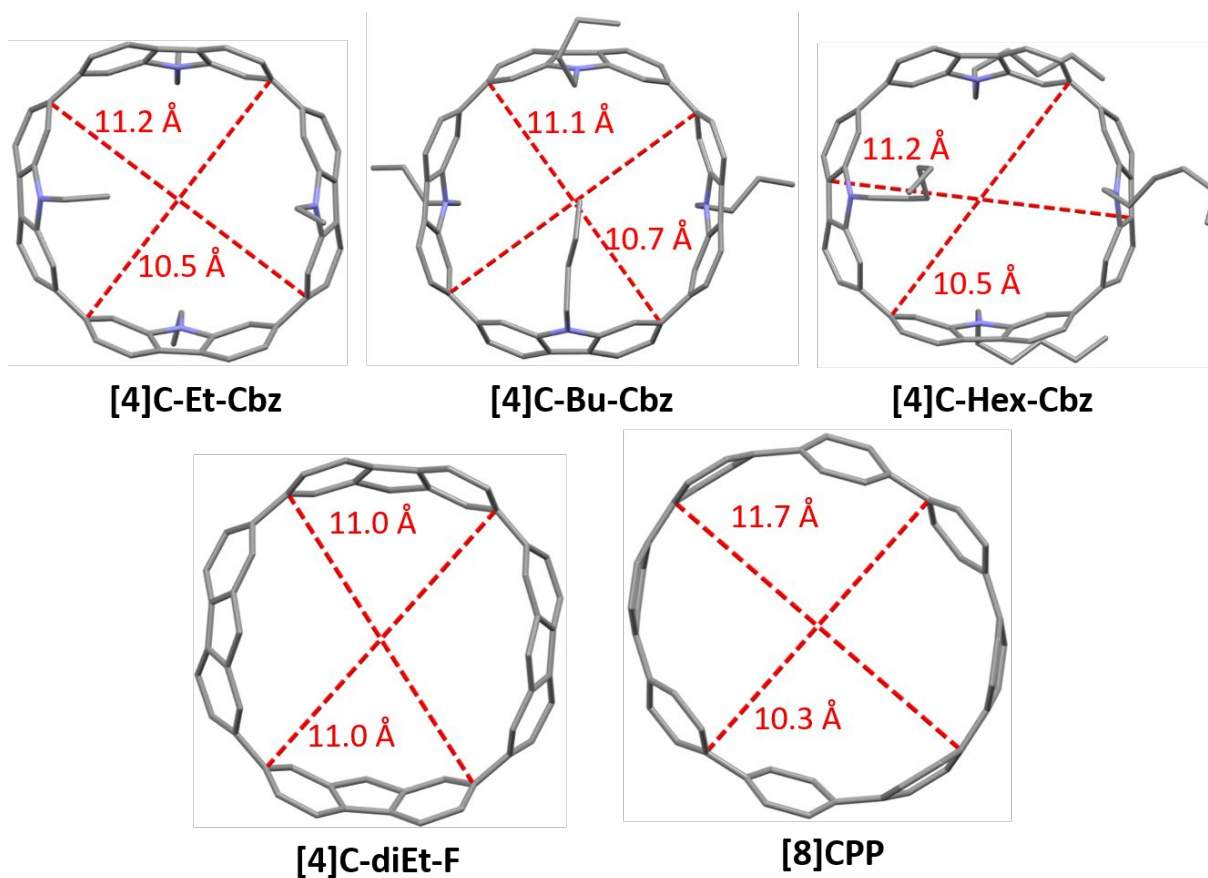


Figure S 7 Minimal and maximal C-C axes in [4]C-Et-Cbz [4]C-Bu-Cbz, [4]C-Hex-Cbz, [4]C-diEt-F and [8]CPP.

Table S 2 Axes and mean diameter values

	Axes (Å)	Mean diameter \emptyset (Å)
[4]C-Et-Cbz	10.60	10.82
	10.51	
	10.49	
	10.64	
	11.10	
	11.07	
	11.19	
	10.94	
[4]C-Bu-Cbz	10.75	10.86
	10.71	
	10.74	
	11.12	
	11.12	
	10.99	
	10.86	

	10.89	
[4]C-Hex-Cbz	10.51	10.90
	10.51	
	10.86	
	10.86	
	11.06	
	11.06	
	11.18	
	11.18	
[4]C-diEt-F	10.98	10.98
	10.98	
	10.98	
	10.98	
	10.98	
	10.98	
	10.98	
	10.98	
[8]CPP	10.87	11.06
	10.34	
	10.93	
	10.38	
	11.34	
	11.25	
	11.65	
	11.68	

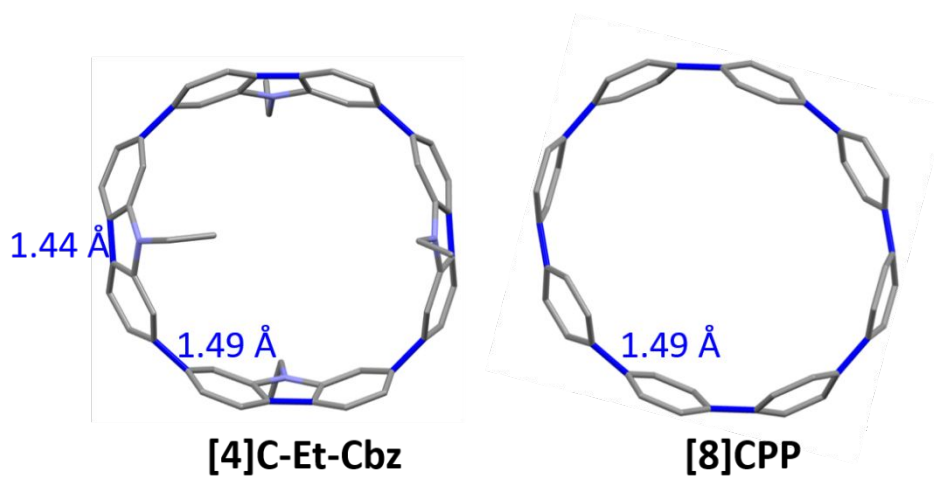


Figure S 8 Average biphenyl bonds in [4]C-Et-Cbz and [8]CPP

Torsion angle

Definition of a torsion angle: The external torsion angle (θ_{ext}) is the dihedral angle between two carbazole building units. Two angles are measured for each C2-C7 link (C8-C7-C2-C3 and C6-C7-C2-C1). The internal torsion angles (θ_{int}) are the dihedral angles within a building unit (C4-C β -C γ -C5 and C α -C β -C γ -C δ).

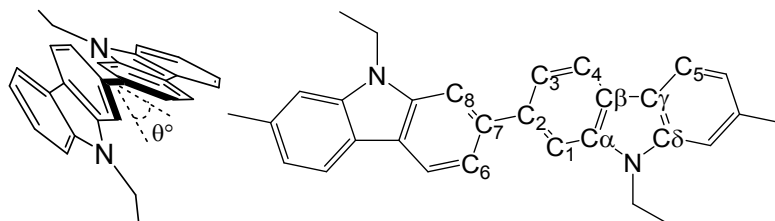


Figure S9 Definition of the torsion angle between two carbazole units

Table S3 Torsion angle values

	□ _{ext}		□ _{int}		θ□
	Values	Average	Values	Average	
[4]C-Et-Cbz	38.7	40.6	0.09	0.8	20.7
	41.2				
	40.7				
	40.4				
	42.4				
	40.7				
	40.4				
	40.5				
[4]C-Bu-Cbz	39.5	37.7	0.1	0.3	19.0
	41.3				
	36.8				
	34.6				
	35.7				
	36.6				
	37.8				
	39.3				
[4]C-Hex-Cbz	41.1	41.1	0.0	0.5	20.3
	43.2				
	40.4				
	39.7				
	40.4				
	39.7				
	43.2				
	41.1				
[8]CPP	42.5	24.3			24.3
	40.4				
	24.9				
	23.1				
	1.5				
	1.6				

	31.3				
	29.4				
	42.5				
	40.4				
	24.9				
	23.1				
	1.5				
	1.6				
	31.3				
	29.4				
[4]C-diEt-F	41.5	41.5	0.0	0.0	20.8
	41.5		0.0		
	41.5		0.0		
	41.5		0.0		
	41.5		0.0		
	41.5		0.0		
	41.5		0.0		
	41.5		0.0		

Displacement angle

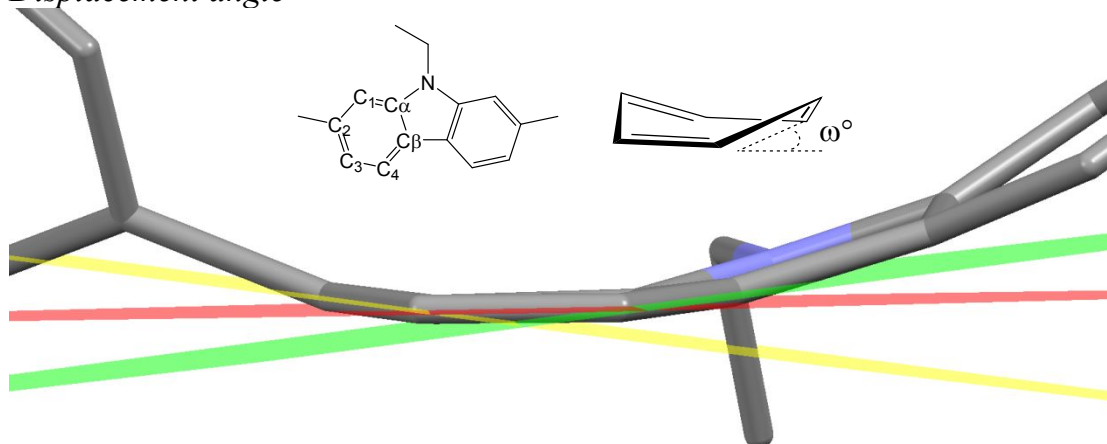


Figure S10 Measurement of a displacement angle

The displacement angle can represent the deformation of a phenyl unit.

Definition of a displacement angle: The mean planes passing by C α -C1-C3-C4 (red), C1-C2-C3 (yellow) and C α -C β -C4 (green) are drawn. The external displacement angle (ω_{ext}) is measured between red and yellow planes, and, the internal displacement angle (ω_{int}) between red and green planes. Then, the mean displacement angle is calculated taking into account two ω_{ext} and two ω_{int} for each carbazole building units.

Table S4 Displacement angle values

	ω_{ext}		ω_{int}		ω
	Values	Average	Values	Average	
[4]C-Et-Cbz	8.4°	7.9	6.1°	6.6	7.2
	7.3°		6.4°		
	8.4°		7.8°		
	8.0°		6.3°		
	6.9°		6.2°		
	8.1°		6.2°		
	8.5°		6.1°		
	7.4°		7.3°		
[4]C-Bu-Cbz	7.4	7.8	5.3	6.3	7.1
	7.2		6.2		
	8.9		7.6		
	7.4		5.1		
	7.6		6.5		
	8.0		7.2		
	7.8		6.1		
	8.2		6.7		
[4]C-Hex-Cbz	8.3	7.6	7.0	6.4	7.0
	8.3		7.0		
	6.8		5.2		
	8.0		6.3		
	7.5		7.2		
	7.5		7.2		
	8.0		6.3		
	6.8		5.2		
[8]CPP	10.8				9.6
	11.4				
	8.1				
	8.3				
	7.7				
	7.2				
	11.1				
	12.1				
	10.8				
	11.4				
	8.1				
	8.3				
	7.7				
	7.2				
	11.1				
12.1					
[4]C-diEt-F	10.7	6.4	10.3	7.4	6.9
	5.8		5.7		
	6.1		5.9		
	9.9		9.1		
	7.7		6.4		

	7.1		6.1	
	4.3		4.4	
	9.2		8.7	

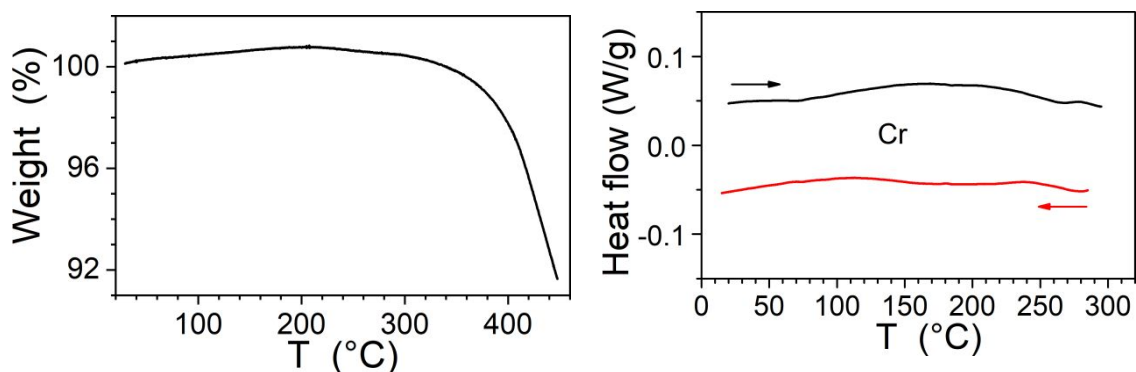


Figure S 11 left: TGA curves (Q50 from TA Instruments; conditions : 5°C/min, air) of **[8]CPP**. Sample amount was insufficient to obtain appropriate baseline, but results are enough to demonstrate that the weight loss from degradation starts around 350°C and reaches 5% at $T_{5\%} = 420^{\circ}\text{C}$. Right: DSC curves on heating and on cooling (DSC Q1000 from TA Instruments; conditions: 5°C/min, endotherm up) that do not display any phase transition peak.

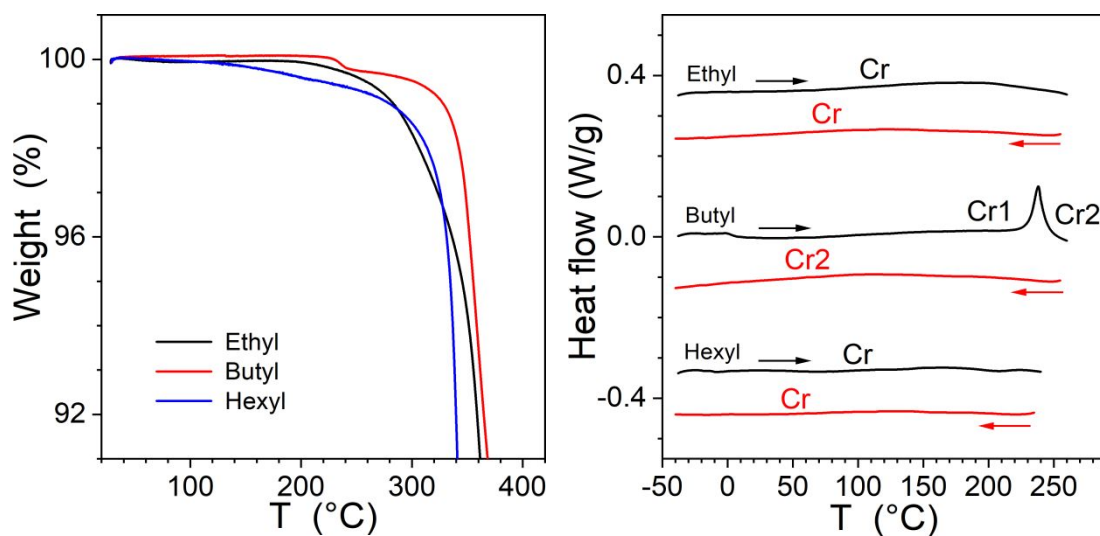


Figure S 12 Left: TGA curves (5°C/min, air). Right: DSC curves on first heating and on cooling (conditions: 5°C/min, endotherm up) and identification based on polarizing optical microscopy (POM) observations of the nanoring series

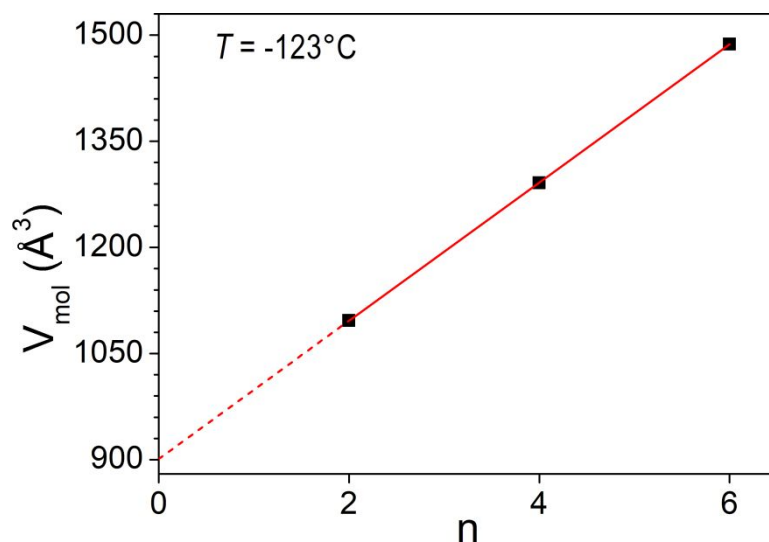


Figure S 13 Variation of molecular volume as a function of alkyl chain length (n =number of carbon atoms in the chain) in [4]C-R-Cbz single-crystal structures.

