Supporting Information

Nine-ring Fused Biscarbazoloanthracene Displaying A Solid State

Based Excimer Emission Suitable for OLED Application

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General Experimental

¹H and ¹³C NMRs were recorded on a Bruker AV-300 spectrometer at 300 and 75 MHz, or Bruker DPX400 at 400 and 100 MHz respectively. Chemical shifts are given in parts per million (ppm) and referenced to the NMR solvent residual peak. Infra-red spectra were run as neat films on a Thermo Nicolet 380 FT-IR spectrometer with a Smart Orbit Goldengate attachment. Samples were analysed using a solariX (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with Fourier Transform Ion Cyclotron Resonance (FT-ICR). Mass spectra were recorded using positive/negative ion atmospheric pressure photoionisation.



Scheme S1. Full synthetic route to 3

Synthesis of 3-bromocarbazole



Using modified procedure (*J. Mater. Chem.*, **2011**, *21*, 9139). In a 250 ml conical flask with a large stir bar was put carbazole (16.72 g, 0.1 mole) and mostly dissolved in N-methylpyrrolidone (70 ml) (or DMF or DMAc). The mixture was cooled below 5 °C with ice/cold water bath. Next solid N-bromosuccinimide (17.80 g, 0.1 mole) was added portion wise within 10-20 minutes with vigorous stirring so that temperature never exceeded 5 °C to avoid dibromination. After adding of all NBS no substrate could be detected (TLC-dichloromethane : hexane 1:1). After 15 minutes of stirring at RT the content of the flask was poured onto stirred water (400 ml) in a 600 ml beaker to yield copious amounts of white precipitate. The solids were filtered off on a wide Buchner funnel and washed water (3 x 100 ml) and dried in air to yield chalk white solid (24 g, 97%). The solid was crystallised from boiling chloroform:isopropanol 1:1 (v/v) (250 ml) with subsequent freezing of the brown solution at -25°C for 16-24h. White flakes and crystals with green tan were collected and washed with methanol (75 ml) (17.17 g, 69.8 %). By concentrating of mother liquor additional 2 g of product could be recovered.



Using modified procedure (*J. Org. Chem.* **2010**, *75*, 6771–6781). In a 100 ml conical flask with a large magnetic stir bar was put 3-bromocarbazole (8.12 g, 0.033 mole) and dimethylacetamide (50 ml) (or DMF or NMP). Next solid sodium *t*-butoxide (3.84 g, 0.04 mole) was introduced in one portion to form pale yellow solution with negligible exothermic effect. Next 2-ethyl-1-hexylbromide (7.15 g, 0.037 mole) was added neat portion wise in 2 minutes. After 5 minutes the mixture became turbid due to precipitation of sodium bromide and the mixture heated itself to 45 °C. The exothermic effect was unaided. TLC (hexane) indicated no change after 30 minutes and if the reaction was not complete at this moment the flask was heated on a hot plate at 50 °C for another 30 minutes. The mixture was diluted with hexane/ethyl acetate (150 ml) and was washed with water (3x150 ml) to remove NaBr and DMAc. The organic layer was dried with anhydrous magnesium sulphate and the solvents evaporated for 30 minutes at 60 °C. The oily yellow residue was passed through 10 cm silica plug (50 ml of silica used) using hexane as eluent. After evaporation of combined fractions (250 ml) of very viscous oil was obtained (7.33 g, 62 %). We did not observe significant difference when t-BuONa was replaced with t-BuOK.

