Supporting Information

An Electron-Poor C₆₄ Nanographene by Palladium-Catalyzed Cascade C–C Bond Formation: One-Pot Synthesis and Single-Crystal Structure Analysis

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Supporting Information

Table of Contents

1. Materials and methods ...........................................................................................................................................S1
2. Synthesis and characterization of new compounds ..............................................................................................S2
3. UV/Vis and fluorescence spectra ..........................................................................................................................S4
4. Cyclic and square wave voltammetry ...................................................................................................................S5
5. DFT calculations .....................................................................................................................................................S6
6. X-Ray structure analysis .........................................................................................................................................S7
7. NMR spectra ..........................................................................................................................................................S9
8. MS spectra ..............................................................................................................................................................S11
9. Literature ...............................................................................................................................................................S12
1. Materials and methods

Chemicals, reagents and solvents were purchased from chemical suppliers. Column chromatography was performed on silica gel (particle size 0.040–0.063 mm) with freshly distilled solvents as eluents. All other commercially available reagents and solvents were of reagent grade and used without further purification. The solvents for the spectroscopic measurements were of spectroscopic grade. UV/Vis absorption spectra were recorded on a Perkin Elmer Lamda 35 spectrometer. Steady-state and time-dependent fluorescence spectra were recorded on a PTI QM4-2003 fluorescence spectrometer. The absolute fluorescence quantum yields were determined with an integrating sphere of Hamamatsu (A10094, C8849, C10027-01, E7536). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DMX 400 or a Bruker DMX 600 spectrometer. $^{13}$C NMR spectra were broad band proton decoupled. Chemical shifts ($\delta$) are listed in parts per million (ppm) and are reported relative to tetramethylsilane (TMS). Coupling constants ($J$) are quoted in Hertz (Hz). Spectra are referenced internally to residual proton solvent resonances or natural abundance carbon resonances. MALDI-TOF mass spectra were recorded on a Bruker Daltronik GmbH (Autoflex II) mass spectrometer. High resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument (Bruker Daltronik GmbH). For cyclic and square wave voltammetry, a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three-electrode single-compartment cell was used. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was recrystallized from ethanol/water. The measurements were carried out using ferrocene/ferrocenium (Fc/Fc$^+$) as an internal standard for the calibration of the potential. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively, and a Ag/AgCl reference electrode was used. Elemental analyses were performed with an Elementar vario micro cube instrument.
2. Synthesis and characterization of new compounds

2,6-diisopropylphenyl-substituted naphthalimide boronic acid pinacol ester (3)[51], tetra-substituted pyrene boronic acid pinacol esters (5)[52] and N-(2,6-diisopropylphenyl)-4,5-dibromo-1,8-naphthalimide (6)[53] were synthesized according to literature procedures.

**Compound 4**

[Bis(dibenzylideneacetone)palladium(0)] (85.0 mg, 0.15 mmol, 15 %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (120 mg, 0.29 mmol, 30 %) and Cs₂CO₃ (3.2 g, 9.8 mmol, 3.0 equiv.) were added to a suspension of 510 mg (0.98 mmol, 1.0 equiv.) 1,3,6,9-tetrabromopyrene 2 and 2.4 g (4.9 mmol, 5.0 equiv.) 2,6-diisopropylphenyl-substituted naphthalimide boronic acid pinacol ester 3 in a mixture of toluene (10 mL) and water (5 mL). After stirring at 80 °C for 23 h, the reaction mixture was cooled down to room temperature and extracted three times with each 30 mL of dichloromethane. The combined organic layers were washed with water, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (gradient of dichloromethane/acetone from 1:0 to 15:1) to yield 4 as a yellow solid.

Yield: 580 g (357 μmol, 37 %). Mp.: > 350 °C. ¹H NMR (TCE-D₂, 600 MHz, 70 °C): δ = 1.10–1.16 (m, 48H), 2.68–2.77 (m, 8H), 7.26–7.29 (m, 8H), 7.42 (t, J = 7.8 Hz, 4H), 7.63–7.68 (m, 4H), 7.77–7.80 (m, 4H), 7.94–8.07 (m, 8H), 8.22–8.25 (m, 2H), 8.62–8.64 (m, 4H), 8.74–8.77 (m, 4H) ppm. ¹³C NMR (TCE-D₂, 151 MHz, 70 °C): δ = 24.2, 24.3, 29.5, 120.6, 123.2, 123.6, 124.2, 125.6, 126.8, 127.7, 127.8, 129.4, 129.6, 129.9, 130.0, 130.1, 130.5, 131.2, 131.3, 131.9, 132.0, 132.8, 133.0, 134.9, 135.0, 144.9, 146.0, 164.0, 164.2 ppm. HRMS (ESI) calculated for C₁₁₂H₉₅N₄O₈: 1623.71444, found 1623.71493 [M+H]+. Elemental analysis: calculated for C₁₁₂H₉₅N₄O₈: C 82.83; H 5.83, N 3.45, found: C 82.55; H 5.93, N 3.43.

