Increasing and Dispersing Strain in Pyrene-Fused Azaacenes

Javier Mateos-Martín,# Marco Carini,# Manuel Melle-Franco* and Aurelio Mateo-Alonso*#

# POLYMAT, University of the Basque Country UPV/EHU, Av. Tolosa 72, E-20018 Donostia-San Sebastián, Spain.
# CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal
# Ikerbasque, Basque Foundation for Science, Bilbao, Spain.

Supporting Information
**Figure S1.** X-ray standard ORTEP plot for compound 7.
Figure S2. C\textsubscript{sp2}-C\textsubscript{sp2} bond alternation for the lowest energy structures at the B3LYP-6-31G(d,p) is rendered in a colour continuum ranging from red (1.33 Å) to white (1.40 Å) to blue (1.47 Å).
Figure S3. NICS(0) values of compounds 12, 13 and 14 (respectively 1st to 3rd from top to bottom) compared with those of the unsubstituted core (4th row) at the B3LYP-6-311+G(2d,p) level.
Figure S4. NICS(1) values of compounds 12, 13 and 14 (respectively 1\textsuperscript{st} to 3\textsuperscript{rd} from top to bottom) compared with those of the unsubstituted core (4\textsuperscript{th} row) at the B3LYP-6-311+G(2d,p) level.
Figure S5. Normalized cyclic voltammograms of 12, 13 and 14 in 0.1 M nBu₄NPF₆ in CH₂Cl₂ (scan rate = 100 mV/s) internally referenced to ferrocene (0.16 M)
The HOMO–1 and HOMO orbitals show density on both quinoxaline residues of 12 and 13, but in the case of 14, the electronic densities are localized in opposite quinoxaline residues in the HOMO–1 and HOMO, respectively. Also, while in the case of 12 and 13, the LUMO and LUMO+1 densities are almost identical, but in the case of 14 LUMO and the LUMO+1 are exchanged.

Figure S6. Frontier orbitals of 12, 13 and 14.
**Figure S7.** Simulated absorption spectra computed at the TD-B3LYP-CH$_2$Cl$_2$-6-311+G(2d,p)/B3LYP-6-31G(d,p) level.
At twist angles >30°, the LUMO density corresponds to the LUMO+1 density of the flat system, exactly as we observed for 14 with respect to 12 and 13 (Figure S6).

Figure S8. a) Twisting energy as a function of the angle from 0° flat, $D_{2h}$ symmetry, to 60° computed by partial optimizations at the B3LYP-6-31G(d,p) level. Front views (with LUMO density) and side views are shown for each selected angle.
**Figure S9.** Absorption spectra for different twist angles computed with four excited states at the TD-B3LYP-CH$_2$Cl$_2$-6-31G(d,p)/B3LYP-6-31G(d,p) level.
|    | $\lambda_{\text{ONSET}}$ (nm)$^a$ | $\lambda_{\text{MAX}}$ (nm)$^a$ | $\lambda_{\text{EM}}$ (nm)$^a$ | $E_G$ (eV)$^{a,b}$ | $E_{I, 1/2}$ (V)$^a$ | $E_{II, 1/2}$ (V)$^a$ | $E_{\text{LUMO}}$ (eV)$^{a,c}$ | $E_{\text{HOMO}}$ (eV)$^d$ |
|----|----------------------------------|----------------------------------|----------------------------------|-------------------|-----------------|-----------------|-------------------|-----------------|
| 12 | 491                              | 464                              | 520                              | 2.53              | −1.61           | −1.72           | −3.26             | −5.79           |
| 13 | 492                              | 464                              | 524                              | 2.52              | −1.67           | −1.78           | −3.17             | −5.69           |
| 14 | 501                              | 472                              | 538                              | 2.48              | −1.64           | −1.75           | −3.21             | −5.69           |

*Table S1. Photophysical and electrochemical experimental properties.*  
$^a$ Measured in dichloromethane.  
$^b$ Estimated from absorption onset according to $E_g = 1240/\lambda_{\text{ONSET}}$.  
$^c$ Estimated from CV $E_{\text{RED,ONSET}}$ according to $E_{\text{LUMO}} = -4.8 - e (E_{\text{RED,ONSET}} - E_{1/2}^{Fc})$ where $E_{1/2}^{Fc}$ was measured in situ according to $E_{1/2}^{Fc} = - (E_{\text{ONSET}^{\text{red}}} - E_{\text{ONSET}^{\text{ox}}})$ (eV).  
$^d$ $E_{\text{HOMO}} = E_{\text{LUMO}} - E_g$. 
|   | LUMO+2 | LUMO+1 | LUMO  | HOMO  | HOMO-1 | HOMO-2 | $E_g$ | EA   | IP   |
|---|--------|--------|-------|-------|--------|--------|------|------|------|
| 12| -1.84  | -2.77  | -2.85 | -5.71 | -5.72  | -6.12  | 2.86 | -2.92| -5.65|
| 13| -1.84  | -2.79  | -2.85 | -5.7  | -5.71  | -6.13  | 2.85 | -2.92| -5.65|
| 14| -1.9   | -2.82  | -2.86 | -5.69 | -5.7   | -6.17  | 2.83 | -2.92| -5.64|