Synthesis of 9-(2-ethylhexyl)-3-carbazoleboronic acid



Using modified procedure (J. Org. Chem. 2010, 75, 6771-6781). In a 100 ml 3-necked round bottom flask was put of 3-bromo-9-(2-ethylhexylcarbazole) (7.40 g, 20.65 mmole) and anhydrous THF (60 ml). Under argon, the colourless mixture was cooled to -70 °C with dry ice/acetone bath and stirred for 15 minutes. Next n-BuLi solution was added (2.5 M in hexanes, 12 ml, 30 mmole) at a rate so that the internal temperature did not exceed -65 °C (15-25 minutes, see note below). Then the mixture was stirred for 10-20 minutes at -70 °C to assure complete halogen lithium exchange. The green solution was then charged with neat triisopropoxyboron (4.50 ml, 4.15 g, 40 mmole) within 15 minutes so that the internal temperature does not exceed -65°C. After 30 min of stirring at -70 °C the colourless solution was brought to 0 °C within 1 hour. TLC (hexane : dichloromethane 1:1) analysis showed that small amount of organolithium compound hydrolysed. Next 2N HCl (30 ml) was added in one portion and stirred at RT for 10 minutes. Resulting pale green biphasic mixture was diluted with ethyl acetate (120 ml) and transferred to the separation funnel and washed with water (2 x 150 ml). The organic layer was dried with anhydrous MgSO₄ for 15 minutes and after removing of drying agent evaporated at 50°C. The resulting brown-yellow oil was quickly diluted with petroleum ether (75 ml) with swirling of the flask. After a few minutes white precipitate appeared and the flask was put in the fridge for several hours. Heavy white-gray precipitate was collected and washed with hexane (2x25 ml) and dried in air to yield very pure product (2.85 g, 43%). The filtrate was evaporated, rediluted with hexane (30 ml) and frozen for 24 h to give another 0.4g (6%) of slightly less pure boronic acid. Boronic acid is stable after storage at RT for minimum 15 months (light exclusion).

Note: In the scaled up experiments high exothermic effect must be taken into consideration. If the reaction mixture is allowed to heat above -65°C for too long the yield was only 33% and 9-(2-ethylhexyl)carbazole resulting from resulting from protonation of the organolithium intermediate was recovered with 27% yield.

¹**H-NMR** (400 MHz, CDCl₃, δ /ppm): 9.00 (s, 1H), 8.43 (d, J_{ortho} = 8 Hz, 1H), 8.37 (d, J_{ortho} = 8 Hz, 1H), 7.58 (t, J_{ortho} = 8 Hz, 1H), 7.51 (d, J_{ortho} = 8 Hz, 1H), 7.45 (d, J_{ortho} = 8 Hz, 1H), 7.41 (t, J_{ortho} = 8 Hz, 1H), 4.16-4.07 (m, J₁ = 4Hz, 2H), 2.15 (m, J_{ortho} = 8 Hz, 1H), 1.55-1.30 (m, 8H), 1.05-0.85 (6H, m).

¹³**C-NMR** (100 MHz, CDCl₃, δ/ppm): 143.7 (C), 141.1(C), 133.0 (CH), 128.5 (CH), 125.5 (CH), 123.2 (C), 122.6 (C), 120.6 (CH), 120.3 (broad, C-B), 119.2 (CH), 109.0 (CH), 108.4 (CH), 47.3 (CH₂), 39.3 (CH), 31.0 (CH₂), 28.8 (CH₂), 24.4 (CH₂), 23.0 (CH₂), 14.0 (CH₃), 10.9 (CH₃).

IR (neat) v_{max}/cm^{-1} : 3048 (w), 2957 (m), 2927 (m), 2858 (w), 1624 (w), 1593 (m), 1454 (m), 1428 (m), 1327 (vs), 1250 (s), 1205 (m), 1140 (m), 1056 (w), 1023 (w), 912 (w), 810 (w), 771 (w), 749 (s), 710 (s).

Synthesis of 1,4-dibromo-2,5-di(tetradec-1-yn-1-yl)benzene (1):



A 50 mL Schlenk flask equipped with a stirrer bar was charged with 1,4-dibromo-2,5-diiodobenzene (*J. Am. Chem. Soc.* **1997**, *119*, 4578-4593) (2.00 g, 4.10 mmol), $Pd(PPh_3)_2Cl_2$ (0.173 g, 0.246 mmol) and copper iodide (0.094 g, 0.494 mmol) and evacuated/refilled with argon three times. A degassed solution of 1-tetradecyne (2.02 mL, 8.21 mmol) in TEA/DMF (2:1, 20 mL) was added via needle, syringe and rubber 'subaseal'. The solution was stirred at rt for 3 days, diluted with saturated ammonium chloride (100 mL) and extracted with diethyl ether (4 x 30 mL). The organic layers were combined, washed (brine) and dried (MgSO₄) and the solvent evaporated to give an orange oil. The crude product was purified by column chromatography (hexane) to give a yellow solid (2.17 g, 85%). Compound may be stored for more than one year in large quantities.

¹**H-NMR** (400 MHz, CDCl₃, δ/ppm): 7.59 (2H, s), 2.46 (4H, t, J = 6.9 Hz), 1.67-1.59 (4H, m), 1.52-1.45 (4H, m), 1.31-1.27 (32H, m), 0.96 (6H, t, J = 6.7 Hz).