**Compound 1**

1,3,6,9-Tetra-substituted pyrene boronic acid pinacol ester 5 (137 mg, 194 μmol, 1.0 equiv.), N-(2,6-diisopropylphenyl)-4,5-dibromo-1,8-naphthalimide 6 (450 mg, 873 μmol, 4.5 equiv.), 223 mg (388 μmol, 2.0 equiv.) [Pd(dba)₂] and 318 mg (776 μmol, 4.0 equiv.) SPhos were dissolved in 24 mL degassed toluene. Subsequently, a solution of 379 mg (1.16 mmol, 6.0 equiv.) Cs₂CO₃ in 6 mL of water was added
to the reaction mixture and was heated to 90 °C for 5 days. After cooling down to room temperature, the solution was extracted three times with each 50 mL of dichloromethane after adding 15 mL of water and the combined organic layers were washed with water. The organic solution was dried over MgSO₄ and concentrated under vacuum. The crude product was purified by column chromatography (silica gel, gradient of DCM to DCM/1 % MeOH), followed by washing with toluene and MeOH and finally size exclusion chromatography on bio beads SX3 (DCM/MeOH 9:1). The isolated solid was washed with hexane and dried in vacuum to yield 1 as a dark purple solid.

Yield: 48 mg (29.6 μmol, 15 %). Mp.: > 350 °C. $^1$H NMR (CDCl₃, 600 MHz): δ = 1.34 (m, 48 H), 3.06 (m, 8 H), 7.50 (d, J = 8.2 Hz, 8 H), 7.64 (t, J = 8.2 Hz, 4 H), 9.71 (m, 4 H), 10.43 (m, 4 H), 11.19 (s, 4 H), 11.90 (s, 2 H) ppm. $^{13}$C NMR (CDCl₃, 151 MHz): δ = 24.4, 29.6, 120.1, 122.2, 123.4, 123.6, 124.5, 125.4, 127.1, 128.4, 128.5, 129.2, 129.3, 130.1, 130.4, 130.9, 135.0, 138.0, 146.0, 164.5 ppm. MS (MALDI, negative mode, DCTB in chloroform): calculated for C₁₁₂H₈₂N₄O₈: 1610.61, found 1610.68. HRMS (ESI, positive mode, acetonitrile/chloroform): calculated for C₁₁₂H₈₃N₄O₈: 1611.62054, found 1611.62137 [M + H]$^+$.

Elemental analysis: calculated for C₁₁₂H₈₂N₄O₈: C 83.46, H 5.13, N 3.48, found: C 83.26, H 5.69, N 3.93.
3. UV/Vis and fluorescence spectra

Figure S1: UV/Vis and steady state fluorescence spectra of 1 in CH$_2$Cl$_2$ at room temperature (left) and its time resolved fluorescence decay ($\lambda_{\text{ex}}$ = 572 nm, $\lambda_{\text{det}}$ = 608 nm).

Table S1. Summary of the optical properties of compounds 1.

| Compound | Abs: $\lambda_{\text{max}}$/ nm | $\varepsilon$/ M$^{-1}$cm$^{-1}$ | Fl: $\lambda_{\text{max}}$/ nm | $\Phi_{\text{fl}}$/ %$^b)$ | $\tau$/ ns |
|----------|-------------------------------|---------------------------------|--------------------------------|---------------------------|----------|
| 1        | 584, 489                      | 141200, 278300                  | 608                            | 67 $\pm$ 1                | 13.38 $\pm$ 1.17 |

$^a$ Spectra were measured in dichloromethane at room temperature. $^b$ Absolute fluorescence quantum yields were determined in an integrating sphere. The compound was excited at different wavelengths and the values with deviations were averaged over 5 different measurements.
4. Cyclic and square wave voltammetry

Figure S2: Cyclic voltammogram of 1 (dashed line represents the square wave voltammogram) in CH$_2$Cl$_2$ solutions (0.1 M TBAHFP), scan rate 100 mV/s.