*Table S2.* Orbital energies, Electron Affinity (EA) and Ionization Potential (IP) computed at the B3LYP-CHCl$_2$-6-311+G(2d,p)/B3LYP-6-31G(d,p) level.
|   | eV  | nm  | Osc. Strength | Contributions       |       |
|---|-----|-----|---------------|---------------------|-------|
| 12| 2.43| 511 | 0.00          | H-1->L+1            | 18%   |
|   |     |     |               | HOMO->LUMO          | 81%   |
| 12| 2.44| 507 | 0.61          | H-1->LUMO           | 68%   |
|   |     |     |               | HOMO->L+1           | 31%   |
| 13| 2.43| 511 | 0.00          | H-1->L+1            | 27%   |
|   |     |     |               | HOMO->LUMO          | 72%   |
| 13| 2.43| 509 | 0.59          | H-1->LUMO           | 64%   |
|   |     |     |               | HOMO->L+1           | 35%   |
| 14| 2.39| 518 | 0.15          | HOMO->LUMO          | 60%   |
|   |     |     |               | HOMO->L+1           | 31%   |
| 14| 2.41| 515 | 0.47          | H-1->LUMO           | 63%   |
|   |     |     |               | H-1->L+1            | 25%   |

**Table S3.** First transition (dark for 12 and 13 in italics) and second transition (active for all) computed at the TD-B3LYP-CH₂Cl₂-6-311+G(2d,p)/B3LYP-6-31G(d,p) level.
S1. General Experimental Methods

All reagents and solvents were purchased from Fisher Scientific, ABCR, Alfa Aesar, Sigma Aldrich or VWR, and were used without further purification unless specified otherwise. Preparation of air moisture sensitive materials was carried out in flamed-dried flasks under nitrogen atmosphere employing standard Schlenk techniques. Anhydrous THF was dried using an Innovative Pure Solve solvent purification system. Commercial chlorotriisopropylsilane was dried by distillation under reduced pressure and stored with molecular sieves under argon atmosphere in a freezer until its use.

Column chromatography was performed on Silica gel 60 (40-60 μm) from Scharlab, employing petroleum ether and dichloromethane as eluents. Analytical thin layer chromatography (TLC) was carried out using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck). UV-active compounds were detected using a UV-lamp from CAMAG at wavelength λ = 254 or 366 nm. NMR spectra in solution were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometer at 298K using partially deuterated solvents as internal standards.

High Resolution Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) Mass Spectrometry experiments were recorded in CICbiomaGUNE in a Ultraflex III (Bruker Daltonics) MALDI-ToF (frequency-tripled (355 nm) Nd:YAG laser) by Dr. Javier Calvo. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) Mass Spectrometry MALDI- ToF experiments were recorded in POLYMAT Fundazioida in a Bruker REFLEX spectrometer by Dr. Estibaliz San Román.

X-ray data collections were performed in an Agilent Supernova diffractometer equipped with an Atlas CCD area detector, and a CuKα micro-focus source with multilayer optics (λ = 1.54184Å, 250μm FWHM beam size) by Dr. Leire Sanfelices (SGiker, University of the Basque Country). The quality of the crystals was checked under a polarizing microscope, and a suitable crystal or fragment was mounted on a Mitegen Micromount™ using Paratone-N inert oil and transferred to the diffractometer. Samples were kept at 150(10)K with an Oxford Cryosystems Cryostream 700 cooler.

Absorption spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer.

Fluorescence spectra were recorded on a LS55 Perkin-Elmer Fluorescence spectrometer.

Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with glassy-carbon disc working electrode (φ = 3mm), a platinum wire counter electrode (φ = 0.5mm) and a silver wire pseudoreference electrode. The cell and the electrodes were custom made. All the potential values are reported versus the redox potential of the ferrocene/ferrocenium couple.
Preparation of starting materials.

Some compounds were synthesized according literature:

1: 2,7-diterbutyl-pyrene-4,5,9,10-tetraone.\textsuperscript{1}
2: 2,7-diiodo-pyrene-4,5,9,10-tetraone.\textsuperscript{1b, 2}
9: 4,7-dibromo-2,1,3-benzothiadiazole.\textsuperscript{3}
S2. Synthesis and Analytical Data

3: 2,7-diiodo-4,5,9,10-tetrahexyloxyppyrene.

In a flame dried Schlenk flask 2.11 g of 2 (4.11 mmol) was suspended in 48 mL of a mixture DMF/H$_2$O 3:2, the suspension was purged with N$_2$ for 15 minutes, then 924 mg of tetrabutylammonium bromide 98% (TBAB, 2.87 mmol, 0.7 eq.) and 4287 mg of sodium dithionite (Na$_2$S$_2$O$_4$, 24.63 mmol, 6 eq.) were added under nitrogen stream. Once the solution turns black, 5671 mg of potassium carbonate 99% (41.05 mmol, 10 eq.) and 5.76 mL of 1-bromohexane 98% (41.05 mmol, 1.176 g/mL, 10 eq.) were added under inert atmosphere. Reaction was refluxed for 4 hours under nitrogen. The reaction was cooled to room temperature, water was added. The product was extracted with diethyl ether (3x50 mL), washed with brine and dried over sodium sulfate. Solvent was removed by rotary evaporation. Resulting solids were loaded onto a chromatography column with hexane as eluent. Desired product is precipitated on methanol, affording 1560 mg (2.59 mmol) of white solid 3 in 63% yield.