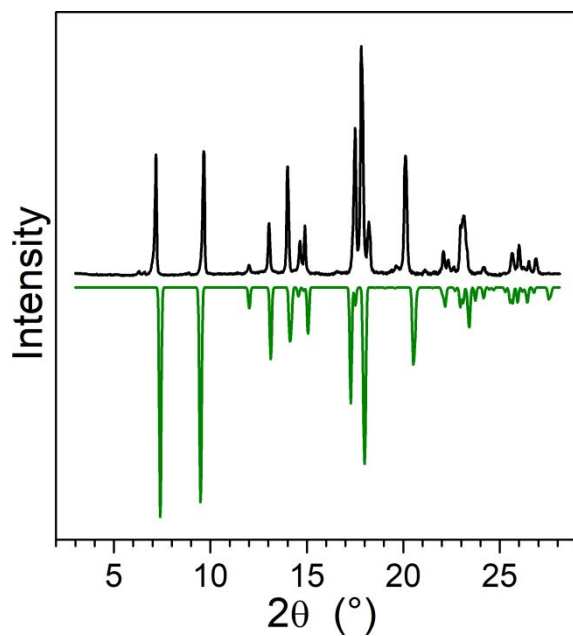


Figure S 14 Powder XRD patterns of 8CPP powder at 20°C and pattern simulated from single-crystal structure CSD-KEBKAL

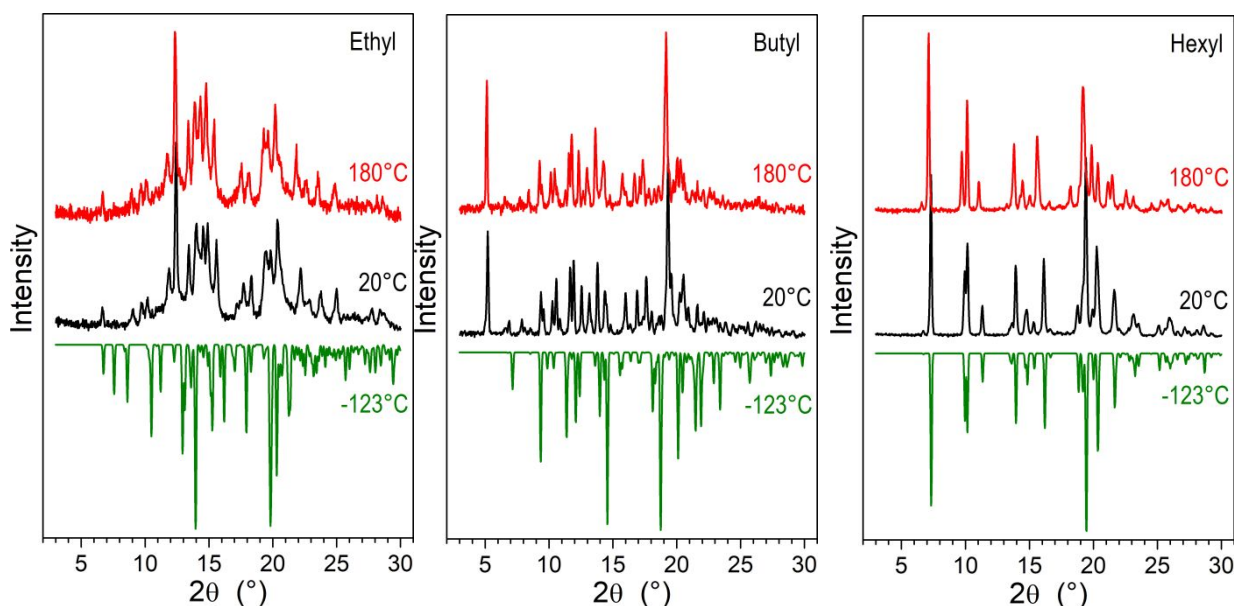


Figure S 15 Small- and wide-angle scattering (S/WAXS) patterns of [4]C-Et-Cbz (Left), [4]C-Bu-Cbz (Middle) and [4]C-Hex-Cbz (Right) at 20°C and 180°C (black and red lines), as compared to simulated powder XRD pattern from single crystal structures acquired at -123°C (green line).

Table S 5 Cell parameters and cell compacity at temperature of measurement T . V , ρ , Z , V/Z : cell volume, density, number of molecules per cell and cell volume per molecule; V_{solv} : solvent volume calculated from density database; $V_{\text{mol}} = V/Z - V_{\text{solv}}$: molecular volume.

Compound	T [°C]	Cell parameters [Å, °, Å ³]	ρ [g/cm ³]	V/Z [Å ³]	V_{solv} [Å ³]	V_{mol} [Å ³]
[4]C-Hex-Cbz	-123	$a = 9.4194, b = 26.193, c = 12.3056, \beta = 101.590$ $\alpha = \gamma = 90, V = 2974.3 (Z = 2)$	1.114	1487.1	0	1487.1
[4]C-Hex-Cbz	20	$a = 9.419, b = 26.27, c = 12.341, \beta = 101.80$ $\alpha = \gamma = 90, V = 2989.1 (Z = 2)$	1.108	1494.5	0	1494.5
[4]C-Hex-Cbz	180	$a = 9.438, b = 26.66, c = 12.687, \beta = 103.43$ $\alpha = \gamma = 90, V = 3105.0 (Z = 2)$	1.067	1552.5	0	1552.5
[4]C-Bu-Cbz	-123	$a = 17.0612, b = 17.9109, c = 18.9041, \beta = 90$ $\alpha = \gamma = 90, V = 5776.7 (Z = 4)$	1.124	1444.2	153	1291
[4]C-Et-Cbz	-123	$a = 26.355, b = 9.1895, c = 41.286, \beta = 96.498$ $\alpha = \gamma = 90, V = 9935 (Z = 8)$	1.233	1241.9	145	1097
[8]CPP	20	$a = 13.327, b = 8.060, c = 19.254, \beta = 108.08$ $\alpha = \gamma = 90, V = 1952.8 (Z = 2)$	1.035	976.4	0	976.4
[8]CPP	-173	$a = 12.9325, b = 8.0103, c = 19.3676, \beta = 105.363$ $\alpha = \gamma = 90, V = 1934.66 (Z = 2)$	1.045	967.63	0	967.63

Table S 6 Structural parameters at temperature of measurement T .

Compound T [°C] Structure type	2D-sublattice parameters [\AA , °, \AA^2] 3D-cell parameters [\AA , °] Columnar lattice parameters [\AA , °, \AA^2]	h_{mol} [\AA] D_{row} [\AA]	D_{mol} [\AA] d_{lam} [\AA]	A_{mol} [\AA^2] S_{mol} [\AA^2]	ψ [°] h_{stack} [\AA]	s_{ring} [\AA^2] σ_{ring} [\AA^2]	$D_{\text{ring, cyl}}$ [\AA] $D_{\text{ring, cav}}$ [\AA]
	[4]C-Hex-Cbz -123 LamCol	$a_{2D} = 26.193, b_{2D} = 9.4194, \gamma_{2D} = 90, A = 246.72$ ($Z_{2D} = 2$) $c' = 12.3056$ ($N_L = 1$), $\alpha' = 101.590, \beta' = 90$ $a_{\text{col}} = 26.193, b_{\text{col}} = 12.0547, \gamma_{\text{col}} = 90, A_{\text{col}} = 315.75$ ($Z_{\text{col}} = 2$)	9.4194 13.097	12.055 12.055	123.36 157.88	51.4 5.88	95.7 153.4
[4]C-Hex-Cbz 20 LamCol	$a_{2D} = 26.27, b_{2D} = 9.419, \gamma_{2D} = 90, A = 247.4$ ($Z_{2D} = 2$) $c' = 12.341$ ($N_L = 1$), $\alpha' = 101.80, \beta' = 90$ $a_{\text{col}} = 26.27, b_{\text{col}} = 12.080, \gamma_{\text{col}} = 90, A_{\text{col}} = 317.3$ ($Z_{\text{col}} = 2$)	9.419 13.135	12.08 12.08	123.7 158.7	-	-	-
[4]C-Hex-Cbz 180 LamCol	$a_{2D} = 26.66, b_{2D} = 9.438, \gamma_{2D} = 90, A = 251.6$ ($Z_{2D} = 2$) $c' = 12.687$ ($N_L = 1$), $\alpha' = 103.43, \beta' = 90$ $a_{\text{col}} = 26.193, b_{\text{col}} = 12.340, \gamma_{\text{col}} = 90, A_{\text{col}} = 329.0$ ($Z_{\text{col}} = 2$)	9.438 13.330	12.34 12.34	125.8 164.5	-	-	-
[4]C-Bu-Cbz $\bullet\text{C}_6\text{H}_5\text{CH}_3$ -123	$a_{2D} = 18.9041, b_{2D} = 17.9109, \gamma_{2D} = 90, A = 338.59$ ($Z_{2D} = 2$) $c' = 17.0612$ ($N_L = 2$), $\alpha' = 90, \beta' = 90$	8.9554 9.4520	8.5306 -	169.29 161.26	36.8 -	-	10.92
[4]C-Et-Cbz $\bullet\text{CHCl}_3$ -123 LamCol	$a_{2D} = 26.355, b_{2D} = 9.1895, \gamma_{2D} = 90, A = 242.19$ ($Z_{2D} = 2$) $c' = 41.286$ ($N_L = 4$), $\alpha' = 90, \beta' = 96.498$ $a_{\text{col}} = 41.286, b_{\text{col}} = 26.355, \gamma_{\text{col}} = 96.498, A_{\text{col}} = 1081.10$ ($Z_{\text{col}} = 8$)	9.1895 13.178	10.255 41.021	121.10 135.14	50.8 5.80	98.1 155.3	13.39 10.84
[8]CPP -173 Col	$a_{2D} = 12.9325, b_{2D} = 8.0103, \gamma_{2D} = 90, A = 103.59$ ($Z_{2D} = 1$) $c' = 19.3676$ ($N_L = 2$), $\alpha' = 90, \beta' = 105.363$ $a_{\text{col}} = 19.3676, b_{\text{col}} = 12.9325, \gamma_{\text{col}} = 105.363, A_{\text{col}} = 241.52$ ($Z_{\text{col}} = 2$)	8.0103 12.9325	9.338 -	103.59 120.76	43.8 5.78	103.6 167	13.9 11.0
[8]CPP 20 Col	$a_{2D} = 13.237, b_{2D} = 8.060, \gamma_{2D} = 90, A = 106.69$ ($Z_{2D} = 1$) $c' = 19.254$ ($N_L = 2$), $\alpha' = 90, \beta' = 108.08$ $a_{\text{col}} = 19.254, b_{\text{col}} = 13.237, \gamma_{\text{col}} = 108.08, A_{\text{col}} = 242.3$ ($Z_{\text{col}} = 2$)	8.060 13.237	9.15 -	106.7 121.1	-	-	-

LamCol: lamello-columnar structure; col: columnar structure; $a_{2D}, b_{2D}, \gamma_{2D}, A, Z_{2D}$: sublattice parameters, area and number of molecules per sublattice in the molecular layer plane; c', N_L, a', b' : cell parameters after referential change ($a' = a_{2D}$: direction of row juxtaposition; $b' = b_{2D}$: direction of rows; c' : direction of layer normal; N_L : number of layers per cell); $a_{\text{col}}, b_{\text{col}}, \gamma_{\text{col}}, A_{\text{col}}, Z_{\text{col}}$: columnar lattice parameters, lattice area and number of columns per lattice ([4]C-Hex-Cbz: $b_{\text{col}} = c' \times \cos(\alpha')$); h_{mol} : molecular spacing along rows/columns; D_{row} : row/columns spacing in the layer plane; D_{mol} : thickness of molecular layers; $d_{\text{lam}} = N_L \times D_{\text{mol}}$: lamellar periodicity; $A_{\text{mol}} = V_{\text{mol}}/D_{\text{mol}} = A/Z_{2D}$: molecular area in the layer plane; $S_{\text{mol}} = V_{\text{mol}}/h_{\text{mol}} = A_{\text{col}}/Z_{\text{col}}$: molecular section in the columnar/piling plane; ψ : tilt angle of rings; $h_{\text{stack}} = h_{\text{mol}} \times \cos(\psi)$: stacking distance of rings; $S_{\text{ring}} = V_{\text{ring}}/h_{\text{mol}}$: cross-sectional area of stacked rings in the columnar plane; $s_{\text{ring}} = V_{\text{ring}}/h_{\text{stack}}$: cross-sectional area of rings; $D_{\text{ring, cyl}} = \sqrt{(2/\sqrt{3}) \times s_{\text{ring}}}$: diameter of equivalent cylinder of cross-sectional area s_{ring} ; $D_{\text{ring, cav}}$: average ring cavity diameter from C-C distances (the shape of the [8]CPP ring is approximately elliptical: $D_1 = 11.66 \text{ \AA}, D_2 = 10.36 \text{ \AA}, D_{\text{ring, cav}} = \sqrt{(D_1 \times D_2)} = 10.99$; flattening: $e = 1 - D_2/D_1 = 0.1114 = 1/8.97$)