Table S2. Redox potentials$^a$ and HOMO and LUMO levels$^b$ of compound 1.

| Comp. | $E_{\text{ox}}$ [M/M$^+$]/V | $E_{\text{red}}$ [M/M]/V | $E_{\text{red}}$ [M/M$^2$]/V | $E_{\text{red}}$ [M$^2$/M$^3$]/V | $E_{\text{red}}$ [M$^3$/M$^4$]/V | $E_{\text{HOMO}}$/eV$^b$ | $E_{\text{LUMO}}$/eV$^b$ |
|-------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 1     | 1.03                | -0.99               | -1.18               | -1.59               | -1.68               | -5.83               | -3.81               |

$^a$ Half-wave potentials were determined by cyclic or square wave voltammetry measured in DCM (0.1 M TBAHFP) vs. Fc/Fc$^+$. $^b$Calculated according to literature known procedure using the experimentally determined redox potentials ($E_{\text{LUMO}} = -[E (M/M^+) + 4.8 \text{ eV}]$ and $E_{\text{HOMO}} = -[E (M/M^+) + 4.8 \text{ eV}]$) and the energy level of Fe/Fe$^+$ with respect to the vacuum level (−4.8 eV).$^{[54]}$
5. DFT calculations

DFT calculations were performed using the Gaussian 09 program package\textsuperscript{[S5]} with B3-LYP\textsuperscript{[S6]} as functional and def2-SVP\textsuperscript{[S7]} as basis set. The structure was geometry optimized, followed by frequency calculations on the optimized structure, which confirmed the existence of a minimum.

Time-dependent (TD)-DFT calculations were carried out on the optimized structure using the same functional (B3-LYP) and basis set (def2-SVP) as for the geometry optimization. The UV/Vis spectra were simulated using the GaussView 5\textsuperscript{[S8]} visualization software package. A half-width of 0.15 eV was assumed for proper simulation.

Figure S3: Calculated UV/Vis spectra of 1 with the most prominent transitions and their transition dipole moments ($\mu_{eq}$) as well as oscillator strengths ($f$) obtained by TD-DFT calculations.
6. X-Ray structure analysis

Single-crystal X-ray diffraction data for 1 was collected at 100 K on a Bruker D8 Quest Kappa diffractometer with a Photon100 CMOS detector and multi-layered mirror monochromated CuKα radiation. The structure was solved using direct methods, expanded with Fourier techniques and refined with the Shelx software package.[59] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions.

Single crystals of 1 suitable for X-ray structural analysis were grown by slow diffusion of hexane into a solution of 1 in chloroform. The single crystals thus obtained were highly sensitive towards temperature. Therefore, the crystalline material was directly immersed (from the remaining solution) into a film of perfluoropolyether which was precooled to 200 K on a copper substrate. Subsequently, the investigated single crystal was transferred on a Teflon loop to a Bruker D8 Quest Kappa diffractometer continuously cooled by evaporated liquid nitrogen. The refinement showed at least 3 more disordered chloroform molecules which could not be modelled satisfactorily. Therefore, the SQUEEZE routine of PLATON was used to remove the respective electron density.[510] The remaining structure could be refined nicely.

**Crystal data for 1** (C_{112}H_{82}N_{4}O_{5} • 4 CHCl_{3}): \( M_r = 2089.28 \), \( 0.35 \times 0.22 \times 0.22 \) mm\(^3\), triclinic space group \( P\overline{1} \), \( a = 14.8784(4) \) Å, \( b = 15.1215(4) \) Å, \( \beta = 87.9040(10)° \), \( c = 16.8294(4) \) Å, \( \gamma = 62.1650(10)° \), \( V = 3214.70(15) \) Å\(^3\), \( Z = 1 \), \( \rho(calcd) = 1.079 \) g·cm\(^{-3}\), \( \mu = 2.753 \) mm\(^{-1}\), \( F_{(000)} = 1078 \), \( GooF(F) = 1.073 \), \( R_1 = 0.0702 \), \( wR^2 = 0.1825 \) for \( I > 2\sigma(I) \), \( R_1 = 0.0773 \), \( wR^2 = 0.1883 \) for all data, 12636 unique reflections \( [\theta \leq 72.319°] \) with a completeness of 99.8 % and 765 parameters, 13 restraints.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1452370 (1). This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.ac.uk/data.request/cif](http://www.ccdc.ac.uk/data.request/cif).
Figure S4: Molecular structure of 1 in the solid state. a) Top view on the aromatic π-surface. b) and c) packing arrangement of 1 in the solid state with included chloroform molecules (green) and solvent accessible voids (illustrated in dark yellow).
7. NMR spectra

**Figure S5:** $^1$H NMR spectrum of 4 in tetrachloroethane-D$_2$ (600 MHz, 343 K) with residual water peak at 1.46 ppm.

**Figure S6:** $^{13}$C NMR spectrum of 4 in tetrachloroethane-D$_2$ (151 MHz, 343 K).
Figure S7: $^1$H NMR spectrum of 1 in CDCl$_3$ (600 MHz, 298 K) with traces of toluene at 2.36 and 7.17 ppm.

Figure S8: $^{13}$C NMR spectrum of 1 in CDCl$_3$ (151 MHz, 298 K) with traces of toluene.
8. MS spectra

Figure S9: HRMS (ESI, pos. mode, acetonitrile/chloroform) spectrum of 4 [M+H]^+.

Figure S10: HRMS (ESI, pos. mode, acetonitrile/chloroform) spectrum of 1 [M+H]^+. 
9. Literature

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