$^1$H NMR (400 MHz, CDCl$_3$-d$_1$): δ = 8.51 (4H, s), 4.29 (8H, J = 6.6 Hz, t), 1.95 (8H, J = 7.5 Hz, m), 1.61 (8H, m), 1.41 (16H, m) and 0.94 (12H, J = 6.7 Hz, t).

$^{13}$C NMR (400 MHz, CDCl$_3$-d$_1$): δ = 143.36, 130.37, 127.94, 119.39, 93.07, 74.06, 31.84, 30.55, 26.07, 22.88, 14.26.

MS: MS (MALDI-ToF) (m/z) [M+H]$^+$ calcd. for C$_{40}$H$_{56}$I$_2$O$_4$: 854.227; found: 854.190.

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4: 2,7-bis(triisopropylsilyl)-4,5,9,10-tetrahexyloxyppyrene.

In a flame dried Schlenk flask 800 mg (0.94 mmol) of 3 was dissolved in 10 mL of dry THF, the resultant solution is freeze-pump-thawed three times, then cooled to −94 °C and 5 mL of n-BuLi 1.6M in hexanes (7.94 mmol, 8eq.) was added. After three hours 1.6 mL of chlorotriisopropylsilane (7.94 mmol, 0.91 g/mL, 8 eq.) previously dried was added dropwise under inert atmosphere. The reaction was allowed to reach room temperature and reacted overnight. Ammonium chloride is added at 0°C, then extracted with diethyl ether (3x50mL). Resultant organic phase was washed with brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting solids were purified by flash chromatography.
(eluent mixture hexanes/dichloromethane 95:5). Product 4 was precipitated on methanol affording 601 mg (0.66 mmol) of white solid in 70% yield.

$^1$H NMR (500 MHz, CDCl$_3$-d$_2$): $\delta = 8.58$ (4H, s), 4.32 (8H, $J = 6.6$ Hz, t), 1.95 (8H, m), 1.65 (8H, m), 1.41 (22H, m), 1.19 (36H, $J = 7.5$ Hz, d) and 0.94 (12H, $J = 7.0$ Hz, t).

$^{13}$C NMR (500 MHz, CDCl$_3$-d$_2$): $\delta = 144.20$, 132.47, 127.67, 125.55, 121.21, 74.23, 32.08, 30.94, 26.41, 22.88, 18.93, 14.25, 11.30.

HRMS (MALDI-ToF) (m/z) [M+H]$^+$ calcd. for C$_{58}$H$_{98}$O$_4$Si$_2$: 914.7001; found: 914.7006.

5: 2,7-bis(triisopropylsilyl)-pyrene-4,5,9,10-tetraone.

In a round bottom flask 360 mg (0.404 mmol) of 4 and 257 mg of sodium carbonate (2.43 mmol, 6 eq.) were suspended on 10 mL of chloroform and cooled below 0°C, then 1 mL of a solution 1.62M of bromide (3.1 g/mL, 4 eq.) in chloroform was slowly added. After 15 minutes the reaction was stopped. More solvent was added, and the organic phase was treated with a 10% aqueous solution of sodium thiosulfate, then washed with water and brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting crude was dissolved in 6 mL of a mixture 1:5 chloroform/acetonitrile and 442 mg of cerium-ammonium-nitrate 99% (CAN, 0.808 mmol, 2 eq.) was added. Reaction was heated up to 70°C overnight. When reaction was completed dichloromethane was added, the organic phase was washed with water and brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting crude was purified by flash chromatography (eluent mixture hexanes/DCM 9:1) affording 106 mg (0.189 mmol) of red solid 5 in 47% yield over two steps.

$^1$H NMR (400 MHz, CDCl$_3$-d$_2$): $\delta = 8.55$ (4H, s), 1.59 (6H, $J = 15.2$, 7.4 Hz, hept), 1.15 (36H, $J = 6.7$ Hz, d).

$^{13}$C NMR (400 MHz, CDCl$_3$-d$_2$): $\delta = 178.71$, 143.17, 141.43, 134.7, 129.86, 18.54, and 10.75.

MS (MALDI-ToF) (m/z) [M+Na]$^+$ calcd. for C$_{34}$H$_{46}$NaO$_4$Si$_2$: 597.283; found: 597.184.
In a flame dried Schlenk flask 714 mg (0.84 mmol) of 3 was dissolved in dry THF, the resultant solution is freeze-pump-thawed three times, then cooled to −94°C and 3.66 mL of n-BuLi 1.6M in hexanes (5.86 mmol, 7 eq.) was added. After three hours 1.8 g of chlorotriphenylsilane 96% (5.86 mmol, 7 eq.) previously dissolved in dry THF was added dropwise under inert atmosphere. The reaction was allowed to reach room temperature and reacting overnight. Ammonium chloride was added at 0°C, then extracted with diethyl ether (3 x 50 mL). The organic phase was washed with brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting solids were loaded onto a chromatography column (elucent mixture hexanes/dichloromethane 7:3). The desired product is precipitated on methanol, affording 544 mg (0.487 mmol) of white solid 6 in 58% yield

1H NMR (500 MHz, CDCl₃-d⁴): δ = 8.66 (4H, s), 7.72 (12H, J = 8.0 Hz, d), 7.50 (6H, J = 7.4 Hz, t), 7.44 (12H, J = 7.2 Hz, t) 4.16 (8H, J = 6.8 Hz, t), 2.06 (8H, m), 1.71 (8H, J = 14.6, 6.9 Hz, p), 1.29 (16H, m) and 0.89 (12H, J = 6.9 Hz, t).