¹³C-NMR (100 MHz, CDCl₃, δ/ppm): 136.02 (2CH), 126.49 (2C), 123.47 (2C), 98.24 (2C), 78.30 (2C), 31.92 (2CH₂), 29.65 (4CH₂), 29.62 (2CH₂), 29.52 (2CH₂), 29.34 (2CH₂), 29.10 (2CH₂), 28.85 (2CH₂), 28.38 (2CH₂), 22.68 (2CH₂), 19.63 (2CH₂), 14.11 (2CH₃).

IR (neat) v_{max}/cm⁻¹: 2952 (m), 2916 (s), 2847 (s), 2224 (w), 1462 (s), 1086 (m), 889 (m), 724 (m).

HRMS (APPI): *m/z* calc. for C₃₄H₅₃Br₂ (M+H)⁺ 619.25085, found 619.25152.

UV (hexane, $\lambda / nm(\epsilon)$) 240 (75700), 286 (86700).

Melting point 56-57 °C.





In a 25 ml 3-necked round bottom flask was put 1,4-dibromo-2,5-di(1-tetradecyn-1yl)benzene (0.62 g, 1 mmole), 9-(2-ethylhexyl)carbazol-3-ylboronic acid (0.71 g, 2.2 mmole, 2.2 eq.), sodium carbonate (0.424 g, 4 mmole, minimum 4 eq. required, see note below) and then degassed THF (20 ml) and distilled water (5 ml). Everything was purged with argon at RT for 30 minutes. Next bis(triphenylphosphine)palladium dichloride (14 mg, 0.02 mmole) was added and the mixture refluxed for 6 hours. After 1 h (TLC-hexane) the mixture contained equal amounts of substrate, monocoupled product and dicoupled one. After another hour substrate was gone but monocoupled product dominated. Hence another 0.194 g of boronic acid was added (+0.6 eq.) and a few milligram of catalyst. After 2 hours the discoupled product was accompanied only by a small amount of monocoupled one and the reaction was carried for final two hours. The mixture was cooled and diluted with ethyl acetate : hexane 1:3 (v/v) (100 ml). The organic layer was washed with water (3 x 150 ml) and dried with anhydrous magnesium sulphate. After evaporation of the solvent at 50 °C the 1.5 g of the residue was rinsed with methanol (3 x 50 ml) by adding it to the flask and decanting. This operation removed most of the impurities (about 0.2 g). The unreacted boronic acid was removed by dissolving of the oil in hexane (40 ml) and filtering through silica plug (10 cm height, 50 ml of silica used, 1 inch wide column, hexane for filling) using 20:1 hexane : diethyl ether (v/v). The product eluted in 50 ml fraction. After drying at 50°C for 45 minutes, very viscous red oil was obtained which solidified within a few hours to a brown resin. (0.9 g, 88.5 %). No decomposition could be detected by NMR for a sample stored one year at RT.

Note: Reaction when sluggish should be accelerated by adding more equivalents of base or by using stronger base like K_3PO_4 . Too extended reaction times will lead to homocoupling of boronic acid (LRMS (APPI+) found 556.4, calc for $C_{40}H_{48}N_2$ 556.4)– a side product very difficult to separate from target compound.

¹**H-NMR** (300 MHz, CDCl₃, δ /ppm): 8.48 (d, J_{meta} = 1.5 Hz, 2H), 8.17 (d, J_{ortho} = 7.5 Hz, 2H), 7.83 (d, J_{ortho} = 8.4 Hz, J_{meta} = 1.8 Hz, 2H), 7.75 (s, 2H), 7.55-7.43 (m, 6H), 7.32-7.25 (m, 2H, overlaps with solvent), 4.28-4.22 (m, J = 7.2 Hz, 4H), 2.43 (t, J = 6.9 Hz, 4H), 2.22-2.12 (m, J = 6.9 Hz, 2H), 1.55-1.10 (m, 56H), 1.05-0.85 (m, 18H).

¹³C-NMR (75 MHz, CDCl₃, δ/ppm): 142.3 (C), 141.3 (C), 140.4 (C), 134.4 (CH), 130.6 (C), 127.2 (CH), 125.5 (CH), 123.1 (C), 122.6 (C), 121.8 (C), 121.1 (CH), 120.3 (CH), 118.8 (CH), 109.0 (CH), 108.3 (CH), 94.3 (acetylenic), 80.7 (acetylenic), 47.6 (N-CH₂), 39.5 (CH), 31.9 (CH₂), 31.1 (CH₂), 29.7 (3xCH₂), 29.5 (CH₂), 29.4 (CH₂), 29.1 (CH₂), 28.9 (CH₂), 28.8 (CH₂), 28.6 (CH₂), 24.4 (CH₂), 23.1 (CH₂), 22.7 (CH₂), 19.7 (CH₂), 14.1 (CH₃), 14.0 (CH₃), 10.9 (CH₃).