Packing diagrams

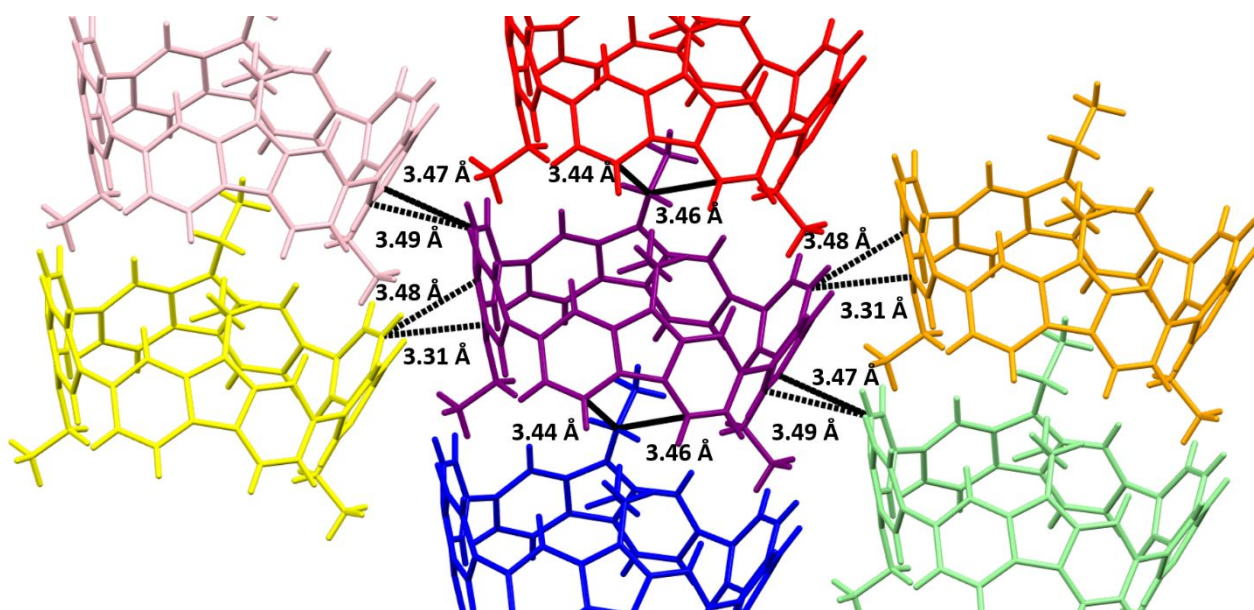


Figure S 16 Short C-C distances in [4]C-Et-Cbz single crystal packing diagram

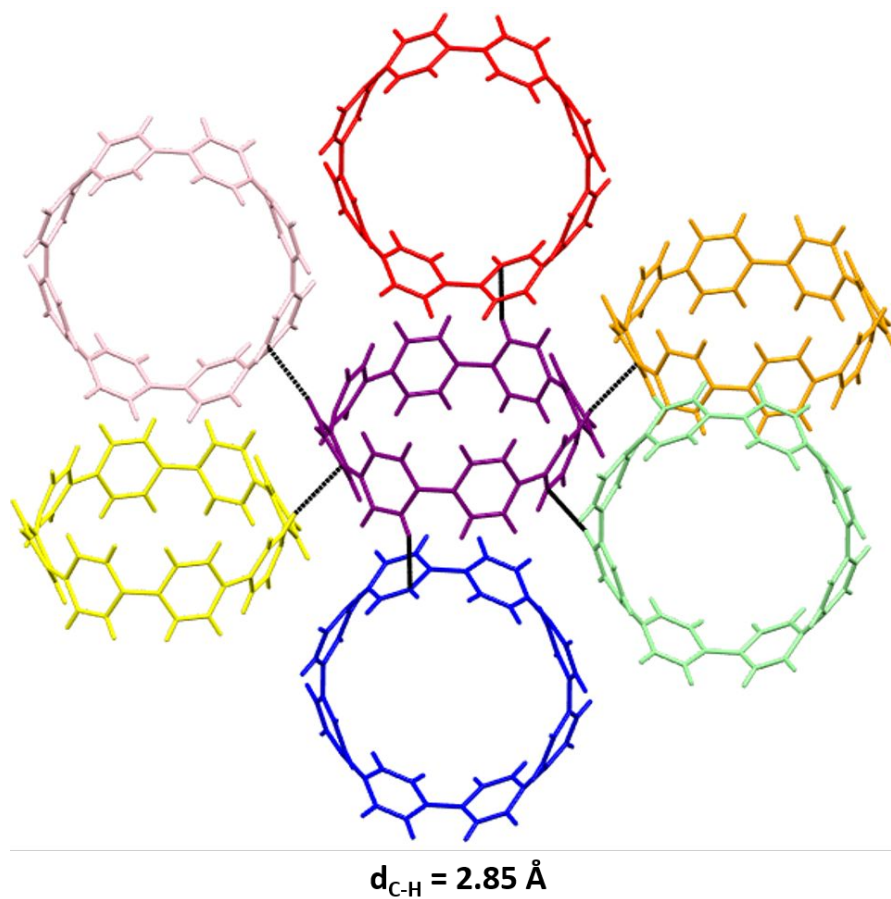


Figure S 17 Short C-H distances in [8]CPP single crystal packing diagram

5 Electrochemical studies

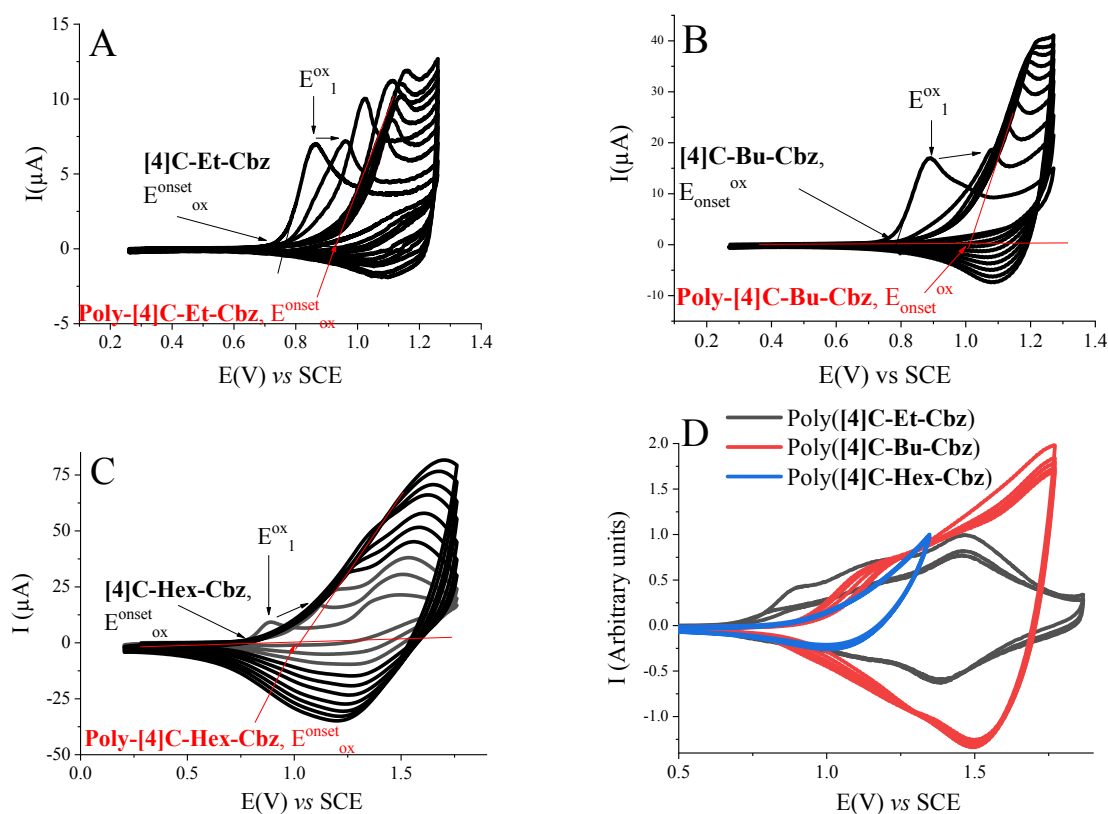


Figure S 18 Cyclic voltammograms recorded in DCM + Bu_4NPF_6 0.2 M in presence of [4]C-Et-Cbz (A), [4]C-Bu-Cbz (B) and [4]C-Hex-Cbz (C). Ten recurrent cycles. Platinum Working electrode, 100 mV/s. Cyclic voltammograms recorded in DCM + Bu_4NPF_6 0.2 M in absence of the cyclocarbazoles [4]C-alkyl-Cbz (D). Poly([4]C-alkyl-Cbz) modified platinum electrode. 100 mV/s.

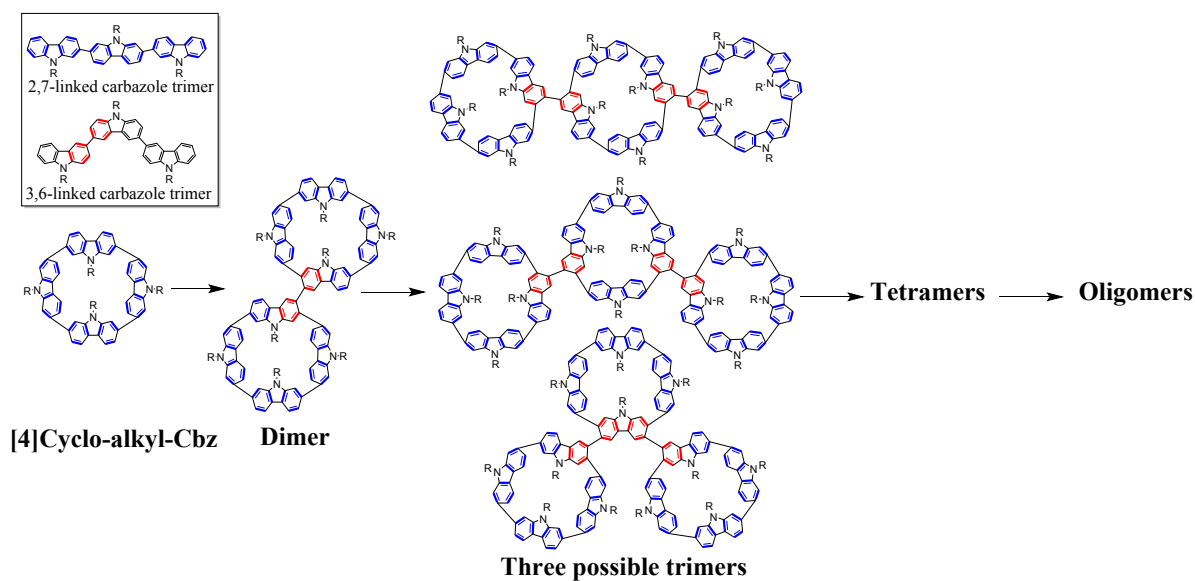


Figure S 19 Proposed carbon-carbon coupling leading to electrodeposition process along recurrent cycles.

6 Photophysical properties

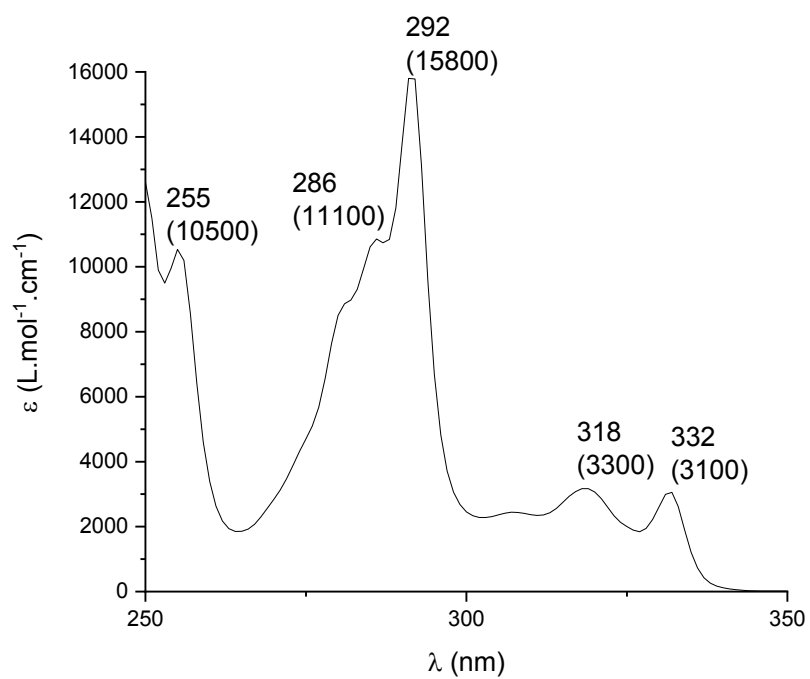


Figure S 20. Absorption spectra of **Cbz** in cyclohexane

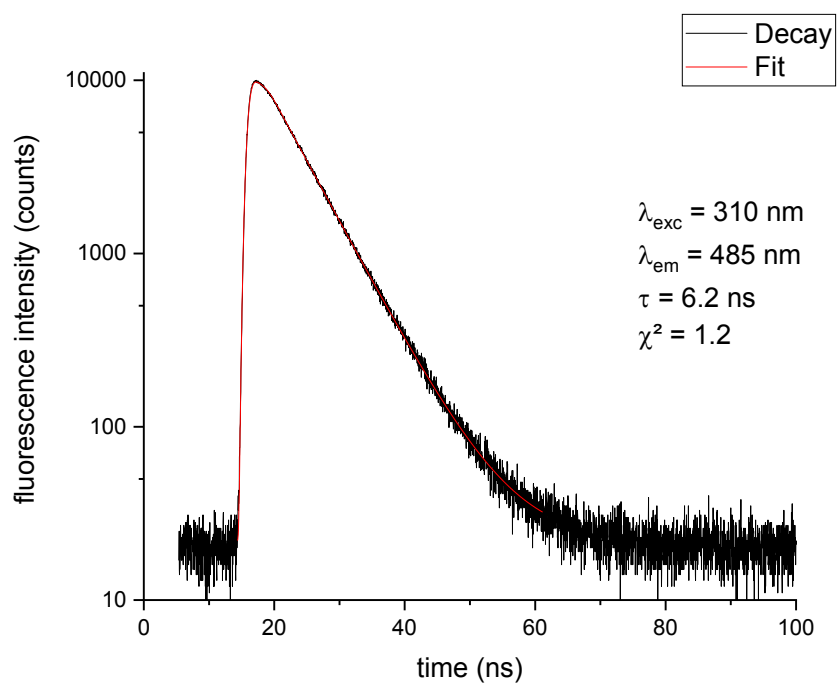


Figure S 21 Fluorescence decay of [4]C-Et-Cbz in cyclohexane

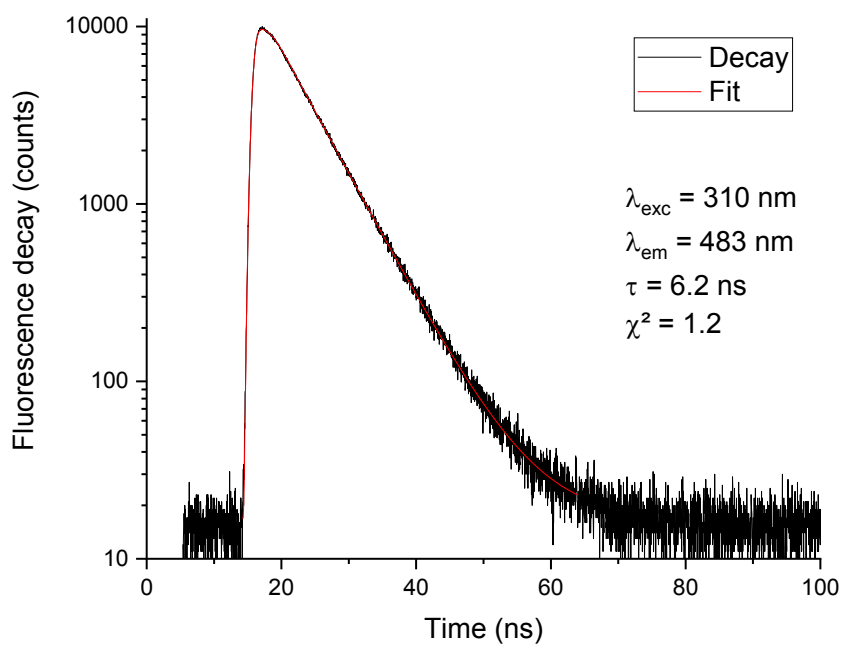


Figure S 22 Fluorescence decay of [4]C-Bu-Cbz in cyclohexane

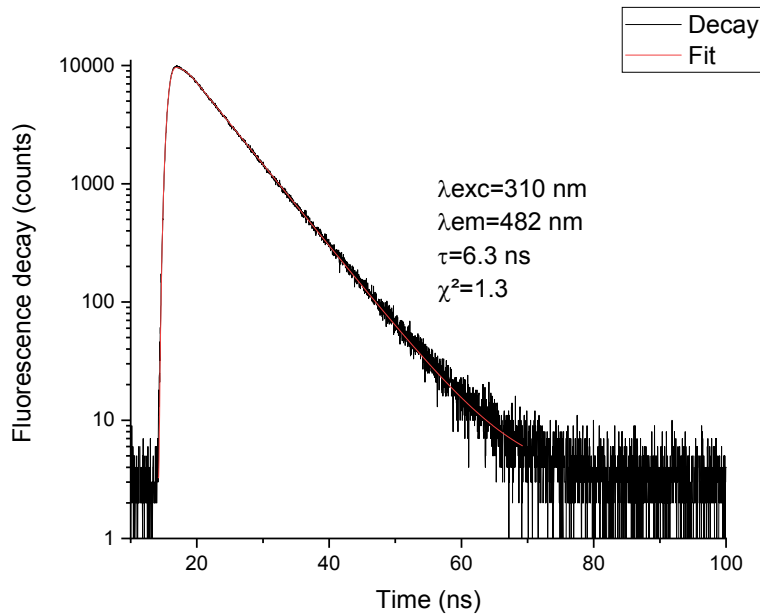


Figure S 23 Fluorescence decay of [4]C-Hex-Cbz in cyclohexane

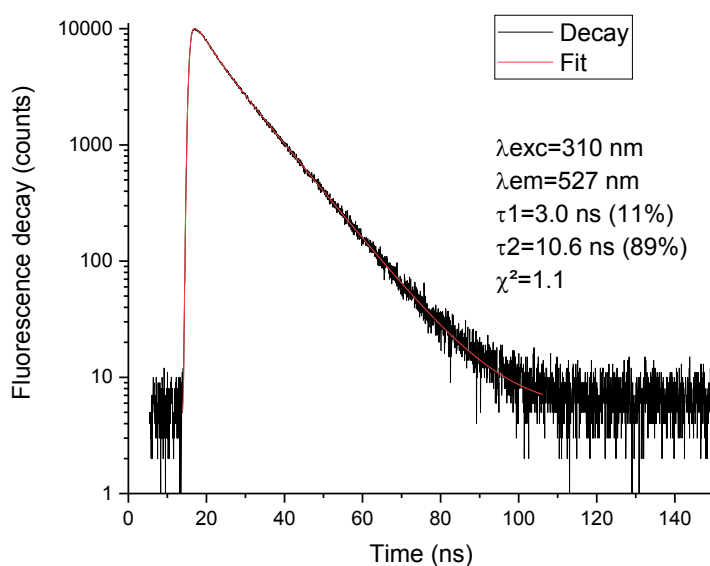


Figure S 24 Fluorescence decay of [8]CPP in cyclohexane

7 Organic field effect transistor and space-charged-limited current diode measurements

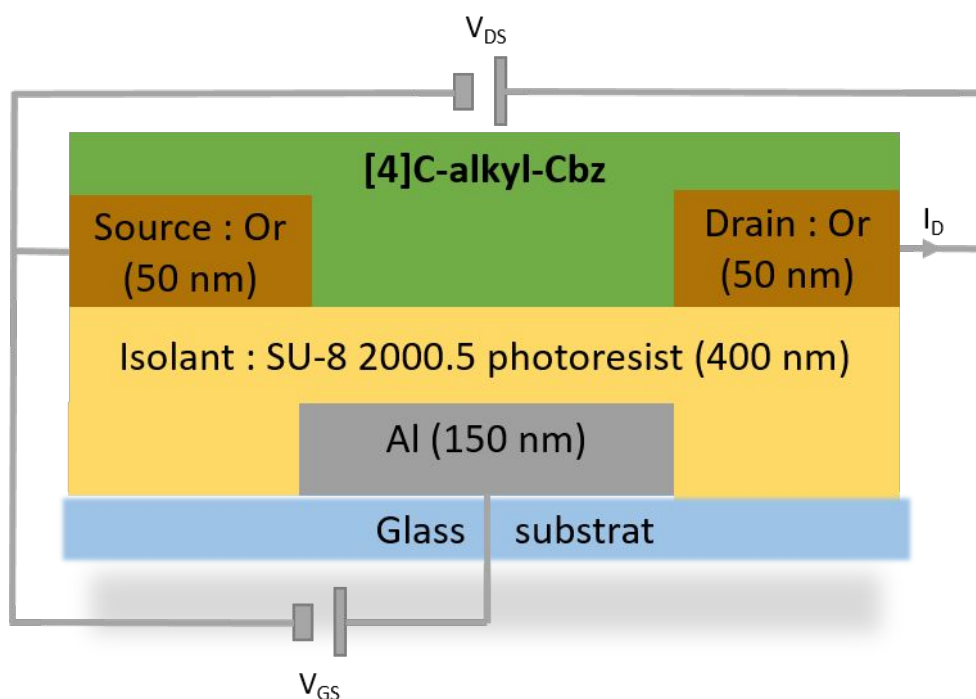


Figure S 25 Structure of the bottom-gate bottom-contact p-type channel OFETs on glass substrat

For the three nanorings the carrier mobility is extracted using the Mott-Gurney formalism in the area where $m = 2$ where the traps are no longer involved in the electrical conduction through the semiconducting layer.

$$J_{SCLC} = \frac{9}{8} \epsilon_0 \epsilon_r \Theta \mu \frac{V^2}{L^3} \quad (1)$$

$$\Theta = \frac{n_f}{n_f + n_t} \quad (2)$$

$$m = \frac{\partial \text{Log}(J)}{\partial \text{Log}(V)} \quad (3)$$

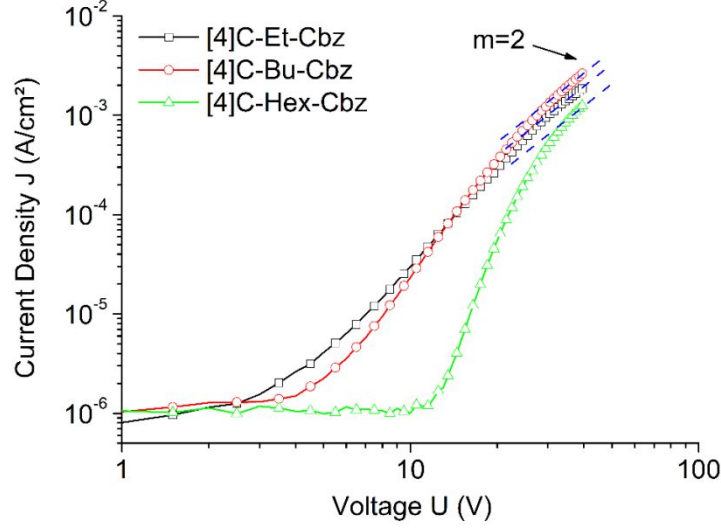


Figure S 26 I-V characteristics of Au/OSC/Au structures for [4]C-Et-Cbz, [4]C-Bu-Cbz and [4]C-Hex-Cbz.