13C NMR (500 MHz, CDCl₃-d⁴): δ = 144.40, 136.72, 134.56, 132.34, 129.75, 128.23, 128.03, 126.88, 121.53, 74.26, 31.84, 30.48, 25.87, 22.71, 14.23.

HRMS (MALDI-ToF) (m/z) [M+H]+ calcd. for C₇₆H₈₆O₄Si₂: 1118.6062; found: 1118.6211

7: 2,7-bis(triphenylsilyl)-pyrene-4,5,9,10-tetraone.

In a round bottom flask 210 mg (0.188 mmol) of 6 and 120 mg of sodium carbonate (1.13 mmol, 6 eq.) were suspended on chloroform and cooled below 0°C, then 1 mL of a 0.75M solution of bromide (3.1 g/mol, 4 eq.) in chloroform was slowly added. After 15 minutes the reaction was stopped. More solvent was added, and the organic phase was treated with a 10% aqueous
solution of sodium thiosulfate, then washed with water and brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting crude was dissolved in 6 mL of 1:5 mixture chloroform/acetonitrile and 206 mg of cerium-ammonium-nitrate 99% (0.376 mmol, 2 eq.) was added. Reaction was heated up to 70 °C overnight. When reaction was completed dichloromethane is added, the organic phase was washed with water and brine, dried over sodium sulfate and filtered. Solvent was removed by rotary evaporation. Resulting crude was purified by flash chromatography (eluent mixture hexanes/DCM 3:2) affording 60mg (0.0771 µmol) of red solid 7 in 45% yield over two steps. Crystals for 7 were obtained by chloroform evaporation.

1H NMR (400 MHz, CDCl₃-d): δ = 8.67 (4H, s), 7.55 (12H, J = 8.0 Hz, s), 7.48 (6H, J = 7.4 Hz, t), 7.42 (12H, J = 7.2 Hz, t).

13C NMR (500 MHz, CDCl₃-d): δ = 178.32, 146.34, 144.09, 141.19, 136.39, 135.07, 131.80, 130.66, 130.26 and 128.59.

MS (MALDI-ToF) (m/z) [M+Na]⁺ calcld. for C₅₂H₃₄NaO₄Si₂: 801.189; found: 801.408.

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8: (tris(trimethylsilyl)silyl)acetylene.

In a Schlenk flask 4 g of chlorotris(trimethylsilyl)silane 97% (14.15 mmol) were dissolved in 20 mL of dry THF and freeze-pump-thawed twice. In a 250 mL round bottom flask 85ml of ethynyl magnesium bromide in hexane (42.4 mmol) was placed under nitrogen and cooled below 0°C. Then the silane solution was added dropwise over the previous solution, allow to react overnight at RT under nitrogen. The solution was cooled to 0°C and quenched with ammonium chloride. The product was extracted with dichloromethane (3x100 mL), washed with brine, dried over sodium sulfate. Rotary evaporation afforded 3.66g (13.43 mmol) of yellow oil 8 that solidifies with time, in 95% yield.

1H NMR (400 MHz, CDCl₃-d): δ = 2.30 (1H, s) and 0.21 (27H, s).

All analytical data agrees with literature.⁴

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10: 4,7-bis((tris(trimethylsilyl)silyl)ethynyl)benzo[c][1,2,5]thiadiazole.

In a flame dried Schlenk 1176 mg (4 mmol) of 8, 140 mg (0.2 mmol, 0.05 eq.) of catalyst PdCl₂(PPh₃)₄, 15.24 mg (0.08 mmol, 0.02 eq) of Cu were dissolved in 30 mL of THF/Et₃N 1:1 and freeze-pump-thawed twice. Then 3.272g (12 mmol, 3 eq.) of 9 was added under nitrogen atmosphere. Solution was heated at room temperature overnight. Resulting solution was cooled
to room temperature and filtered through Celite pad. Solvents were rotary evaporated, crude was redissolved in hexanes and washed with brine, dried over sodium sulfate and the organic phase was removed by rotary evaporation. Resulting solid was purified by flash chromatography (eluent hexane/dichloromethane 95:5) and desired product was triturated on methanol. Recrystallization by dichloromethane evaporation afforded 2.02 g (2.95 mmol) of 10 as bright yellow crystals in 74% yield.

**1H NMR (400 MHz, CDCl$_3$-d$_6$):** $\delta$ = 7.53 (2H, s) and 0.28 (27H, s).

**13C NMR (400 MHz, CDCl$_3$-d$_6$):** $\delta$ = 154.36, 131.80, 117.52, 103.96, 98.74, 0.29.

**HRMS (MALDI-ToF) (m/z) [M+Ag]$^+$ calcd. for C$_{28}$H$_{56}$AgN$_2$SSi$_8$: 789.1361; found: 783.1369.

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**11:** 3,6-bis((tris(trimethylsilyl)silyl)ethynyl)benzene-1,2-diamine.