IR (neat, v_{max}/cm^{-1}): 3047 (w), 2956 (m), 2921 (s), 2851 (s), 2218 (w, acetylenic), 1627 (w), 1599 (w), 1461 (vs), 1378 (w), 1329 (m), 1216 (m), 1150 (m), 883 (m), 800 (s), 743 (s), 726 (s).

UV-vis (CHCl₃, nm): 286, 299 (shoulder), 342 (shoulder), 352 (shoulder).

LRMS (APPI⁺) M⁺ calc. for C₇₄H₁₀₀N₂ 1016.8, found. 1016.8

Synthesis of biscarbazoloanthracene (3)



In a 20 ml finger flask with argon inlet was put 1,4-bis[9-(2-ethylhexyl)carbazol-3-yl]-2,5-di(1-tetradecyn-1yl)benzene (0.20 g, 0.20 mmole), 1,8-diazabicyclo-7-undecene (0.1 g, 0.66 mmole) and N-methylpyrrolidone (5 ml) which were heated to reflux for 3 days under rigorous air exclusion. Next, the reaction mixture was cooled to RT. The mixture was diluted in chloroform (60 ml) and washed with water (2 x 150 ml). The organic layer was evaporated the residue was treated with slow addition of methanol. After cooling overnight in the refrigerator the precipitate was filtered off on a narrow Schott funnel and washed with methanol (3 x 10 ml) and dried in air. The amorphous solid was crystallised by suspending in ethanol (25 ml) and adding a few ml of ether to dissolve it. After slow evaporation in RT bright yellow fibre fluffy solids were collected on a small sinter funnel and washed with methanol (3 x 10 ml) and dried in air. (80 mg, 40%). Compound could be stored at RT with light exclusion for over 1 year without decomposition.

¹**H-NMR** (300 MHz, CDCl₃, δ /ppm): 9.12 (s, 2H), 9.00 (d, J_{ortho} = 9.0 Hz, 2H), 8.36 (d, J_{ortho} = 8.0 Hz, 2H), 8.14 (s, 2H), 7.78 (d, J_{ortho} = 9.0 Hz, 2H), 7.56 (br d, J_{ortho}=8 Hz, 2H), 7.51 (br t, J_{ortho}=7.5 Hz, 2H), 7.32 (br t, J_{ortho} = 7.5 Hz, 2H), 4.35 (d, J = 7.5 Hz, 4H), 3.67 (t, J = 7.5 Hz, 4H), 2.25-2.15 (m, J = 6.9 Hz, 2H), 1.80 - 1.68 (m, 4H), 1.55-1.10 (m, 52H), 1.00-0.80 (m, 18H).

¹³C-NMR (75 MHz, CDCl₃, δ/ppm): 141.0 (C), 140.5 (C), 137.0 (C), 129.8 (C), 128.5 (C), 128.4 (C), 127.8 (CH), 125.1 (CH), 124.8 (C), 124.2 (CH), 123.8 (C), 121.8 (CH), 120.5 (CH), 118.2 (CH), 117.2 (C), 109.2 (CH), 109.1 (CH), 47.5 (N-CH₂), 39.7 (CH), 35.5 (CH₂), 32.8 (CH₂), 31.9 (CH₂), 31.1 (CH₂), 29.7 (CH₂), 29.6 (2CH₂), 29.5 (2CH₂), 29.4 (CH₂), 29.3 (CH₂), 28.9 (CH₂), 24.5 (CH₂), 23.1 (CH₂), 22.7 (CH₂), 14.1 (CH₃), 14.0 (CH₃), 11.0 (CH₃).

IR (neat, v_{max}/cm^{-1}): 3047 (w), 2956 (m), 2920 (s), 2851 (m), 1613 (w), 1563 (m), 1498 (m), 1466 (w), 1423 (w), 1334 (w), 1314 (w), 1156 (m), 901 (m), 802 (m), 784 (s), 703 (s).

UV-vis (CHCl₃, nm): 259, 279, 320, 335, 350, 406, 437.