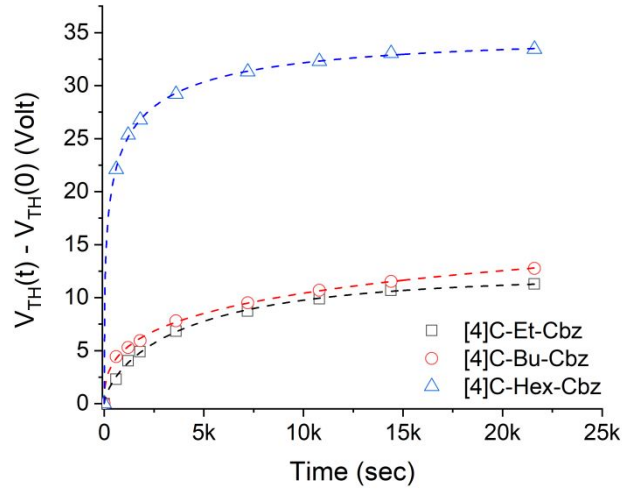


Figure S 27 Evolution of ΔV_{TH} with the stress time for [4]C-Et-Cbz, [4]C-Bu-Cbz and [4]C-Hex-Cbz based OFETs under $V_{GSstress} - V_{TH} = 40V$ and $V_{DS} = 10V$. The dashed lines are the fit with stretched exponential equation (4).

$$V_{TH}(t) - V_{TH}(0) = V_{TH}(\infty) \left\{ 1 - \exp \left[- \left(\frac{t}{t_0} \right)^{\beta_1} \right] \right\} \quad (4)$$

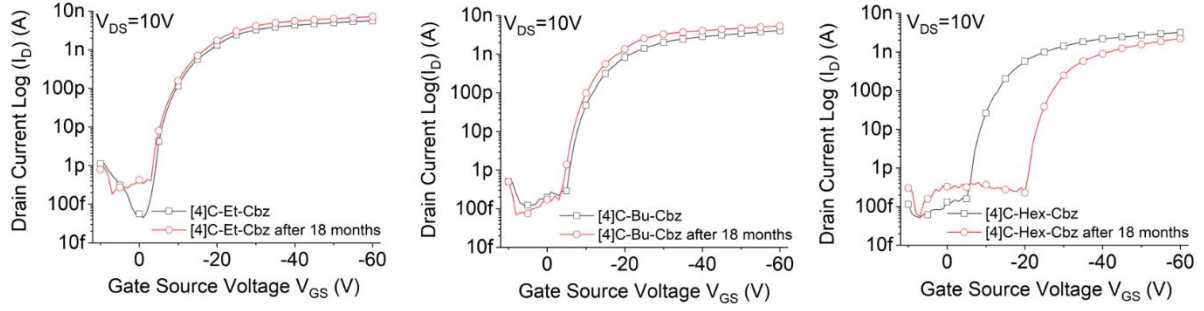


Figure S 28 Transfer characteristics in linear regime before and after 18 months of **[4]C-Et-Cbz** (left), **[4]C-Bu-Cbz** (middle) and **[4]C-Hex-Cbz** (right).

Table S 7 Stretched Exponential fit parameters. $V_{TH}(\infty)$ is the maximum threshold voltage shift after infinite stress time, β is the stretched-exponential exponent and t_0 represents the characteristic trapping time of carriers.

	$V_{TH}(\infty)$ (V)	β	t_0 (s)	R^2
[4]C-Et-Cbz	11.9	0.697	4623.4	0.9988
[4]C-Bu-Cbz,	23.3	0.384	39045.2	0.9992
[4]C-Hex-Cbz	34.7	0.335	558.9	0.9999

Table S 8 Roughness parameters extracted from AFM images ($500 \times 500 \text{nm}^2$)

	R_a (Arithmetic Average Roughness) [nm]	R_q (RMS Roughness) [nm]	R_{max} (Maximum Roughness depth) [nm]
[4]C-Et-Cbz	0.658	0.837	4.81
[4]C-Bu-Cbz,	0.332	0.421	3.15
[4]C-Hex-Cbz	1.18	1.47	9.46
[8]CPP	2.79	3.67	29.8

8 Molecular modelling

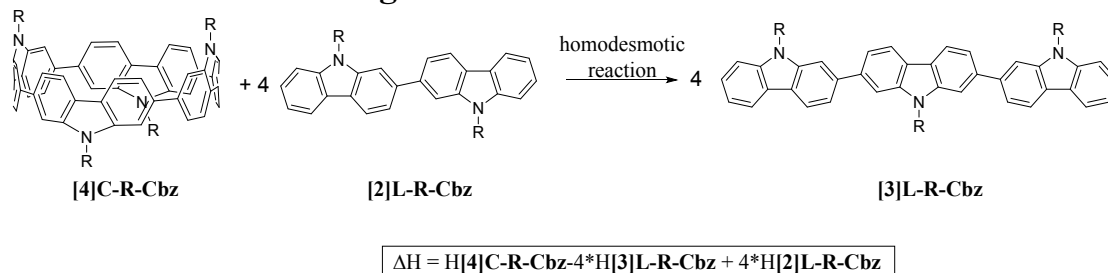
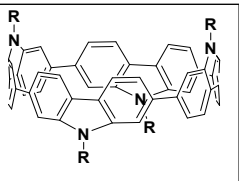
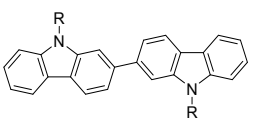
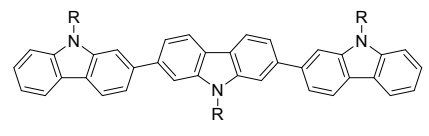


Figure S 29 Strain energy (ΔH) calculation (b3lyp/6-31g(d))

Table S 9 Strain energies of [4]C-Et-Cbz, [4]C-Bu-Cbz and [4]C-Hex-Cbz. Energies are given in kcal.mol⁻¹.

				ΔH
[4]C-Et-Cbz	-1492599.30	-747070.99	-1120239.18	73
[4]C-Bu-Cbz	-1689807.53	-845674.36	-1268144.22	72
[4]C-Hex-Cbz	-1887008.40	-944273.71	1416044.15	73

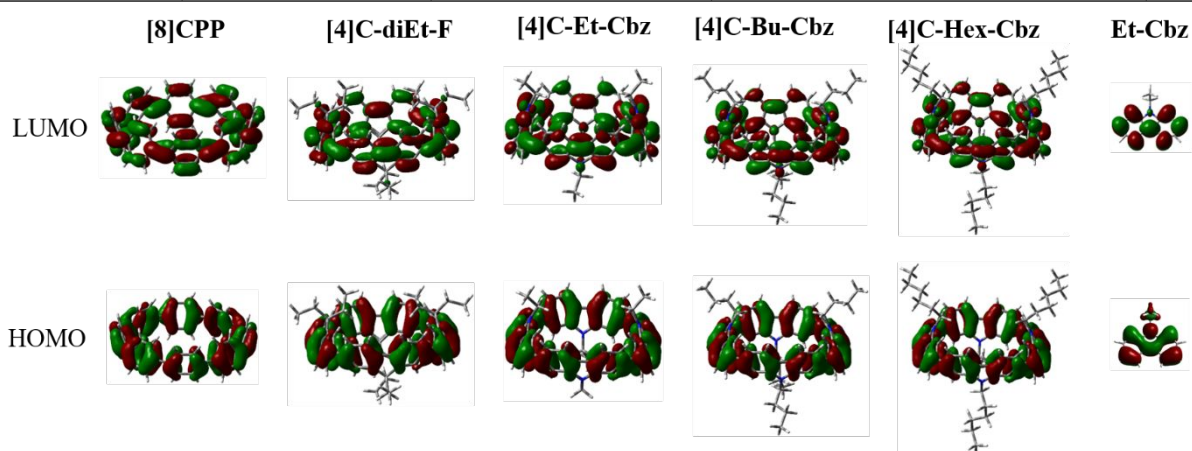


Figure S 30 Representation of the frontier orbitals of [8]CPP, [4]C-diEt-F, [4]C-Et-Cbz, [4]C-Bu-Cbz, [4]C-Hex-Cbz and Cbz obtained by DFT, B3LYP/6-311 + G(d,p), shown with an isovalue of 0.02 [$e \text{ bohr}^{-3}$]^{1/2}.

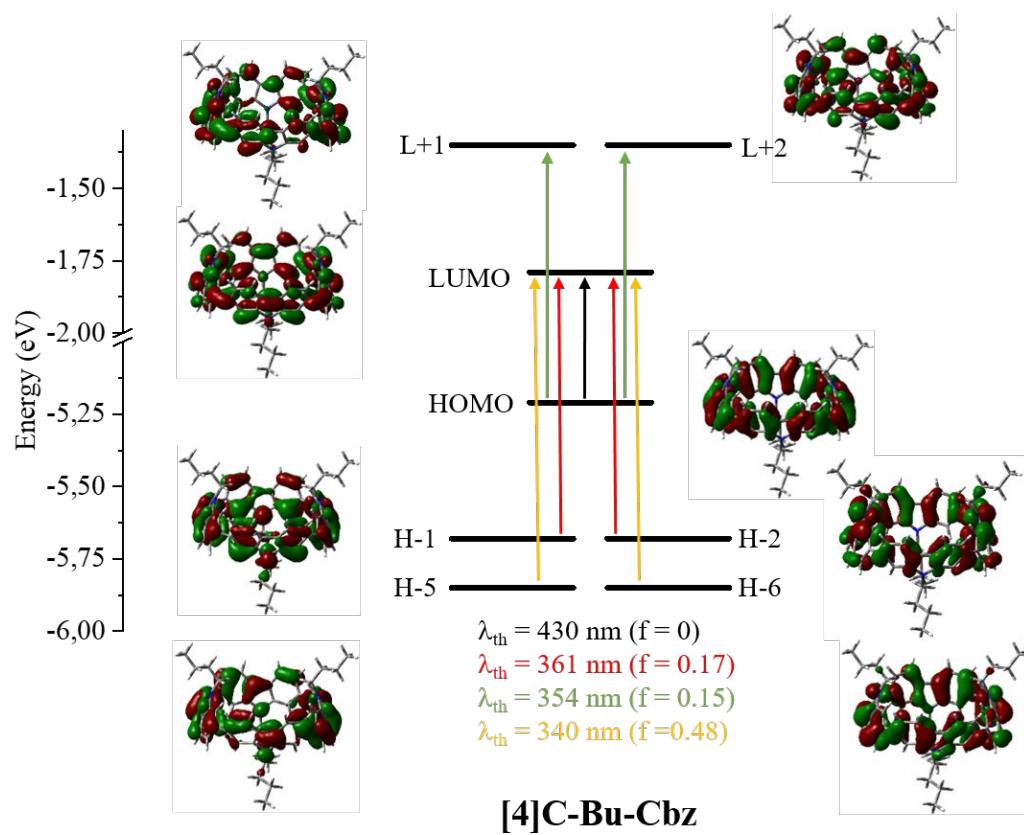


Figure S 31 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of [4]-Bu-Cbz obtained by TD-DFT, B3LYP/6-311 + G(d,p), shown with an isovalue of 0.02 [$e \text{ bohr}^3$]^{1/2}. For clarity purposes, only the major contribution of each transition is shown.

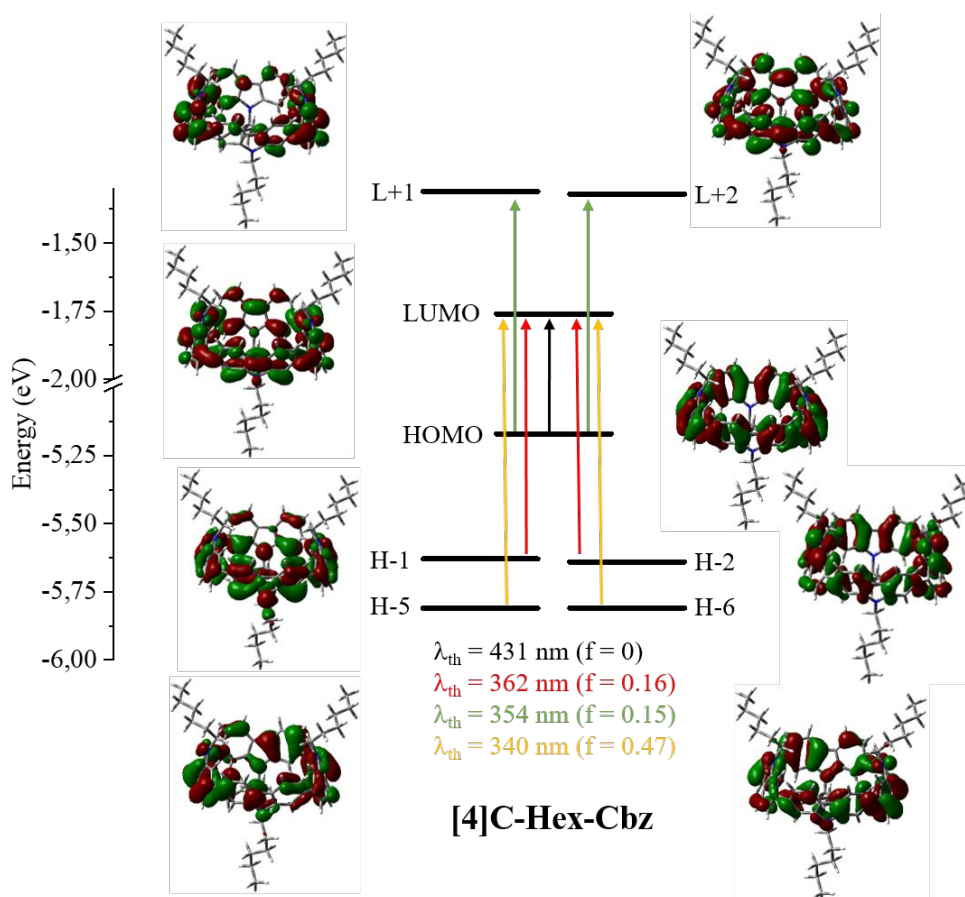


Figure S 32 Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of **[4]-Hex-Cbz** obtained by TD-DFT, B3LYP/6-311 + G(d,p), shown with an isovalue of $0.02 [e \text{ bohr}^{-3}]^{1/2}$. For clarity purposes, only the major contribution of each transition is shown.

Table S 10 TD-DFT results of **[4]C-Et-Cbz** (b3lyp/6-311+g(d,p).