In a two-neck 250 mL round bottom flask 500 mg (0.747 mmol) of 10 was dissolved in 35 mL of dry diethyl ether and cooled to −15°C, then under nitrogen atmosphere 300 mg (7.47 mmol, 10 eq.) of LiAlH$_4$ was slowly added. Reaction was allowed to reach room temperature, after two hours was quenched with ammonium chloride and extracted with hexane. Organic phase was washed with water and brine, dried over sodium sulfate and solvent was removed by rotary evaporation. Trituration on methanol afforded 176 mg (0.26 mmol) of pale yellow solid 11 in 35% yield.

**1H NMR (400 MHz, CDCl$_3$-d$_6$):** $\delta$ = 7.26 (2H, s) and 0.24 (27H, s).

**13C NMR (400 MHz, CDCl$_3$-d$_6$):** $\delta$ = 136.23, 122.10, 105.10, 94.99, 0.53.

**HRMS (MALDI-ToF):** (m/z) [M+Ag]$^+$ m/z calcd. for C$_{28}$H$_{60}$AgN$_2$Si$_8$: 648.2911, found 648.3079.

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**12:** TTMS-TBU-TTMS-dibenzotetrazahexacene.

In a Schlenk flask 13 mg of tetraketone 1 (36 µmol, 1 eq.) and 52 mg of diamine 11 (80 µmol, 2.2 eq.) were dissolved in little amount chloroform and 1.5 mL of acetic acid was added. Mixture was heated up to 40°C for three hours under nitrogen atmosphere. Reaction was cooled to room temperature. Chloroform was removed, methanol was added, and the suspension was filtered.
Resulting solids were purified by flash chromatography (eluent mixture hexane/DCM 7:3). Desired product was isolated by precipitation on methanol affording 49.4 mg (30 µmol) of yellow solid 12 in 83% yield. Crystals were obtained by low vapor diffusion of ethanol over a toluene solution of 12.

\[ ^1H \text{NMR (400 MHz, CDCl}_3-d^1\text{)}: \delta = 9.88 (4H, s), 7.96 (4H, s), 1.72 (18H, s) and 0.36 (108H, s) \]

\[ ^13C \text{NMR (400 MHz, CDCl}_3-d^1\text{)}: \delta = 150.88, 143.18, 141.72, 135.66, 129.43, 126.39, 125.57, 124.72, 106.592, 98.53, 35.94, 32.52 and 0.92 \]

HRMS (MALDI-ToF): \( \langle m/z \rangle [M]+H^+ \) calcd. for \( C_{80}H_{135}N_{4}Si_{16} \): 1599.6991; found: 1599.6955.

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13: TTMS-TIPS-TTMS-dibenzotetrazahexacene.

In a Schlenk flask 20 mg of tetraketone 5 (34 µmol, 1 eq.) and 65 mg of diamine 11 (104 µmol, 3 eq.) were suspended in 1.5 mL of acetic acid. Mixture is heated up 40° for three hours under nitrogen atmosphere. Reaction was cooled to room temperature, methanol was added, and the suspension was filtered. Resulting solids were purified by flash chromatography (eluent mixture hexane/DCM 4:1). Desired product was isolated by precipitation on methanol affording 23.8 mg (14 µmol) of yellow solid 13 in 40% yield. Crystals were obtained by low vapor diffusion of ethanol over a toluene solution of 13.

\[ ^1H \text{NMR (400 MHz, CDCl}_3-d^1\text{)}: \delta = 9.83 (4H, s), 7.95 (4H, s), 1.78 (6H, J = 7.4 Hz, p), 1.23 (36H, J = 7.5 Hz, d) and 0.35 (108H, s) \]

\[ ^13C \text{NMR (400 MHz, CDCl}_3-d^1\text{)}: \delta = 142.93, 141.52, 136.37, 135.94, 135.11, 128.68, 128.55, 124.87, 107.68, 99.04, 31.75, 29.87, 22.82, 19.41, 11.54 and 0.91 \]

HRMS (MALDI-ToF): \( \langle m/z \rangle [M]+H^+ \) calcd. for \( C_{90}H_{159}N_{4}Si_{18} \): 1799.8412; found: 1799.8580.
14: TTMS-TPS-TTMS-dibenzotetrazahexacene.

In a Schlenk flask 20 mg of tetraketone 7 (26 µmol, 1 eq.) and 50 mg of diamine 11 (77 µmol, 3 eq.) were suspended in 3 mL of acetic acid. Mixture was heated at 40 °C for three hours under nitrogen atmosphere. Reaction was cooled to room temperature, methanol was added, and the suspension was filtered. Resulting solids were purified by flash chromatography (eluent mixture hexane/DCM 4:1). Desired product was isolated by precipitation on methanol affording 23.8 mg (12 µmol) of yellow solid 14 in 47% yield. Crystals were obtained by low vapor diffusion of ethanol over a toluene solution of 14.