LRMS (APPI⁺) M⁺ calc. for C₇₄H₁₀₀N₂ 1016.8, found. 1016.8



Figure S1. ¹HNMR spectrum of crude **3** (300 MHz, CDCl₃,NS=16, d1=1s) . Diagnostic peaks ascribed to asymmetric isomer **3**' are marked with asterisks



Figure S2. ¹HNMR spectrum of 1 (300 MHz, CDCl₃,NS=16, d1=1s)



Figure S3. ¹³CNMR spectrum of 1 (saturated solution) (100 MHz, CDCl₃,NS=512, d1=2s)



Figure S4. DEPT135 NMR spectrum of 1 (saturated solution)(100 MHz, CDCl₃,NS=256, d1=2s)



Figure S5. ¹HNMR spectrum of 9-(2-ethylhexyl)-3-carbazoleboronic acid (400 MHz, CDCl₃,NS=16, d1=1s)



Figure S6. ¹³CNMR spectrum of 9-(2-ethylhexyl)-3-carbazoleboronic acid (100 MHz, CDCl₃,NS=512, d1=2s), C-B signal at 120.3 ppm



Figure S7. DEPT135 NMR spectrum of 9-(2-ethylhexyl)-3-carbazoleboronic acid (100 MHz, CDCl₃,NS=256, d1=2s)



Figure S8. ¹HNMR spectrum of 2 (400 MHz, CDCl₃,NS=16, d1=1s)



Figure S9. ¹³CNMR spectrum of 2 (100 MHz, CDCl₃,NS=512, d1=2s)



Figure S10. DEPT135 NMR spectrum of 2 (100 MHz, CDCl₃,NS=256, d1=2s)



Figure S11. ¹HNMR spectrum of 3 (300 MHz, CDCl₃,NS=16, d1=1s)



Figure S12. ¹HNMR spectrum of 3 (300 MHz, CDCl₃,NS=16, d1=1s) extended aromatic region



Figure S13. ¹³CNMR spectrum of 3 (75 MHz, CDCl₃,NS=512, d1=1s)



Figure S14. ¹³CNMR spectrum of 3 (75 MHz, CDCl₃,NS=512, d1=1s) extended aromatic region



Figure S15. DEPT135 NMR spectrum of 3 (75 MHz, CDCl₃,NS=256, d1=1s)







Figure S17. IR spectrum of 9-(2-ethylhexyl)-3-carbazoleboronic acid



Figure S18. IR spectrum of 2



Figure S19. IR spectrum of 3



Figure S20. TGA of 3.



Figure S21. DSC plot for **3** (second heating-cooling cycle). The first exothermic transition correspond to a crystallisation from the amorphous phase obtained during the cooling cycle under this conditions

Table S1. The bond lengths (Å) of the polyaromatic moiety of **3.** All the C–C and C–N bond lengths are almost the same for the "chair" and "boat" isomers (the deviations not exceed 0.001 Å).

Bond	Bond lengths						
a	1.399	g	1.367	m	1.403	S	1.405
b	1.430	h	1.459	n	1.456	t	1.390
c	1.402	i	1.418	0	1.424	u	1.403
d	1.428	j	1.436	р	1.391	v	1.391
e	1.459	k	1.377	q	1.392		
f	1.435	1	1.417	r	1.399		



Figure S22. The NICS(0) indexes for the "boat" and "chair" isomers of 3 molecule calculated by the B3LYP/6-311++G(d,p) method.



Figure S23. The HOMO and LUMO orbitals for the "boat-like" isomer



Figure S24. The shapes of the HOMO-1 and LUMO+2 of 3



Figure S25. Photoelectron emission spectra of the solid state films of 3



Figure S26. X-ray pattern for the thin film of 3.



Figure S24. AFM topographical images with normalized Z axis in nm of vacuum deposited films of **3** on quartz substrates: (a) as deposited and (b) aged for 10 months at room temperature. The images were acquired in air using contact mode.



Figure S27. Photography of the operating electroluminescent device of 3 (ITO/CuI/3/Bphen/Ca:Al with vacuum deposited 3)



Figure S28. EL spectrum (black line) of the spin coated electroluminescent device of **3** in configuration: ITO/PVK:PBD+5% **3** blend/LiF/Al and comparison to the PL spectrum of the blend (red line)



Figure S29. a) Current density-voltage (black line) and luminance-voltage (red line) characteristics b) Current efficiency – voltage characteristics of the electroluminescent device of 3 in configuration: ITO/PVK:PBD+5% **3** blend/LiF/Al