λ (nm)	Oscillator strength	Major contributions	Minor contributions
430	0	HOMO→LUMO (97%)	
361	0.17	H-1→LUMO (60%) HOMO→L+1 (12%)	H-6→LUMO (7%), H-5→LUMO (2%), H-3→L+2 (3%), HOMO→L+2 (7%)
361	0.16	H-2→LUMO (59%) HOMO→L+2 (11%)	H-6→LUMO (2%), H-5→LUMO (7%), H-3→L+1 (3%), H-3→L+2 (2%), HOMO→L+1 (8%)
358	0.001	H-3→LUMO (88%)	H-6→L+2 (3%), H-5→L+1 (3%)
356	0.06	H-4→LUMO (84%)	H-2→L+2 (3%), H-1→L+1 (4%), HOMO→L+5 (3%)
354	0.13	H-2→LUMO (12%) H-1→LUMO (13%) HOMO→L+1 (72%)	

354	0.14	H-2→LUMO (12%) H-1→LUMO (11%) HOMO→L+2 (74%)	
340	0.48	H-5→LUMO (78%)	H-4→L+2 (4%), H-2→LUMO (7%), H-1→LUMO (3%), HOMO→L+2 (2%)
340	0.47	H-6→LUMO (78%)	H-4→L+1 (4%), H-2→LUMO (3%), H-1→LUMO (6%), HOMO→L+1 (2%)
325	0.0001	H-2→L+1 (16%) H-1→L+2 (16%) HOMO→L+3 (55%)	H-2→L+2 (2%), H-1→L+1 (2%)
321	0.006	H-4→LUMO (12%) H-2→L+2 (28%) H-1→L+1 (41%)	H-3→L+3 (5%), H-2→L+1 (6%), H-1→L+2 (3%)
319	0	H-2→L+1 (17%) H-2→L+2 (36%) H-1→L+1 (24%) H-1→L+2 (19%)	
317	0.0001	H-2→L+1 (38%) H-2→L+2 (15%) H-1→L+1 (18%) H-1→L+2 (19%)	H-4→L+3 (2%), H-3→LUMO (3%)
317	0	H-2→L+1 (15%) H-1→L+2 (34%) HOMO→L+3 (38%)	H-2→L+2 (6%)
316	0.006	H-4→L+2 (26%) H-3→L+1 (23%) H-3→L+2 (20%)	H-6→LUMO (2%), H-5→LUMO (5%), H-4→L+1 (8%), H-2→LUMO (4%), H-2→L+3 (5%)
315	0.005	H-4→L+1 (38%) H-3→L+1 (16%) H-3→L+2 (13%)	H-6→LUMO (5%), H-5→LUMO (2%), H-4→L+2 (9%), H-1→LUMO (4%), H-1→L+3 (5%), HOMO→L+8 (2%)
313	0.13	H-4→L+1 (22%) H-4→L+2 (11%) H-3→L+1 (34%) H-3→L+2 (26%)	
312	0.01	H-6→L+2 (37%) H-5→L+1 (39%)	H-4→L+2 (4%), H-4→L+3 (4%), H-3→LUMO (6%), H-3→L+1 (3%)
312	0.12	H-4→L+1 (14%) H-4→L+2 (33%) H-3→L+1 (14%)	H-6→L+2 (2%), H-5→L+1 (3%)

		H-3→L+2 (28%)
308	0	H-6→L+1 (46%) H-5→L+2 (45%)

Table S 11 TD-DFT results of [4]C-Bu-Cbz (b3lyp/6-311+g(d,p)).

λ (nm)	Oscillator Strength	Major contributions	Minor contributions
430	0.00	HOMO→LUMO (97%)	
362	0.14	H-1→LUMO (65%)	H-5→LUMO (7%), H-3→L+1 (3%), H-3→L+2 (3%), HOMO→L+1 (9%), HOMO→L+2 (7%)
361	0.17	H-2→LUMO (63%), HOMO→L+2 (10%)	H-6→LUMO (8%), HOMO→L+1 (8%)
358	0.01	H-3→LUMO (86%)	H-5→L+1 (2%)
357	0.06	H-4→LUMO (84%)	H-2→L+1 (2%), H-2→L+2 (2%), HOMO→L+5 (2%)
354	0.15	H-1→LUMO (15%), HOMO→L+1 (74%)	H-2→LUMO (6%), HOMO→L+2 (2%)
354	0.15	H-2→LUMO (16%), HOMO→L+2 (75%)	H-1→LUMO (5%), HOMO→L+1 (2%)
340	0.48	H-6→LUMO (30%), H-5→LUMO (50%)	H-4→L+2 (4%), H-2→LUMO (7%), H-1→LUMO (2%)
340	0.47	H-6→LUMO (50%), H-5→LUMO (31%)	H-4→L+1 (4%), H-2→LUMO (3%), H-1→LUMO (6%)
325	0.00	H-2→L+1 (10%), H-1→L+1 (10%), H-1→L+2 (11%), HOMO→L+3 (52%)	H-2→L+2 (9%)
322	0.01	H-4→LUMO (11%), H-2→L+1 (19%), H-2→L+2 (16%), H-1→L+1 (25%), H-1→L+2 (18%)	H-3→L+3 (5%)
320	0.00	H-2→L+1 (18%), H-2→L+2 (29%), H-1→L+1 (25%), H-1→L+2 (25%)	

Table S 12 TD-DFT results of [4]C-Hex-Cbz (b3lyp/6-311+g(d,p)).

λ (nm)	Oscillator Strength	Major contributions	Minor contributions
431	0.00	HOMO→LUMO (97%)	

362	0.14	H-1→LUMO (67%), HOMO→L+1 (12%)	H-6→LUMO (2%), H-5→LUMO (5%), H-3→L+2 (5%), HOMO→L+2 (2%)
362	0.16	H-2→LUMO (64%), HOMO→L+2 (13%)	H-6→LUMO (6%), H-5→LUMO (3%), H-4→L+1 (3%), H-3→L+1 (2%), HOMO→L+1 (3%)
359	0.01	H-3→LUMO (85%)	
357	0.07	H-4→LUMO (84%)	H-2→L+1 (4%), H-1→L+2 (2%), HOMO→L+5 (2%)
354	0.15	H-1→LUMO (17%), HOMO→L+1 (76%)	HOMO→L+2 (2%)
354	0.15	H-2→LUMO (19%), HOMO→L+2 (75%)	
340	0.47	H-6→LUMO (33%), H-5→LUMO (47%)	H-4→L+1 (2%), H-2→LUMO (8%)
340	0.46	H-6→LUMO (48%), H-5→LUMO (34%)	H-1→LUMO (8%)
325	0.00	H-2→L+2 (14%), H-1→L+1 (19%), HOMO→L+3 (51%)	H-2→L+1 (4%), H-1→L+2 (5%)
322	0.01	H-4→LUMO (10%), H-2→L+1 (30%), H-1→L+1 (12%), H-1→L+2 (32%)	H-3→L+3 (5%), H-2→L+2 (6%)
320	0.00	H-2→L+2 (38%), H-1→L+1 (39%), H-1→L+2 (12%)	H-2→L+1 (6%)

Table S 13 Atomic coordinates of [4]C-Et-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	-2.650892	4.261788	1.01839
C	-3.711753	3.378971	1.223109
H	-3.738279	2.746007	2.103337
C	-4.59059	3.117319	0.161492
C	-4.50676	3.912552	-1.007301
H	-5.22298	3.750001	-1.808292
C	-3.466955	4.819434	-1.194471
H	-3.38576	5.36034	-2.134089
C	-2.468039	4.941042	-0.215479
C	-1.093831	5.408487	-0.222778
C	-0.237471	5.91758	-1.211812

H	-0.640649	6.292934	-2.149144
C	1.14147	5.834433	-1.037153
H	1.800798	6.140202	-1.845105
C	1.704005	5.260211	0.128764
C	0.858069	4.934896	1.199299
H	1.273192	4.451838	2.077065
C	-0.522999	4.986266	1.007293
C	-1.25861	3.692752	3.045927
H	-2.186304	3.707239	3.627628
H	-0.526978	4.272858	3.618144
C	-0.768397	2.251121	2.854207
H	-1.50248	1.654025	2.304718
H	-0.603509	1.779475	3.829755
H	0.173309	2.224611	2.297498
C	4.214071	2.710864	-0.795184
C	3.329154	3.777361	-0.961094
H	2.706605	3.846543	-1.846564
C	3.045753	4.604071	0.135339
C	3.822475	4.471551	1.312224
H	3.64424	5.150451	2.141808
C	4.729851	3.42764	1.464802
H	5.255929	3.303357	2.408126
C	4.873389	2.476364	0.441857
C	5.343904	1.104567	0.402171
C	5.825604	0.207651	1.369054
H	6.179577	0.572311	2.330169
C	5.741661	-1.162783	1.138991
H	6.028336	-1.854329	1.926726
C	5.190295	-1.677089	-0.060148
C	4.895784	-0.789124	-1.104842
H	4.434498	-1.167631	-2.010816
C	4.947945	0.583709	-0.857973
C	3.782255	1.402172	-2.934311
H	3.094388	2.230027	-3.120428
H	3.173535	0.488565	-2.915652

C	4.826169	1.325833	-4.052684
H	5.404888	2.253638	-4.10579
H	4.335206	1.166817	-5.019576
H	5.524618	0.499867	-3.884088
C	2.623407	-4.217236	0.717975
C	3.689221	-3.343957	0.940533
H	3.744177	-2.766667	1.857431
C	4.530259	-3.014513	-0.13226
C	4.410505	-3.740931	-1.34239
H	5.101379	-3.530062	-2.154277
C	3.366796	-4.638763	-1.549193
H	3.255276	-5.122113	-2.516647
C	2.401399	-4.823509	-0.546509
C	1.026947	-5.287921	-0.539528
C	0.145094	-5.736008	-1.53605
H	0.526104	-6.057059	-2.502393
C	-1.228385	-5.661739	-1.324859
H	-1.908192	-5.921532	-2.131872
C	-1.759362	-5.153036	-0.114428
C	-0.887338	-4.8912	0.951717
H	-1.286009	-4.459109	1.863153
C	0.489613	-4.934222	0.7279
C	1.349268	-3.835032	2.855652
H	0.281814	-3.792793	3.083678
H	1.707402	-2.797227	2.844311
C	-4.294105	-2.560185	-0.828155
C	-3.412661	-3.613588	-1.076492
H	-2.813348	-3.631525	-1.980315
C	-3.100115	-4.499678	-0.035828
C	-3.845924	-4.435037	1.166484
H	-3.645856	-5.159422	1.951426
C	-4.748941	-3.402685	1.401458
H	-5.249643	-3.33188	2.36392
C	-4.919712	-2.39624	0.437431
C	-5.392117	-1.025442	0.486904

C	-5.846686	-0.184507	1.51525
H	-6.173366	-0.602589	2.464228
C	-5.769204	1.196804	1.359552
H	-6.033519	1.843039	2.19231
C	-5.250996	1.777886	0.176214
C	-4.985144	0.949811	-0.92391
H	-4.547187	1.378436	-1.819032
C	-5.031535	-0.434769	-0.752836
C	-3.928518	-1.135265	-2.904973
H	-3.264652	-1.962006	-3.167034
H	-3.301937	-0.234947	-2.851571
C	-5.009588	-0.970862	-3.977826
H	-5.606985	-1.883855	-4.067502
H	-4.550145	-0.758899	-4.949998
H	-5.685881	-0.145897	-3.732172
N	-1.510238	4.410765	1.803998
N	4.374851	1.598182	-1.620176
N	1.501637	-4.397453	1.522699
N	-4.479778	-1.404406	-1.585888
C	2.084723	-4.64235	3.929773
H	3.158044	-4.690973	3.719615
H	1.949189	-4.177731	4.913121
H	1.701105	-5.666754	3.973993

Number of imaginary frequency: 0

Table S14 Atomic coordinates of [2]L-Et-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	6.634592	0.523154	0.539932
C	5.284498	0.235801	0.315914
C	4.866888	-1.035318	-0.164316
C	5.822927	-2.027137	-0.411496
C	7.167711	-1.746168	-0.185357
C	7.565008	-0.482808	0.285179
H	6.957697	1.496459	0.897328
H	5.518564	-3.004592	-0.777113

H	7.9184	-2.508018	-0.375264
H	8.619904	-0.282067	0.452276
C	3.426688	-0.976831	-0.284845
C	2.441086	-1.884544	-0.68736
C	3.035185	0.325755	0.123391
C	1.107662	-1.493377	-0.680343
H	2.713838	-2.884766	-1.014354
C	1.697319	0.723497	0.127458
C	0.716706	-0.1947	-0.275475
H	0.346251	-2.186713	-1.02447
H	1.405111	1.713949	0.461755
C	4.185954	2.433589	0.924414
C	4.316585	3.425286	-0.237019
H	3.478212	3.322351	-0.93372
H	4.326453	4.454338	0.140202
H	5.243284	3.253801	-0.794212
N	4.166274	1.042957	0.501015
H	3.268145	2.624984	1.490642
H	5.015059	2.55691	1.629444
C	-0.716663	0.194785	-0.275461
C	-1.107657	1.49343	-0.680391
C	-1.697256	-0.723432	0.127477
C	-2.441092	1.884563	-0.687412
H	-0.346271	2.186767	-1.024569
C	-3.035132	-0.325735	0.123384
H	-1.405016	-1.713867	0.461805
C	-3.42667	0.976838	-0.284877
H	-2.71387	2.884772	-1.014425
C	-4.866866	1.035314	-0.164284
C	-5.28445	-0.235829	0.315887
C	-5.822922	2.027132	-0.411416
C	-6.63454	-0.523228	0.539877
C	-7.167699	1.746127	-0.185289
H	-5.518578	3.004603	-0.777004
C	-7.564974	0.482733	0.285178

H	-6.957623	-1.496563	0.897205
H	-7.918405	2.507972	-0.375151
H	-8.619868	0.281968	0.452259
C	-4.185917	-2.433595	0.924397
H	-3.267996	-2.625074	1.490427
H	-5.014867	-2.556835	1.629618
C	-4.316914	-3.425279	-0.237001
H	-5.243646	-3.253578	-0.794085
H	-3.47861	-3.32256	-0.933806
H	-4.327008	-4.454322	0.140236
N	-4.166203	-1.042962	0.500999

Number of imaginary frequency: 0

Table S15 Atomic coordinates of [3]L-Et-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	-10.789945	0.432131	-0.665296
C	-9.443891	0.188106	-0.375565
C	-9.044157	-0.932854	0.401828
C	-10.014203	-1.820244	0.88193
C	-11.355053	-1.583324	0.591267
C	-11.734537	-0.467344	-0.174233
H	-11.099446	1.293566	-1.24969
H	-9.723555	-2.68277	1.476263
H	-12.116614	-2.264536	0.960026
H	-12.786691	-0.297935	-0.38707
C	-7.603209	-0.866278	0.508954
C	-6.630705	-1.660292	1.126271
C	-7.193428	0.291227	-0.204514
C	-5.292064	-1.30009	1.030083
H	-6.917797	-2.545702	1.687832
C	-5.850148	0.657695	-0.30067
C	-4.882644	-0.145635	0.320663
H	-4.541267	-1.896859	1.538843
H	-5.54384	1.531341	-0.867237
C	-8.314603	2.157701	-1.495289

C	-8.424564	3.400946	-0.605333
H	-7.586273	3.452224	0.097
H	-8.417174	4.309929	-1.21772
H	-9.352793	3.384056	-0.024924
N	-8.314402	0.909438	-0.74988
H	-7.396537	2.192684	-2.091643
H	-9.144834	2.121821	-2.208634
C	-3.444545	0.215208	0.234093
C	-3.040442	1.570252	0.300054
C	-2.472291	-0.78519	0.086209
C	-1.702715	1.936921	0.219609
H	-3.795239	2.336007	0.450634
C	-1.129735	-0.413724	0.002413
H	-2.774792	-1.824808	0.010285
C	-0.725518	0.946706	0.069753
H	-1.419763	2.984519	0.28451
C	0.714517	0.957533	-0.047771
C	1.121528	-0.396388	-0.187858
C	1.689946	1.960827	-0.047303
C	2.465813	-0.750117	-0.311333
C	3.028901	1.612198	-0.175619
H	1.405347	3.005991	0.044141
C	3.43627	0.26293	-0.306857
H	2.771144	-1.789664	-0.375371
H	3.782628	2.393066	-0.206554
C	0.005535	-2.66728	-0.219017
H	-0.919594	-2.992624	-0.706327
H	0.825992	-2.97437	-0.876499
C	0.147278	-3.324146	1.158674
H	1.081465	-3.019306	1.641243
H	-0.682257	-3.038622	1.813718
H	0.149873	-4.41584	1.061524
N	-0.00431	-1.214064	-0.169862
C	4.875415	-0.081035	-0.43425
C	5.838833	0.623015	0.302958

C	5.289474	-1.121363	-1.300349
C	7.182655	0.272303	0.164325
H	5.529258	1.406053	0.987761
C	6.628674	-1.465034	-1.439053
H	4.541685	-1.638435	-1.893843
C	7.597113	-0.769841	-0.706816
H	6.919159	-2.260471	-2.120703
C	9.037104	-0.853573	-0.600011
C	10.010016	-1.663231	-1.197309
C	9.431745	0.141231	0.335614
C	11.348818	-1.473807	-0.865413
H	9.723339	-2.429388	-1.913224
C	10.775782	0.337384	0.668051
C	11.723377	-0.482571	0.057891
H	12.11257	-2.095306	-1.324136
H	11.081565	1.103363	1.374546
H	12.773988	-0.348178	0.301131
C	8.295664	1.929079	1.72138
H	7.372746	1.879536	2.309113
H	9.119905	1.787289	2.42855
C	8.414874	3.28849	1.023257
H	7.581251	3.445472	0.331047
H	8.406216	4.098066	1.762073
H	9.346639	3.353352	0.452028
N	8.299869	0.802532	0.802428

Number of imaginary frequency: 0

Table S 16 Atomic coordinates of [4]C-Bu-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	-4.57772800	-2.18422200	-0.76055000
C	-3.83321400	-3.34912200	-0.95396500
C	-3.62100700	-4.20660300	0.13529300
C	-4.34504900	-3.98316500	1.33202300
C	-5.11458100	-2.83676900	1.51057600
C	-5.16904100	-1.87210100	0.49198400