$^1$H NMR (400 MHz, CDCl$_3$-d$_1$): δ = 9.90 (4H, s), 7.87 (4H, s), 7.72 (12H, $J = 1.68, 5.8$ Hz, dd), 7.42 (24H, m) and 0.13 (108H, s).

$^{13}$C NMR (400 MHz, CDCl$_3$-d$_1$): δ = 142.28, 141.58, 136.92, 135.07, 134.33, 134.01, 129.75, 129.28, 128.80, 128.21, 106.99, 99.26, and 0.68.

HRMS (MALDI-ToF): (m/z) [M]+H$^+$ calcd. for C$_{108}$H$_{147}$N$_4$Si$_{18}$: 2003.7473; found: 2003.7451.
S3. Crystal structures and X-Ray Diffraction data for compounds 7, 12, 13 and 14

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1997927 (7), 1998202 (12), 1998195 (13) and 1998197 (14). The crystallographic data is shown below.

S3.1 Compound 7

Bond precision: C-C = 0.0050 Å       Wavelength=1.54184

Cell: a=14.4193(9)       b=15.3229(7)       c=18.2720(6)
      alpha=90          beta=93.967(4)      gamma=90

Temperature: 150 K

| Calculated | Reported |
|------------|----------|
| Volume     | 4027.4(3)       | 4027.5(3)       |
| Space group| P 21/c       | P 1 21/c 1       |
| Hall group | -P 2ybc     | -P 2ybc       |
| Moiety formula | C_{52} H_{34} O_{4} Si_{2} | C_{52} H_{34} O_{4} Si_{2} |
| Sum formula | C_{52} H_{34} O_{4} Si_{2} | C_{52} H_{34} O_{4} Si_{2} |
| M_r        | 778.97       | 778.97       |
| D_x (g cm^-3) | 1.285     | 1.285     |
| Z          | 4           | 4           |
| Mu (mm^-3) | 1.177       | 1.178       |
| F000       | 1624.0       | 1624.0       |
| F000'      | 1630.39      |             |
| h,k,l_max  | 17,18,22     | 17,18,22     |
| N_ref      | 7644        | 7641        |
| T_min, T_max | 0.657,0.799 | 0.674,0.836 |
| T_min'     | 0.530       |             |

Correction method= #
Reported T Limits: T_min=0.674 T_max=0.836

AbsCorr = ANALYTICAL

Data completeness= 1.000     Theta(max)= 69.999
R(reflections)= 0.0692 (5190) wR2(reflections)= 0.2211 (7641)

S = 1.033     N_{par}= 650
S3.2 Compound 12

Bond precision: C-C = 0.0038 Å  Wavelength=1.54184

Cell:  
\[ \begin{align*}
a &= 9.8911(2) \\
b &= 16.0352(4) \\
c &= 19.2371(5) \\
\alpha &= 88.170(2) \\
\beta &= 76.903(2) \\
\gamma &= 73.041(2)
\end{align*} \]

Temperature: 150 K

| Calculated | Reported |
|------------|----------|
| Volume     | 2840.61(12) | 2840.61(12) |
| Space group| P -1      | P -1       |
| Hall group | -P 1      | -P 1       |
| Moiety formula | C\textsubscript{80} H\textsubscript{134} N\textsubscript{4} Si\textsubscript{16}, 2(C\textsubscript{7} H\textsubscript{8}) | C\textsubscript{80} H\textsubscript{134} N\textsubscript{4} Si\textsubscript{16}, 2(C\textsubscript{7} H\textsubscript{8}) |
| Sum formula | C\textsubscript{94} H\textsubscript{150} N\textsubscript{4} Si\textsubscript{16} | C\textsubscript{94} H\textsubscript{150} N\textsubscript{4} Si\textsubscript{16} |
| Mr         | 1785.62   | 1785.61    |
| \(\Delta\) (g cm\(^{-3}\)) | 1.044     | 1.044      |
| Z          | 1         | 1          |
| \(\mu\) (mm\(^{-1}\)) | 1.998     | 2.002      |
| F000       | 966.0     | 966.0      |
| F000'      | 971.77    |            |
| \(h,k,l_{\text{max}}\) | 11,19,23  | 11,19,23   |
| \(N_{\text{ref}}\) | 10543     | 10521      |
| \(T_{\text{min}}, T_{\text{max}}\) | 0.544, 0.812 | 0.599, 0.844 |
| \(T_{\text{min}}'\) | 0.394     |            |

Correction method= #
Reported T Limits: \(T_{\text{min}}=0.599\) \(T_{\text{max}}=0.844\)

AbsCorr = ANALYTICAL

Data completeness= 0.998
R(Reflections)= 0.0477 (9007)
\(S = 1.035\)  \(N_{\text{par}}= 576\)

Theta(max)= 68.994
wR2(Reflections)= 0.1419 (10521)
### S3.3 Compound 13

**Bond precision:** C-C = 0.0067Å  
**Wavelength:** 1.54184 Å

**Cell:**
- \(a = 43.6057(12)\)
- \(b = 8.5663(2)\)
- \(c = 33.2570(9)\)
- \(\alpha = 90\)
- \(\beta = 101.568(3)\)
- \(\gamma = 90\)