C	-5.46333800	-0.45192500	0.46057900
C	-5.81385000	0.49162100	1.43952000
C	-5.56888200	1.84255300	1.21298900
C	-4.98185700	2.29033100	0.00434800
C	-4.81507300	1.37819900	-1.04740100
C	-5.03044500	0.02004700	-0.80815700
C	-4.00466200	-0.99810200	-2.90488500
C	-4.84337000	-1.67850000	-3.99813800
C	-6.19352000	-1.00043500	-4.25902000
C	-7.01286400	-1.70513600	-5.34480800
C	-2.10886600	4.49722100	0.73220100
C	-3.26631400	3.75570300	0.97538100
C	-4.16595500	3.53832100	-0.07829300
C	-3.98797300	4.25414100	-1.28749300
C	-2.84839400	5.02080100	-1.51525800
C	-1.84503400	5.08053600	-0.53510100
C	-0.42461300	5.37428000	-0.56027100
C	0.48050700	5.71889700	-1.57681700
C	1.83924800	5.47540100	-1.40078700
C	2.33324500	4.89569200	-0.20672500
C	1.46226200	4.73515800	0.88022100
C	0.09583700	4.94895600	0.69195200
C	-0.84090100	3.93614300	2.83242500
C	-1.47659700	4.78267000	3.94636200
C	-0.78624900	6.13280400	4.17291600
C	-1.44698800	6.96006700	5.28012400
C	4.50865800	2.01553900	-1.00134800
C	3.75695600	3.17120700	-1.21963400
C	3.58424700	4.08081200	-0.16672400
C	4.34855400	3.91517100	1.01408000
C	5.12417800	2.77804000	1.21850900
C	5.14402100	1.76622100	0.24523400
C	5.44628900	0.34769400	0.27492900
C	5.82380300	-0.55029000	1.28597500
C	5.57313200	-1.91045200	1.12693800

C	4.95350100	-2.41452200	-0.04281700
C	4.76061700	-1.55181300	-1.13160900
C	4.98144500	-0.18459500	-0.95654800
C	3.89634400	0.65633100	-3.06590600
C	4.89416700	0.36481500	-4.19771200
C	5.84405500	1.52843400	-4.50499500
C	6.83569600	1.20594600	-5.62726000
C	2.09945500	-4.57464600	0.87067300
C	3.26595100	-3.82826100	1.04524000
C	4.13401200	-3.66272700	-0.04364100
C	3.91789700	-4.43233800	-1.21310000
C	2.77077400	-5.20519900	-1.37068000
C	1.79711300	-5.21676500	-0.35913800
C	0.37705300	-5.51121000	-0.32654700
C	-0.55920600	-5.90325600	-1.29676800
C	-1.91234500	-5.65395400	-1.08878400
C	-2.37007400	-5.02114100	0.09282000
C	-1.46533400	-4.80931100	1.14277200
C	-0.10491500	-5.02809800	0.92014000
C	0.89347000	-3.93328000	2.98708300
C	1.49030500	-4.78734500	4.11495900
C	1.41520100	-4.09351700	5.48057200
C	2.00997700	-4.93733000	6.61259000
H	-3.25349000	-3.48632400	-1.86046100
H	-4.22944300	-4.68164400	2.15649400
H	-5.59386700	-2.65301100	2.46899600
H	-6.19148700	0.16608600	2.40568100
H	-5.75356000	2.55991900	2.00806700
H	-4.32511200	1.70780300	-1.95700000
H	-3.00688000	-1.45418200	-2.85572300
H	-3.85539200	0.05535200	-3.15590600
H	-5.00502800	-2.73003400	-3.72549200
H	-4.24705100	-1.68581300	-4.92176800
H	-6.76921300	-0.96992100	-3.32550700
H	-6.02236100	0.04631100	-4.54915300

H	-7.23026600	-2.74325500	-5.06532100
H	-6.47500900	-1.72542100	-6.30083600
H	-7.96995400	-1.19858000	-5.51187300
H	-3.36918700	3.18213100	1.89029700
H	-4.71812000	4.13451500	-2.08345400
H	-2.70134400	5.49376100	-2.48310700
H	0.11798600	6.09086200	-2.53195300
H	2.52569000	5.65570600	-2.22370300
H	1.82690000	4.25096400	1.77949300
H	0.22134300	3.78632400	3.04283700
H	-1.30017800	2.93893500	2.80728200
H	-1.44926900	4.19173800	4.87308000
H	-2.53759100	4.94511500	3.71376700
H	0.27053200	5.96098100	4.42358400
H	-0.79048900	6.70294800	3.23551700
H	-1.43173400	6.42777600	6.23935800
H	-2.49459400	7.17834800	5.03941500
H	-0.93232100	7.91689000	5.42204000
H	3.14094300	3.27019200	-2.10667400
H	4.26080100	4.65220900	1.80779200
H	5.63847200	2.63857600	2.16620000
H	6.22608000	-0.18257300	2.22672800
H	5.77998500	-2.59051100	1.94895000
H	4.24983200	-1.91675500	-2.01620400
H	3.32524000	1.55859400	-3.30006100
H	3.16980600	-0.16293000	-2.98267500
H	5.47729100	-0.52991200	-3.94151400
H	4.31542400	0.11062100	-5.09726400
H	5.25351400	2.41434600	-4.77986900
H	6.39380100	1.79661800	-3.59414000
H	6.31540100	0.96210300	-6.56188400
H	7.46467300	0.34657200	-5.36471700
H	7.49922600	2.05464600	-5.82718800
H	3.39772300	-3.21389700	1.92954500
H	4.62361600	-4.35152000	-2.03552000

H	2.59430100	-5.72269600	-2.31040800
H	-0.22641400	-6.31868500	-2.24477200
H	-2.62394000	-5.87262700	-1.88042300
H	-1.80244200	-4.28551400	2.03065500
H	-0.15723300	-3.71816200	3.19960900
H	1.40440300	-2.96232000	2.93542100
H	0.95765900	-5.74690500	4.15053600
H	2.53563900	-5.02191900	3.87385600
H	0.36669900	-3.85738100	5.71256400
H	1.93988700	-3.12871700	5.42890700
H	3.06753100	-5.16028900	6.42656200
H	1.48287900	-5.89380600	6.71244800
H	1.94276600	-4.41719500	7.57462800
N	-4.61387800	-1.06167800	-1.58430900
N	-0.95524400	4.53734600	1.51162500
N	4.53123100	0.85198700	-1.77062500
N	0.96911400	-4.57282100	1.68346600

Number of imaginary frequency: 0

Table S 17 Atomic coordinates of [2]L-Bu-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	-5.26824800	-0.48102900	0.55098900
C	-6.64187000	-0.38771700	0.79771300
C	-7.42338000	-1.51744600	0.56187700
C	-6.85755000	-2.71371900	0.08849700
C	-5.48960700	-2.80283300	-0.15532700
C	-4.68065000	-1.68431400	0.07548700
C	-3.26349400	-1.42675600	-0.05148600
C	-2.16481300	-2.19554200	-0.45077800
C	-0.89591700	-1.63006800	-0.44477600
C	-0.68403200	-0.28939600	-0.04329300
C	-1.77958200	0.49067600	0.35399200
C	-3.05388200	-0.07963500	0.34788200
C	-4.50318000	1.83383300	1.19982900
C	-5.04441700	2.80929900	0.14087200

C	-4.07042300	3.11116900	-1.00441300
C	-4.65629200	4.07656100	-2.03994400
C	3.05388100	0.07963400	0.34788300
C	1.77958200	-0.49067600	0.35399200
C	0.68403100	0.28939600	-0.04329300
C	0.89591600	1.63006800	-0.44477700
C	2.16481200	2.19554100	-0.45077800
C	3.26349400	1.42675600	-0.05148600
C	4.68064900	1.68431400	0.07548700
C	5.48960600	2.80283300	-0.15532700
C	6.85754900	2.71371900	0.08849800
C	7.42337900	1.51744600	0.56187800
C	6.64187000	0.38771700	0.79771300
C	5.26824800	0.48102900	0.55098900
C	4.50317900	-1.83383400	1.19982900
C	5.04441900	-2.80929900	0.14087200
C	4.07042500	-3.11116900	-1.00441300
C	4.65629500	-4.07656000	-2.03994500
H	-7.09334500	0.53100500	1.15979100
H	-7.49510800	-3.57540900	-0.08771100
H	-5.05437400	-3.73025600	-0.51886300
H	-2.30158900	-3.22483200	-0.77269300
H	-0.04818900	-2.21605500	-0.78648300
H	-1.62140400	1.51220400	0.68347500
H	-3.55785700	2.20452200	1.60949300
H	-5.20467400	1.77363000	2.04101700
H	-5.30878400	3.74466200	0.65513900
H	-5.97998900	2.40672300	-0.26983800
H	-3.14497000	3.53662700	-0.59000800
H	-3.78413700	2.17399400	-1.49744600
H	-4.92461300	5.03718800	-1.58293300
H	-5.56313400	3.66274300	-2.49756400
H	-3.94051200	4.27851000	-2.84450800
H	1.62140300	-1.51220400	0.68347500
H	0.04818800	2.21605400	-0.78648300

H	2.30158800	3.22483100	-0.77269300
H	5.05437300	3.73025600	-0.51886300
H	7.49510700	3.57540900	-0.08771100
H	7.09334400	-0.53100500	1.15979300
H	3.55785700	-2.20452300	1.60949200
H	5.20467200	-1.77363000	2.04101900
H	5.97999100	-2.40672100	-0.26983700
H	5.30878600	-3.74466100	0.65513900
H	3.14497200	-3.53662800	-0.59000800
H	3.78413800	-2.17399400	-1.49744500
H	4.92461800	-5.03718700	-1.58293400
H	5.56313700	-3.66274000	-2.49756500
H	3.94051500	-4.27851000	-2.84450900
H	8.49317600	1.46854900	0.74669300
H	-8.49317700	-1.46854900	0.74669200
N	-4.27593100	0.48093300	0.71281600
N	4.27593100	-0.48093300	0.71281600

Number of imaginary frequency: 0

Table S 18 Atomic coordinates of [3]L-Bu-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	-9.39029200	-0.19743500	0.88864200
C	-10.69809600	-0.53668100	1.25054900
C	-11.68254000	0.44192200	1.12456100
C	-11.37944400	1.72861600	0.64720000
C	-10.07618700	2.06274200	0.28872100
C	-9.06724600	1.10010300	0.40775400
C	-7.64461700	1.09953400	0.14923700
C	-6.73775900	2.05861100	-0.31480800
C	-5.39455800	1.72645700	-0.43845700
C	-4.91655400	0.43628100	-0.10609100
C	-5.81868000	-0.53335100	0.35522800
C	-7.16797300	-0.19731600	0.47976600
C	-8.17746400	-2.35280100	1.38669000
C	-8.63801100	-3.38867400	0.34720800

C	-7.73915800	-3.49235400	-0.89086700
C	-8.24270700	-4.52752100	-1.90200200
C	-1.15197700	0.72287600	-0.05020000
C	-2.49920500	1.06206400	0.08542800
C	-3.47441100	0.10893100	-0.24406000
C	-3.06893600	-1.16528600	-0.70854400
C	-1.72692200	-1.50046200	-0.84078200
C	-0.74668400	-0.55830000	-0.50992800
C	0.69771500	-0.56133500	-0.50472400
C	1.67314000	-1.50977800	-0.83229800
C	3.01663600	-1.18394100	-0.69615900
C	3.42736600	0.08888100	-0.23266300
C	2.45727800	1.04789600	0.09360500
C	1.10766700	0.71876400	-0.04294000
C	-0.04710900	2.84835400	0.74390900
C	-0.30711500	3.92386200	-0.32436900
C	0.80480500	4.06441500	-1.37092800
C	0.49695800	5.13740300	-2.42046900
C	7.11859600	-0.23254100	0.49684700
C	5.76784400	-0.56258000	0.37185400
C	4.87091800	0.40984000	-0.09362200
C	5.35539300	1.69661600	-0.42986300
C	6.70003200	2.02274600	-0.30570900
C	7.60177100	1.06093300	0.16264400
C	9.02411300	1.05557700	0.42271900
C	10.03775800	2.01300100	0.30165500
C	11.33904400	1.67384000	0.66258500
C	11.63551100	0.38727000	1.14440900
C	10.64627300	-0.58621900	1.27251100
C	9.34047500	-0.24192800	0.90813000
C	8.11692500	-2.39001800	1.41133200
C	8.57399800	-3.43100300	0.37542100
C	7.67645900	-3.53382800	-0.86367900
C	8.17649300	-4.57423400	-1.87117500
H	-10.94762300	-1.52772800	1.61731600

H	-12.17065300	2.46762000	0.55836100
H	-9.84422500	3.05963100	-0.07746300
H	-7.08046300	3.05405800	-0.58570900
H	-4.69660000	2.46042700	-0.82944500
H	-5.45550000	-1.51728300	0.63283900
H	-8.79673900	-2.43265100	2.28862600
H	-7.14795500	-2.55876800	1.69737700
H	-9.66401400	-3.15050800	0.03639700
H	-8.68539200	-4.36538800	0.85025500
H	-7.66927600	-2.51051800	-1.37510200
H	-6.71851400	-3.75435300	-0.57644000
H	-9.24707100	-4.27274200	-2.26166600
H	-8.29464100	-5.52851200	-1.45593000
H	-7.58208700	-4.58503400	-2.77419500
H	-2.79911500	2.03278500	0.46669700
H	-3.82930300	-1.88442900	-0.99751500
H	-1.44430900	-2.48425700	-1.20687900
H	1.38446400	-2.49130100	-1.19977300
H	3.77354700	-1.90788600	-0.98211900
H	2.76508700	2.01772200	0.47009500
H	0.90855200	3.03394900	1.24495500
H	-0.82092200	2.90160100	1.51947300
H	-0.44587300	4.88244600	0.19620700
H	-1.25850300	3.70421600	-0.82705000
H	1.74985400	4.30854900	-0.86446400
H	0.96290900	3.09959200	-1.86845700
H	0.36374900	6.12266300	-1.95661600
H	-0.42371000	4.90200700	-2.96817000
H	1.30736100	5.22064300	-3.15311600
H	5.39965100	-1.54392600	0.65204200
H	4.66137400	2.43233000	-0.82462600
H	7.04787500	3.01557300	-0.57969700
H	9.81093300	3.00979500	-0.06799500
H	12.13385600	2.40878100	0.57218800
H	10.89069600	-1.57725400	1.64273300

H	7.08606500	-2.59029700	1.72124600
H	8.73465600	-2.47016700	2.31430500
H	9.60157900	-3.19862900	0.06543800
H	8.61596900	-4.40652100	0.88126300
H	6.65410200	-3.79000900	-0.55003700
H	7.61202700	-2.55302900	-1.35076000
H	8.22296800	-5.57421200	-1.42223400
H	9.18259300	-4.32529300	-2.23008000
H	7.51687100	-4.63101400	-2.74417100
H	-12.70589100	0.20125700	1.39995800
H	12.65741700	0.14262000	1.42165700
N	-8.23514200	-0.97226300	0.92856300
N	-0.02259500	1.48533700	0.23280400
N	8.18160500	-1.01110600	0.94929700

Number of imaginary frequency: 0

Table S 19 Atomic coordinates of [4]C-Hex-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	-4.76932400	0.57522000	-1.24132600
C	-4.11053500	2.69999400	-1.58060400
C	-3.58303900	1.08084000	-3.43624100
C	2.69632000	4.77125900	-0.02401100
C	0.54556000	5.41240300	-0.19505800
C	-0.20280400	-4.39764400	1.46449100
C	-2.35332800	-3.75814400	1.28489400
C	-3.24770100	3.73571900	-1.94351600
C	-4.77923800	2.68584800	-0.32814500
C	-2.99724800	4.76327900	-1.02265000
C	-3.78827900	4.83760100	0.15015000
C	-1.67220300	5.44149800	-1.14197000
C	-0.83789600	5.35842300	-0.01822000
C	-1.10534200	5.79218600	-2.39170600
C	0.27320800	5.87851700	-2.56062600
C	1.12479300	5.60198400	-1.47900700
C	2.51015200	5.18597800	-1.36920100

C	-4.67235300	3.81872200	0.49425400
C	-5.20707400	1.31680100	-0.11062600
C	-5.68591600	0.61165400	1.00512300
C	-5.56167200	-0.77369600	1.05024400
C	-4.96817800	-1.49319900	-0.01551500
C	-4.67008300	-0.81693100	-1.20719600
C	-4.27157300	-2.79849200	0.18596000
C	-3.44361200	-2.88678600	1.31445400
C	-4.11027200	-3.74457700	-0.85575300
C	-2.09156700	-4.59316200	0.16671400
C	-3.04049300	-4.63546800	-0.86701800
C	-0.70630000	-5.00753400	0.28363500
C	-4.29584800	1.65311400	-4.67399200
C	-5.74406500	1.17875400	-4.87128200
C	-5.89847700	-0.31815400	-5.17523800
C	-7.34952400	-0.72661200	-5.46249400
C	-7.50927500	-2.22092100	-5.75969600
C	2.01009700	5.64529800	3.07084500
C	1.34506300	4.65745400	2.09867700
C	1.89903500	5.23338100	4.54807600
C	0.47039400	5.25753000	5.11408300
C	0.37100600	4.87780100	6.60189200
C	1.03029400	5.87643300	7.56087200
C	3.77661700	3.97450900	0.35884800
C	3.52072500	4.89458100	-2.29934700
C	4.67113800	3.52730900	-0.62424400
C	4.58055000	4.07138500	-1.92901700
C	5.36759300	2.23804800	-0.33781800
C	5.14478000	1.20103900	-1.25522200
C	5.88234100	1.91861800	0.94271600
C	5.22839100	-0.12049700	-0.81316900
C	5.99505500	0.59859400	1.37023700
C	5.58181200	-0.44254200	0.52376000
C	4.54806600	-2.23844600	-0.47371400
C	4.18549800	-1.26678800	-2.79874500