**Temperature:** 150 K

| Calculated | Reported |
|------------|----------|
| Volume     | 12170.5(6) | 12170.5(6) |
| Space group| C 2/c     | C 1 2/c 1  |
| Hall group | -C 2yc    | -C 2yc     |
| Moiety formula | \(C_{90}H_{158}N_4Si_{18}\) [+solvent] | \(C_{90}H_{158}N_4Si_{18}\) |
| Sum formula | \(C_{90}H_{158}N_4Si_{18}\) [+solvent] | \(C_{90}H_{158}N_4Si_{18}\) |
| \(M_r\)   | 1801.82   | 1801.81    |
| \(D_\lambda (g \text{ cm}^{-3})\) | 0.983     | 0.983      |
| \(Z\)     | 4         | 4          |
| \(\mu (\text{mm}^{-1})\)  | 2.049     | 2.049      |
| \(F_{000}\)  | 3912.0    | 3912.0     |
| \(F_{000}'\) | 3936.82   | 3936.82    |
| \(h,k,l_{\text{max}}\) | 52,10,40  | 52,10,40   |
| \(N_{\text{ref}}\)  | 11320     | 11316      |
| \(T_{\text{min}},T_{\text{max}}\) | 0.825,0.868 | 0.552,0.876 |
| \(T_{\text{min}}'\) | 0.299     |            |

**Correction method:** #  
**Reported T Limits:**  
- \(T_{\text{min}} = 0.552\)  
- \(T_{\text{max}} = 0.876\)

**AbsCorr = ANALYTICAL**

**Data completeness:** 1.000  
**Theta(max):** 68.987°  
**R(reflections):** 0.0933 (8597)  
**wR2(reflections):** 0.2693 (11316)  
**S:** 1.023  
**N_{ref}:** 643

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*S25*
**S3.4 Compound 14**

Bond precision: C-C = 0.0148 Å

Wavelength=1.54184

Cell:  
- a=22.1092(12)  
- b=22.3180(13)  
- c=29.0414(13)
- \(\alpha=74.547(4)\)  
- \(\beta=79.773(4)\)  
- \(\gamma=71.053(5)\)

Temperature: 150 K

|                | **Calculated**             | **Reported**   |
|----------------|-----------------------------|----------------|
| Volume         | 12998.3(13)                 | 12998.0(10)    |
| Space group    | P -1                        | P -1           |
| Hall group     | -P 1                        | -P 1           |
| Moiety formula | \(\text{C}_{108}\text{H}_{146}\text{N}_4\text{Si}_{18}\), \(\text{C}_7\text{H}_8\) | \(2(\text{C}_{108}\text{H}_{146}\text{N}_4\text{Si}_{18})\), \(2(\text{C}_7\text{H}_8)\) |
| Sum formula    | \(\text{C}_{115}\text{H}_{154}\text{N}_4\text{Si}_{18}\) | \(\text{C}_{230}\text{H}_{308}\text{N}_8\text{Si}_{36}\) |
| Mr             | 2098.05                     | 4196.07        |
| Dx, g cm\(^{-3}\) | 1.072                      | 1.072          |
| Z              | 4                           | 2              |
| Mu (mm\(^{-3}\)) | 1.988                      | 1.988          |
| F000           | 4496.0                      | 4496.0         |
| F000'          | 4522.55                     |                |
| \(h,k,l_{\text{max}}\) | 26,27,35                   | 26,27,35       |
| Nref           | 48333                       | 48242          |
| \(T_{\text{min}}\) \(T_{\text{max}}\) | 0.658,0.858                | 0.615,0.896    |
| \(T'_{\text{min}}\) | 0.372                      |                |

Correction method= #

Reported T Limits: \(T_{\text{min}}=0.615\) \(T_{\text{max}}=0.896\)

AbsCorr = ANALYTICAL

Data completeness= 0.998  
\(R(\text{reflections})= 0.1286\ (21047)\)

\(S = 1.020\)  
\(N_{\text{par}} = 2431\)
S4. General Methods for Calculations

The geometries from the crystallographic data were first optimized in cartesian space to a very small gradient with the GFN2-xtB method (Geometry, Frequency, Non-covalent, Extended Tight-Binding) and then they were optimized at the B3LYP-6-31G(d,p) level.

S4.1 Strain calculations
The strain energies for the three systems under consideration were estimated with a simplified H-capped molecular analogue where the bulky groups were deleted, the H-capping atoms optimized, and then the molecule allowed to relax.

| H-capped molecules | Aromatic core | Polycyclic core | Acetylenes |
|--------------------|---------------|-----------------|------------|
|                    | Total Strain E. / Kcal/mol | Total Strain E. / Kcal/mol | Total Strain E. / Kcal/mol |
| 12                 | 4.0           | 3.1             | 0.9        |
| 13                 | 8.2           | 5.1             | 3.1        |
| 14                 | 11.2          | 9.8             | 1.4        |
| H-capped molecules | StrainViz |
|--------------------|-----------|
|                    | Total Strain E. / Kcal/mol | Max. bond strain E. / Kcal/mol | Min. bond strain E. / Kcal/mol |
| 12                 | 4.0       | 0.44         | 0.00         |
| 13                 | 8.2       | 0.62         | 0.00         |
| 14                 | 11.2      | 0.45         | 0.01         |
S5. Fluorescence Quantum Yield of products 12, 13 and 14.

Quantum yields were calculated following the next equation:

$$\Phi_f^i = \Phi_f^s \frac{F_i f_i \eta_i^2}{F_s f_s \eta_s^2}$$

where $\Phi_f^s$ stands for the quantum yield of the reference standard, $F_i$ for the measured fluorescence (area) of a solution at known concentration of products 12, 13 and 14 at the selected excitation wavelength, $F_s$ for the measured fluorescence (area) of a solution at known concentration of reference standard at the selected excitation wavelength.

$f_s = 1 - 10^{-A_s(\lambda_{exc})}$ stands for the absorption factor of a solution at known concentration of reference standard at the excitation wavelength, $f_i = 1 - 10^{-A_i(\lambda_{exc})}$ stands for the absorption factor of a solution at known concentration of products 12, 13 and 14 at the excitation wavelength. Finally, $\eta_i$ is the refraction index of the solvent of the solution of compounds 12, 13 and 14; $\eta_s$ refers to the refraction index of the solvent of the solution of the reference standard.

The error of was calculated as follows:

$$\text{Error} = \frac{\sqrt{\sum_{i=n}^{m} (\Phi_{f,i} - \bar{\Phi}_{f,i})^2}}{m}$$

To measure quantum yield of 12, 13 and 14, 9,10-Diphenylanthracene (DPA) was selected as reference standard ($\Phi_f^{DPA} = 0.93$) at 7.57·10$^{-7}$ M in cyclohexane ($\eta_{cHex} = 1.45$). The excitation wavelength was set at 340 nm and three different solutions at different concentration of 12, 13 and 14 were analyzed.

Quantum yields ($\Phi_f^{12}$, $\Phi_f^{13}$ and $\Phi_f^{14}$) are expressed as the average of the three measurements with its associated error.

| Entry | Concentration (mol·L$^{-1}$) | $\Phi_f^{12}$ (%) |
|-------|-----------------------------|------------------|
| 1     | 2.70E-07                    | 19.56            |
| 2     | 4.05E-07                    | 17.58            |
| 3     | 5.40E-07                    | 16.76            |

$\bar{\Phi}_f^{12} = 17.90 \pm 0.68$
| Entry | Concentration (mol·L⁻¹) | $\Phi_f^{13}$ (%) |
|-------|--------------------------|-------------------|
| 1     | 2.50E-07                 | 18.06             |
| 2     | 3.75E-07                 | 15.24             |
| 3     | 5.00E-07                 | 17.57             |

$\bar{\Phi}_f^{13} = 16.91 \pm 0.71$

| Entry | Concentration (mol·L⁻¹) | $\Phi_f^{14}$ (%) |
|-------|--------------------------|-------------------|
| 1     | 1.93E-07                 | 20.55             |
| 2     | 2.90E-07                 | 20.19             |
| 3     | 3.86E-07                 | 19.36             |

$\bar{\Phi}_f^{14} = 20.03 \pm 0.29$
S6. $^1$H and $^{13}$C NMR Spectra

*Figure S10.* $^1$H NMR on CDCl$_3$ of compound 3.

*Figure S11.* $^{13}$C NMR on CDCl$_3$ of compound 3.
Figure S12. $^1$H NMR on CDCl$_3$ of compound 4.

Figure S13. $^{13}$C NMR on CDCl$_3$ of compound 4.
Figure S14. $^1$H NMR on CDCl$_3$ of compound 5.

Figure S15. $^{13}$C NMR on CDCl$_3$ of compound 5.
Figure S16 $^1$H NMR on CDCl$_3$ of compound 6.

Figure S17 $^{13}$C NMR on CDCl$_3$ of compound 6.
**Figure S18** $^1$H NMR on CDCl$_3$ of compound 7.

**Figure S19** $^{13}$C NMR on CDCl$_3$ of compound 7.
Figure S20 $^1$H NMR on CDCl$_3$ of compound 10.

Figure S21 $^{13}$C NMR on CDCl$_3$ of compound 10.
Figure S22 $^1$H NMR on CDCl$_3$ of compound 11.

Figure S23 $^{13}$C NMR on CDCl$_3$ of compound 11.
Figure S24. $^1$H NMR on CDCl$_3$ of compound 12.

Figure S25. $^{13}$C NMR on CDCl$_3$ of compound 12.
**Figure S26.** $^1$H NMR on CDCl$_3$ of compound 13.

**Figure S27.** $^{13}$C NMR on CDCl$_3$ of compound 13.
Figure S28. $^1$H NMR on CDCl$_3$ of compound 14.

Figure S29. $^{13}$C NMR on CDCl$_3$ of compound 14.
S7. MS spectra

**Figure S30.** MS spectra of compound 3.

**Figure S31.** HRMS spectra for compound 4.
Figure S32. MS spectra for compound 5.

Figure S33. HRMS spectra for compound 6.

Figure S34. MS spectra for compound 7.
Figure S35. HRMS spectra for compound 10.

Figure S36. HRMS spectra for compound 11.

Figure S37. HRMS spectra for compound 12.
Figure S38. HRMS spectra for compound 13.

Figure S39. HRMS spectra for compound 14.
S8. References

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