C	5.14617300	-1.80899800	0.74198400
C	3.69457400	-3.34249700	-0.51716900
C	5.27496700	-1.24092200	-3.88514900
C	4.98327900	-2.60857500	1.88457900
C	3.38777500	-4.01481400	0.67446500
C	6.23317100	-2.44212300	-3.87802000
C	4.11143100	-3.69266500	1.84849700
C	2.06651900	-4.70997500	0.71019500
C	5.58350700	-3.78981100	-4.22244500
C	1.16830300	-4.27039300	1.69292300
C	1.57183600	-5.46181700	-0.38339600
C	6.59466900	-4.94136000	-4.30247300
C	0.20505400	-5.61624200	-0.59401300
C	5.94996100	-6.28955900	-4.63937600
C	-1.13210900	-2.92106200	3.32000100
C	-1.90346300	-3.48042900	4.52675400
C	-1.35709100	-4.82281400	5.02957500
C	-1.99820100	-5.37135600	6.31758600
C	-3.49322600	-5.75188100	6.23015000
C	-4.47750300	-4.62725100	6.57971100
H	-2.61978100	3.64393900	-2.82326400
H	-1.75790000	5.91477700	-3.25194600
H	0.68487000	6.07254800	-3.54801400
H	-1.26179300	5.04655500	0.93010100
H	-3.63884100	5.66789300	0.83517700
H	-5.20551400	3.86425300	1.44068400
H	-6.07038900	1.14733500	1.86958800
H	-5.84736500	-1.30671900	1.95308500
H	-3.53029000	-2.14193800	2.09824100
H	-2.89707300	-5.29500000	-1.71935300
H	-4.78986700	-3.71657500	-1.70331400
H	-4.16816700	-1.35362400	-2.00476200
H	-3.54988800	-0.00914600	-3.48814200
H	-2.53990500	1.42444200	-3.41825000
H	-4.28277800	2.74840700	-4.60983800

H	-3.69394100	1.38695200	-5.55464900
H	-6.18140600	1.75422000	-5.69888900
H	-6.33268400	1.43408400	-3.97997400
H	-5.26957000	-0.58279000	-6.03918300
H	-5.52693300	-0.91542300	-4.33062900
H	-7.97687700	-0.45512200	-4.60201900
H	-7.72815600	-0.14092600	-6.31228600
H	-6.91754400	-2.51746100	-6.63473000
H	-8.55494700	-2.47882600	-5.96243400
H	-7.17488100	-2.83159700	-4.91191100
H	0.27074700	4.60077300	2.28405600
H	1.74335200	3.64572400	2.25837500
H	1.56536700	6.63834100	2.92235100
H	3.06908300	5.73767200	2.79928600
H	2.53503700	5.90696400	5.13551600
H	2.32327700	4.22606000	4.67907500
H	0.04197700	6.26062100	4.96773600
H	-0.16467000	4.56858200	4.54075700
H	-0.69047300	4.78102000	6.86632500
H	0.81202500	3.88150800	6.75009800
H	0.60586800	6.88068000	7.43686500
H	0.87642100	5.57778700	8.60404100
H	2.11134900	5.95107300	7.39874400
H	3.80976400	3.53377800	1.34951000
H	3.43518200	5.23286900	-3.32904700
H	5.31014800	3.77247700	-2.67686600
H	4.70993800	1.42935400	-2.22240800
H	6.11446700	2.72454500	1.63376400
H	6.31595300	0.38678800	2.38720600
H	3.56578400	-2.15937100	-2.90422000
H	3.51607400	-0.40524200	-2.92565200
H	3.10656400	-3.55047400	-1.40437000
H	5.85691100	-0.31728700	-3.77460500
H	4.76929100	-1.17404500	-4.85906400
H	5.46429000	-2.33383100	2.82011600

H	7.03590000	-2.24191800	-4.60115200
H	6.71977800	-2.51050500	-2.89585800
H	3.91691700	-4.25268000	2.75923000
H	5.05343600	-3.70534000	-5.18361200
H	4.82111700	-4.04425300	-3.47270500
H	1.53802400	-3.65672600	2.50704000
H	2.27314800	-5.85387800	-1.11508700
H	7.12780300	-5.01936900	-3.34467300
H	7.35728000	-4.70056500	-5.05677600
H	-0.14938500	-6.13056000	-1.48388900
H	5.43456000	-6.25265300	-5.60724200
H	6.69802400	-7.08878600	-4.69120200
H	5.21023100	-6.57556400	-3.88143400
H	-0.07127600	-2.83237000	3.56868300
H	-1.48612400	-1.90892600	3.08236200
H	-0.27642300	-4.71460600	5.20520100
H	-2.96056800	-3.57706400	4.25343500
H	-1.85404700	-2.73167400	5.33026300
H	-1.45985100	-5.57168500	4.23298900
H	-1.42744700	-6.26491300	6.60264400
H	-1.85328700	-4.65122500	7.13683800
H	-3.68067100	-6.58803800	6.91654800
H	-3.71207600	-6.13825200	5.22452700
H	-4.39055900	-3.76989100	5.90443300
H	-5.51307000	-4.98338000	6.52784600
H	-4.30407100	-4.26127500	7.59942500
N	-4.22193000	1.44828800	-2.18103300
N	1.53736400	5.02457200	0.70461900
N	-1.24431000	-3.74811200	2.12721600
N	4.72047000	-1.25279900	-1.44514000

Number of imaginary frequency: 0

Table S 20 Atomic coordinates of [2]L-Hex-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	2.65110700	-0.38208800	0.66558000
C	4.78434600	-1.06635000	0.96020700
C	6.79071700	-2.36586600	1.03286700
C	6.14315200	-1.15656800	1.27977000
C	6.10830600	-3.46226200	0.47834200
C	4.07960600	-2.16711300	0.40264400
C	4.75541000	-3.36895800	0.16265700
C	2.71425400	-1.72876900	0.21736900
C	-7.53099600	2.54007600	0.49874700
C	-6.91282100	1.31101200	0.72231300
C	-6.79678600	3.66485300	0.08523000
C	-5.53043300	1.22946600	0.52417500
C	-5.42054200	3.58056800	-0.10817300
C	-4.77374700	2.35912900	0.11197100
C	-3.37982100	0.54903900	0.39068300
C	-5.10508000	-1.18328900	1.11876200
C	-3.39777500	1.92325300	0.02979900
C	-2.18825500	-0.17798700	0.43208600
C	-5.78041200	-2.01769000	0.01401100
C	-2.19407900	2.55670200	-0.29734500
C	-0.98593500	0.46753000	0.10823200
C	-4.85416500	-2.47558800	-1.12454500
C	-1.00803600	1.83461400	-0.25700200
C	0.29800000	-0.27857200	0.15007200
C	-3.88692900	-3.60414900	-0.74012500
C	1.45809500	0.34256800	0.63456300
C	0.36452700	-1.61876600	-0.30005600
C	-2.98027100	-4.04489100	-1.89676600
C	1.55269800	-2.33802100	-0.26957900
C	-2.01768000	-5.17371800	-1.51402400
C	4.27842000	1.29979800	1.67302000
C	5.00418800	2.23516400	0.68970500
C	4.13368300	2.70249900	-0.48385400

C	4.77966100	3.73302400	-1.42853000
C	6.01161900	3.25000900	-2.22685900
C	7.36715500	3.49737800	-1.55081900
H	6.68407000	-0.31696900	1.70572000
H	4.22941400	-4.21966200	-0.26317000
H	6.64307000	-4.39002100	0.29578000
H	-7.49349200	0.45052600	1.04035700
H	-7.30948300	4.60764400	-0.08307900
H	-4.85432700	4.45325200	-0.42365600
H	-4.23052100	-1.70120000	1.52235600
H	-5.80179100	-1.05417700	1.95642100
H	-2.17292200	-1.21843500	0.73897100
H	-6.60521200	-1.42751900	-0.40352600
H	-6.23851300	-2.89618100	0.49090800
H	-2.18541700	3.60407800	-0.58840400
H	-5.47723200	-2.81973500	-1.96137000
H	-4.28825000	-1.61423600	-1.50447800
H	-0.07794400	2.31714300	-0.54144200
H	-4.46514200	-4.46949100	-0.38241500
H	-3.25629800	-3.29395400	0.10571800
H	1.40871300	1.36259600	1.00083800
H	-0.52885500	-2.08032200	-0.70953200
H	-2.40681300	-3.17865900	-2.25621900
H	-3.60474900	-4.36587200	-2.74253000
H	1.57883600	-3.36300100	-0.63089700
H	-2.56340600	-6.06504500	-1.18052200
H	-1.38806900	-5.46684100	-2.36177800
H	-1.35381300	-4.86860400	-0.69531000
H	3.36454100	1.77471200	2.04459000
H	4.91413900	1.11832600	2.54847600
H	3.21058800	3.14346200	-0.07925600
H	5.89863900	1.72230700	0.31783600
H	5.35621400	3.10675000	1.26032400
H	3.82027100	1.82912500	-1.07098900
H	4.00335100	4.04541100	-2.13920400

H	5.04521600	4.63710100	-0.86041400
H	6.02147900	3.76247100	-3.19772600
H	5.90025300	2.18081400	-2.45660100
H	7.45713400	2.97764900	-0.59137200
H	8.19100200	3.15630600	-2.18868600
H	7.51734200	4.56732200	-1.35994800
H	-8.60411900	2.62694600	0.64662500
H	7.84638400	-2.45928800	1.27336800
N	3.91138300	0.00615300	1.11489500
N	-4.67872400	0.14085400	0.68703100

Number of imaginary frequency: 0

Table S 21 Atomic coordinates of [3]L-Hex-Cbz after geometry optimization (b3lyp/6-31g(d))

Atom	X (Å)	Y (Å)	Z (Å)
C	7.34412400	0.51236400	0.17374100
C	9.57994500	0.59685300	0.48484300
C	-6.89177900	-0.32806100	0.78236200
C	-9.08451900	-0.49222300	1.30280700
C	11.85207900	1.32741200	0.63170800
C	10.92043600	0.29738300	0.74760400
C	11.46573400	2.62654600	0.25947200
C	10.13088600	2.91980900	-0.00616000
C	9.17374500	1.90438900	0.10233700
C	7.74196500	1.84910000	-0.09434900
C	-11.39672200	-0.01567700	1.68499000
C	-10.34673600	-0.93181400	1.71533300
C	-11.20216300	1.30732500	1.25247100
C	-8.87097700	0.84319000	0.86658700
C	-9.94393600	1.74151600	0.84377600
C	-7.46709100	0.94751300	0.53670800
C	8.64527400	-2.53527100	-0.41208900
C	8.47477600	-1.65331700	0.83642400
C	8.59223600	-4.04429600	-0.12094200
C	9.77560600	-4.57977300	0.70080900
C	9.73177600	-6.09534500	0.96305200

C	9.88964800	-6.96465500	-0.29032300
C	6.01134400	0.10917000	0.07669600
C	6.76827400	2.78421400	-0.46149200
C	5.04241600	1.05465300	-0.29027500
C	5.44014000	2.38684800	-0.55657700
C	3.61476800	0.65945100	-0.39699400
C	2.60546900	1.53806900	0.02438600
C	3.25720900	-0.60534400	-0.92245400
C	1.27284700	1.13635800	-0.08350300
C	1.93010600	-1.00418000	-1.02451600
C	0.91670800	-0.13672400	-0.60202100
C	-0.98105900	1.00725400	0.01347300
C	0.09814600	3.15288400	0.87279800
C	-0.52370000	-0.21998700	-0.53925700
C	-2.33936600	1.24769700	0.22898800
C	0.31847700	4.28975000	-0.14285900
C	-1.45899700	-1.20347400	-0.87969600
C	-3.26876600	0.25312300	-0.10992000
C	-0.82369600	4.50383700	-1.14952200
C	-2.81066800	-0.96509900	-0.66580400
C	-4.71965700	0.47841600	0.11513900
C	-2.07772900	5.16082100	-0.55550600
C	-5.53209900	-0.56800400	0.57500800
C	-5.29619200	1.74693000	-0.13344500
C	-3.19754800	5.36818900	-1.58362900
C	-6.64959200	1.98354200	0.07207700
C	-4.44716000	6.02805100	-0.99166800
C	-7.71435400	-2.58379700	1.63497300
C	-8.17421800	-3.59920400	0.57383300
C	-7.33001900	-3.58756900	-0.70707600
C	-7.67925300	-4.66565500	-1.74983800
C	-9.08151100	-4.56638700	-2.39197000
C	-10.18504000	-5.35874800	-1.67782600
H	12.21727300	3.40656500	0.17709100
H	9.83507000	3.92488000	-0.29606500

H	11.23530200	-0.70316100	1.02878200
H	-10.51256500	-1.95162500	2.04914800
H	-9.79575100	2.76631800	0.51284400
H	-12.04230300	1.99579900	1.23832400
H	9.27698200	-1.83412300	1.55848700
H	7.53669600	-1.90095300	1.34742200
H	9.59606000	-2.28134900	-0.89955700
H	7.85335800	-2.27350400	-1.12504800
H	8.54722000	-4.57290000	-1.08109400
H	7.65220200	-4.28294000	0.39989100
H	10.71468700	-4.32973700	0.18411100
H	9.81433100	-4.06443600	1.67008100
H	10.53038600	-6.34899500	1.67288100
H	8.78759000	-6.34688700	1.46717800
H	10.82741800	-6.73662500	-0.81249700
H	9.90563500	-8.02890200	-0.02925800
H	9.06947400	-6.81523000	-1.00132400
H	5.71336400	-0.90872700	0.30705900
H	7.04675300	3.81153200	-0.68244200
H	4.69022200	3.10452900	-0.87487100
H	2.87031700	2.49831600	0.45471900
H	4.04140500	-1.26472900	-1.28164300
H	1.68415200	-1.97942400	-1.43702400
H	-0.85443900	3.27343400	1.39624400
H	0.88034100	3.19239000	1.64099800
H	-2.68354100	2.17226800	0.68021600
H	1.24893200	4.08573500	-0.68654200
H	0.48790800	5.21662300	0.42378700
H	-1.13324400	-2.14461900	-1.31547500
H	-0.45183900	5.13703000	-1.96665400
H	-1.09020200	3.54299700	-1.61029100
H	-3.53900700	-1.71490300	-0.95928200
H	-1.80344100	6.13218000	-0.11701500
H	-2.46780900	4.55559000	0.27572800
H	-5.09209400	-1.53662300	0.78771600

H	-4.66879700	2.54134600	-0.52602500
H	-3.46766500	4.39784300	-2.02396700
H	-2.81684700	5.98086600	-2.41308900
H	-7.06923200	2.96449000	-0.13634900
H	-4.21442700	7.01468800	-0.57228800
H	-5.22517100	6.16447000	-1.75134900
H	-4.87267500	5.41910900	-0.18404000
H	-6.65764800	-2.73866000	1.87618100
H	-8.27346100	-2.74239500	2.56544400
H	-6.27299800	-3.71280900	-0.42906000
H	-9.22600300	-3.40194000	0.33678300
H	-8.13761300	-4.59775700	1.03290200
H	-7.40404800	-2.59891900	-1.17910100
H	-6.92526300	-4.59693800	-2.54487400
H	-7.55249000	-5.66357800	-1.30404500
H	-9.01933000	-4.93246800	-3.42512500
H	-9.37292800	-3.50924200	-2.46862800
H	-10.34286400	-5.02091500	-0.64842100
H	-11.14081200	-5.26283500	-2.20623900
H	-9.93425200	-6.42613300	-1.63822700
H	-12.38630700	-0.33468300	2.00118100
H	12.89960900	1.11785900	0.83128700
N	8.46238100	-0.23022200	0.53963700
N	-7.88205400	-1.19032800	1.24796300
N	0.11779600	1.81976200	0.28587400

Number of imaginary frequency: 0

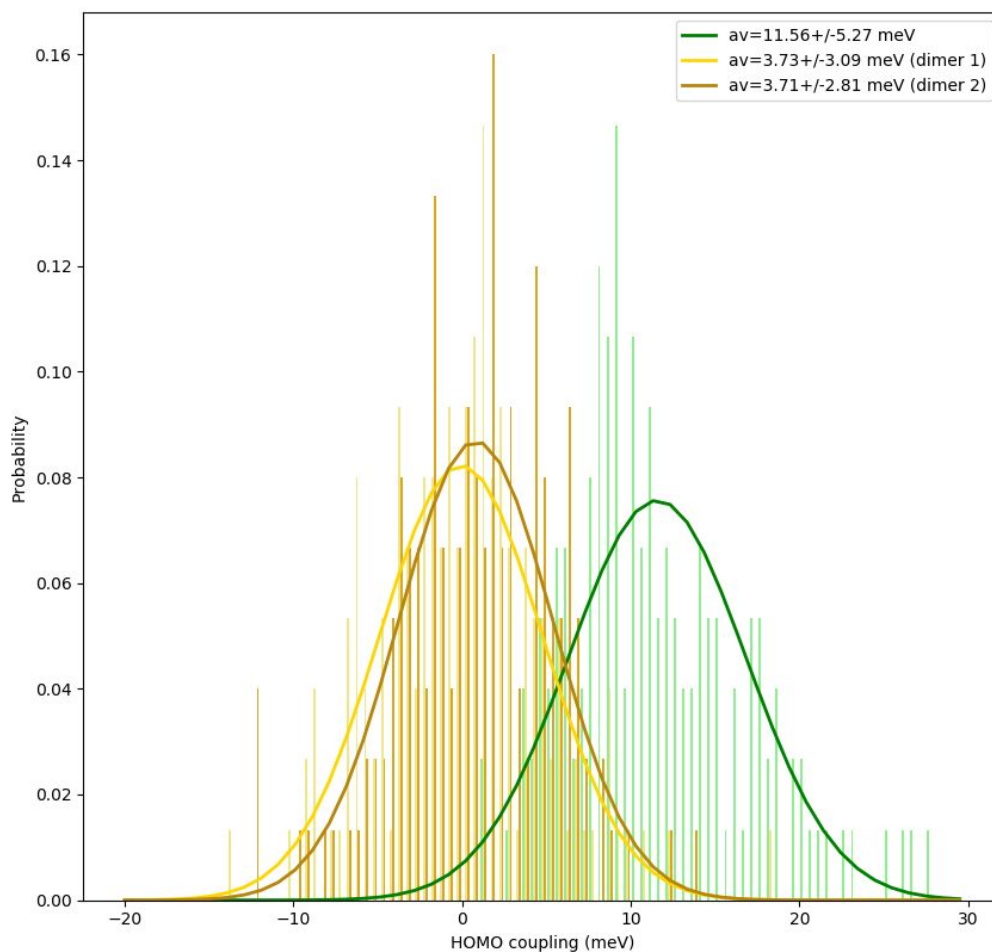


Figure S 33 Electronic coupling distribution and their respective Gaussian fits in [8]CPP. The green distribution corresponds to the green axis in Fig 9b. The two distributions in yellow and red are almost superposed, meaning that thermal noise affects one charge transfer direction as much as the other in the (bc) plane, see orange arrows in Fig.9.

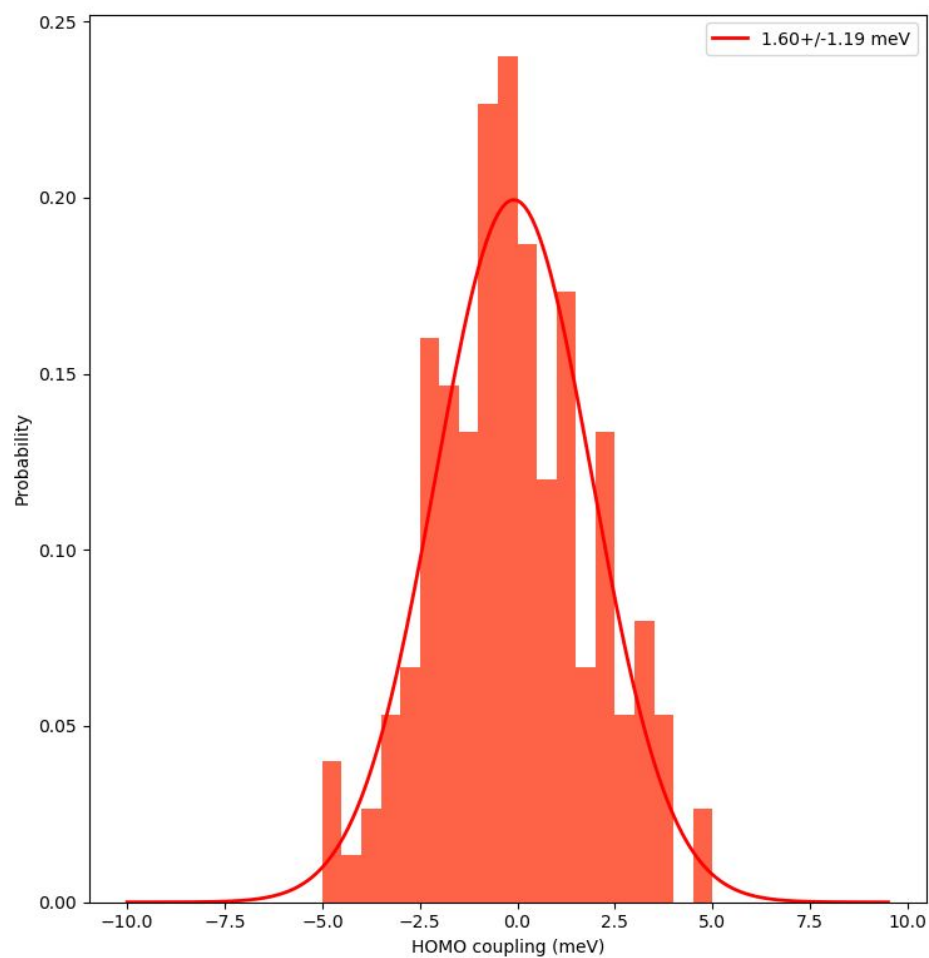


Figure S 34 Electronic coupling distribution in the zigzag molecular columns displayed of [4]C-Bu-Cbz displayed in Fig. 9.

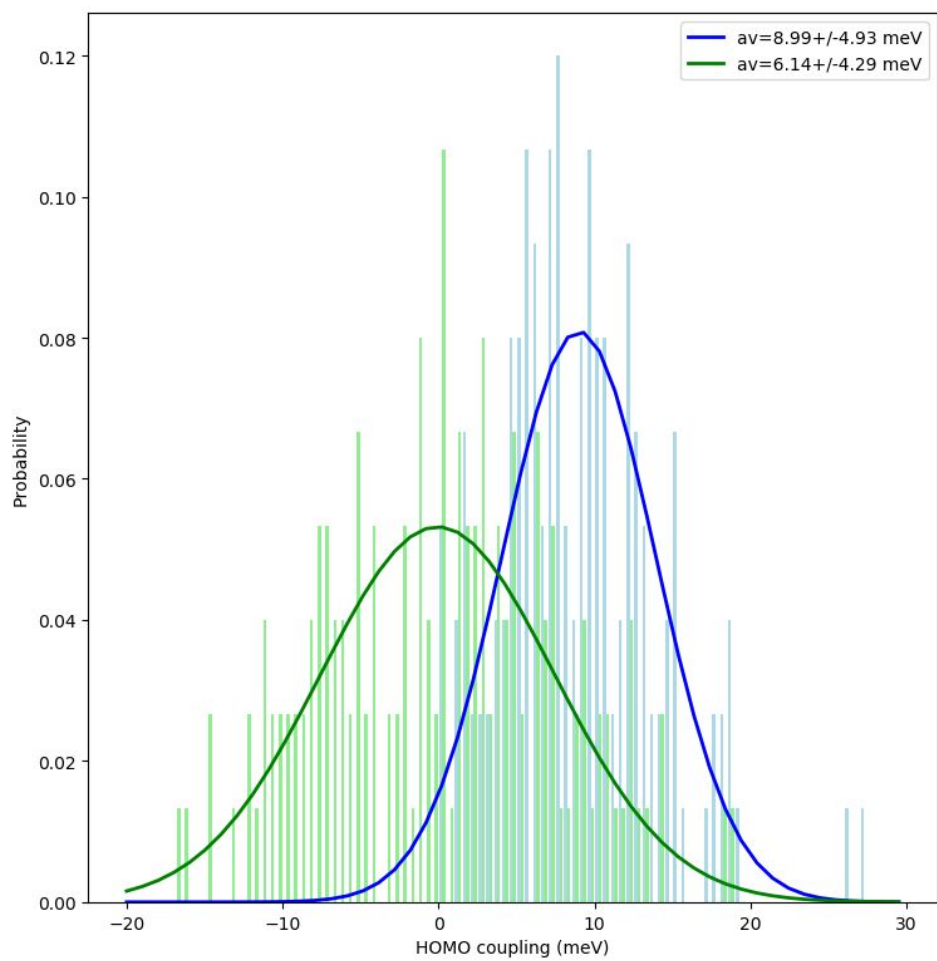


Figure S 35 Electronic coupling distributions in [4]C-Et-Cbz. The colors of the distribution are matched with the molecular columns in Fig. 9. Thermal noise affects both distribution differently.

Table S 22 Summary of the important parameters implicated in the theoretical analysis

Material	X-ray structure Value (meV)	Molecular dynamics Average value (meV)	Molecular Dynamics Standard deviation (meV)
[8]CPP green molecular axis	18.3	11.6	5.27
[8]CPP yellow plane (dimer 1)	10.1	3.71	2.81
[8]CPP yellow plane (dimer 2)	10.3	3.73	3.09
[4]C-Et-Cbz green axis	10.8	6.14	4.29
[4]C-Et-Cbz blue axis	11.6	8.99	4.93
[4]C-Bu-Cbz	7.00	1.06	1.19

9 X-ray diffraction structures and tables

[4]C-Et-Cbz

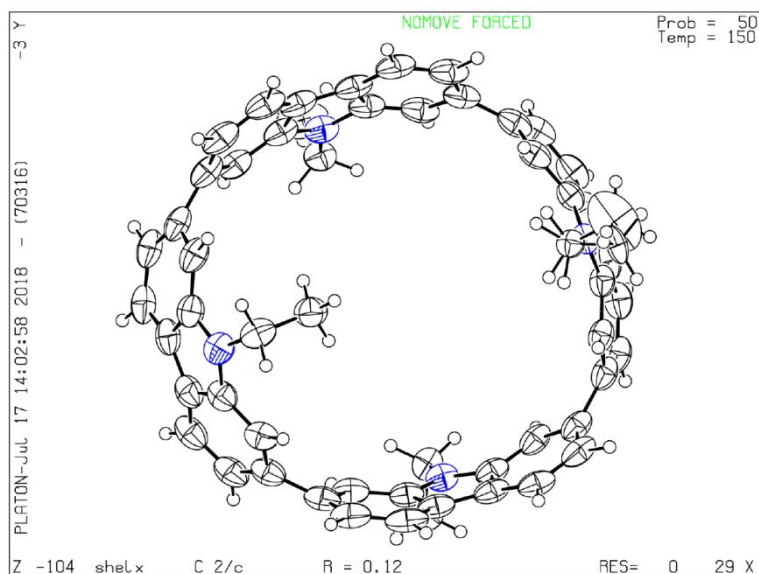


Table S 23 Crystal data and structure refinement for [4]C-Et-Cbz

Identification code	shelx
Empirical formula	C _{57.25} H _{45.25} Cl _{3.75} N ₄
Formula weight	922.16
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 26.355(4) Å α = 90°
	b = 9.1895(13) Å β = 96.498(5)°
	c = 41.286(6) Å γ = 90°
Volume	9935(3) Å ³
Z	8
Density (calculated)	1.233 Mg/m ³
Absorption coefficient	0.266 mm ⁻¹
F(000)	3844
Crystal size	0.13 x 0.03 x 0.02 mm ³
Theta range for data collection	2.349 to 27.637°.
Index ranges	-32 ≤ h ≤ 33, -11 ≤ k ≤ 10, -53 ≤ l ≤ 53
Reflections collected	46522
Independent reflections	11248 [R(int) = 0.0881]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11248 / 3 / 653
Goodness-of-fit on F ²	1.093
Final R indices [I > 2σ(I)]	R1 = 0.1315, wR2 = 0.3529
R indices (all data)	R1 = 0.2068, wR2 = 0.4023
Extinction coefficient	0.0117(10)
Largest diff. peak and hole	2.164 and -0.604 e.Å ⁻³

[4]C-Bu-Cbz

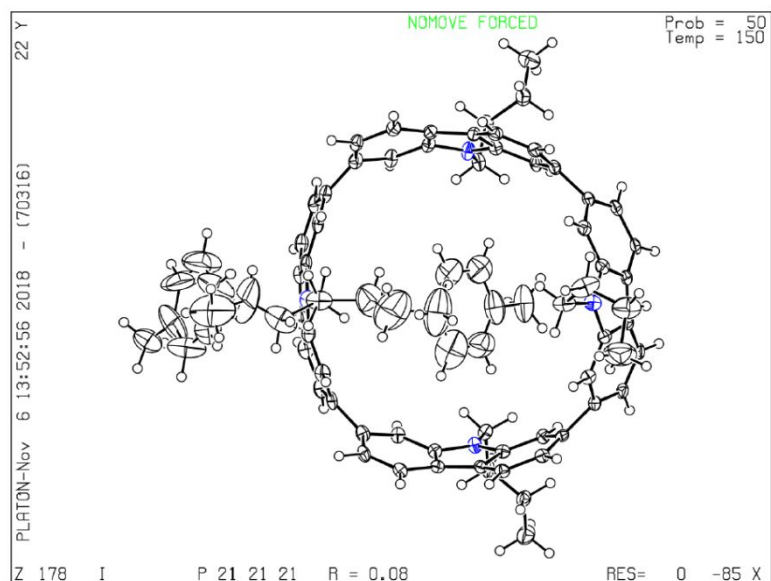


Table S 24 Crystal data and structure refinement for [4]C-Bu-Cbz

Identification code	shelx
Empirical formula	C71 H68 N4
Formula weight	977.29
Temperature	150(2) K
Wavelength	71.073 pm
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 1706.12(12) pm $\alpha = 90^\circ$.
	b = 1791.09(15) pm $\beta = 90^\circ$.
	c = 1890.41(14) pm $\gamma = 90^\circ$.
Volume	5.7767(8) nm ³
Z	4
Density (calculated)	1.124 Mg/m ³
Absorption coefficient	0.065 mm ⁻¹
F(000)	2088
Crystal size	0.13 x 0.05 x 0.04 mm ³
Theta range for data collection	2.155 to 27.513°.
Index ranges	-22 ≤ h ≤ 21, -23 ≤ k ≤ 23, -24 ≤ l ≤ 23
Reflections collected	59586
Independent reflections	13220 [R(int) = 0.0406]
Completeness to theta = 25.242°	99.7 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13220 / 0 / 753
Goodness-of-fit on F ²	1.082
Final R indices [I > 2σ(I)]	R1 = 0.0794, wR2 = 0.2126
R indices (all data)	R1 = 0.0857, wR2 = 0.2206
Absolute structure parameter	0(5)
Extinction coefficient	n/a
Largest diff. peak and hole	1.140 and -0.417 e.Å ⁻³

[4]C-Hex-Cbz

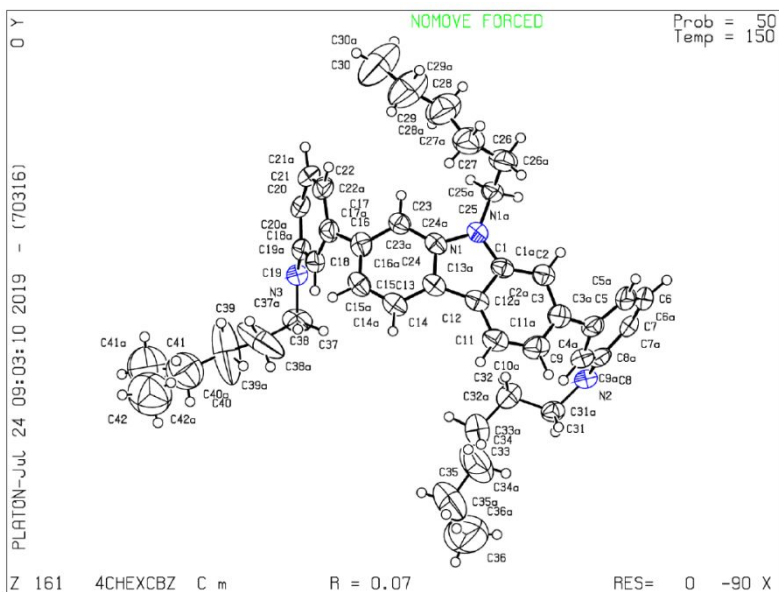


Table S 25 Crystal data and structure refinement for [4]C-Hex-Cbz

Identification code	shelx
Empirical formula	C72 H76 N4
Formula weight	997.36
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C m
Unit cell dimensions	a = 9.4194(14) Å $\alpha = 90^\circ$.
	b = 26.193(3) Å $\beta = 101.590(5)^\circ$.
	c = 12.3056(17) Å $\gamma = 90^\circ$.
Volume	2974.2(7) Å ³
Z	2
Density (calculated)	1.114 Mg/m ³
Absorption coefficient	0.064 mm ⁻¹
F(000)	1072
Crystal size	0.160 x 0.095 x 0.070 mm ³
Theta range for data collection	2.296 to 27.796°.
Index ranges	-12 ≤ h ≤ 12, -27 ≤ k ≤ 34, -16 ≤ l ≤ 15
Reflections collected	21881
Independent reflections	6886 [R(int) = 0.0681]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6886 / 60 / 401
Goodness-of-fit on F ²	1.047
Final R indices [I > 2σ(I)]	R1 = 0.0734, wR2 = 0.1879
R indices (all data)	R1 = 0.1116, wR2 = 0.2128
Absolute structure parameter	0(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.342 and -0.266 e.Å ⁻³

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