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Carbazole-linked porphyrin dimers for organic light emitting diodes: synthesis and initial photophysical studies

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ABSTRACT

Carbazole linked porphyrin dimers were synthesized in good yields via stepwise Suzuki coupling reactions using bromoporphyrins and borylated carbazoles as the precursors, the latter of which were synthesized via known procedures from biphenyl derivatives. For comparative purposes porphyrin–carbazole monomers were synthesized. Single layer organic light emitting diodes (OLEDs) were created to demonstrate the optical properties of these materials. Light emission from these carbazole substituted porphyrins showed better results compared to previously examined bromo substituted porphyrins with better electroluminescence and lower turn-on voltages. Dimers exhibited turn-on voltages of 3 V compared to 6 V for monomeric porphyrin–carbazoles.

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1. Introduction

The development of new and improved organic light emitting diodes (OLEDs) is currently a vibrant area of research, with constant need for enhanced devices for full color displays. Polymers of known chromophoric molecules, such as fluorenes, carbazoles, and oxadiazoles have proven to be extremely efficient as host matrices in OLED devices due to their high stability and as they are green and blue emitters.[1–5] For example, the polymeric carbazole, poly(*N*-vinylcarbazole) (PVK)[6] and polyfluorene (PFO),[7] have been shown to be highly efficient as a host material in OLEDs and are used in commercial devices. To fine-tune the color of the OLED, photoluminescent dyes can be doped into the host matrices producing devices.[8]

Porphyrins are highly chromophoric materials, emit light in the red region and have a narrow emission linewidth.[9] Thus, their incorporation into OLED host matrix materials is of interest for the development of improved displays. As a result, research into developing porphyrins for use in OLEDs is expanding.[10–14] Most previous studies on porphyrin-based OLED materials focused on substituted monomeric porphyrin dopants. For example, tetraphenylporphyrin (TPP)[15] and (2,3,7,8,12,13,17,18-octaethylporphyrinato) platinum(II) (PtOEP).[16] Whilst these studies are promising and show significant enhancement of devices, we wanted to open a different approach by constructing porphyrin dimers linked via a carbazole entity followed by the analysis of the properties of such arrays.

Published studies have incorporated chromophores, such as fluorenes and carbazoles into the porphyrin periphery.[17–19] Recently, it was shown that polymeric porphyrin–fluorene arrays exhibit a lower turn-on voltage in comparison to TPP doped into a PFO matrix.[20] As there is a limit to the scope of dopants into polymeric layers as the porphyrins self-aggregate, an approach of synthesizing polymeric-fluorene porphyrins units is attractive.[21] Our aim was to develop synthetic methods for the introduction of bulky substituents, namely carbazole units, to the porphyrin macrocycle. This should reduce self-aggregation and potentially give new materials suitable as substrates in OLEDs. In addition, we envisaged that the additional porphyrin unit, along with the conduction properties of the carbazole, would act to improve the light emitting properties of OLED devices. Furthermore, if these materials prove promising, there is scope to develop these arrays in a similar fashion to Fei et al.[20b] for enhanced optical properties. Here, we report the synthesis of such porphyrins materials using Suzuki type coupling reactions. Single layer organic light emitting diodes (OLEDs) were created to demonstrate the optical properties of these materials.

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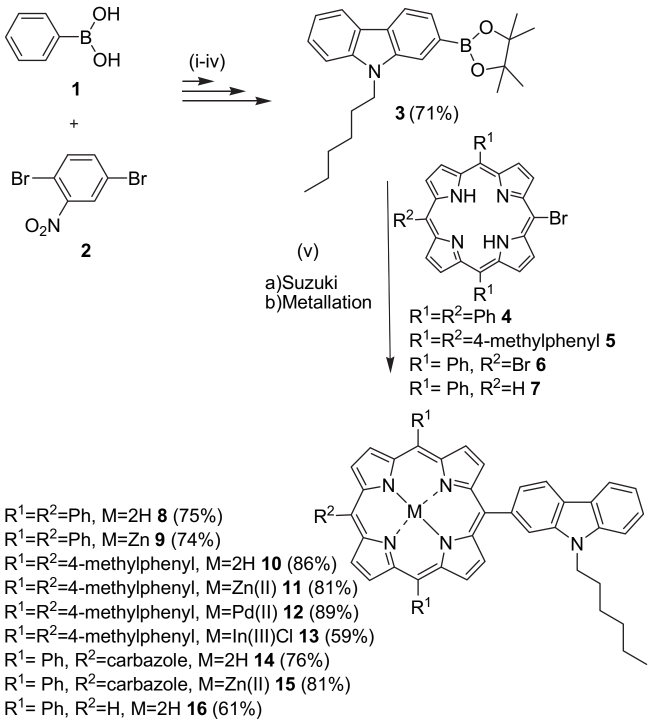
2. Results and discussion

2.1. Synthesis of porphyrin–carbazole units

Carbazole substituted porphyrin monomers and dimers were synthesized with the aim of enhancing the optical properties of the porphyrin. Based on the general applicability of Suzuki reactions in porphyrin chemistry[22] and our current developments thereof[23] we focused on the coupling of respective bromo and borylated building blocks.

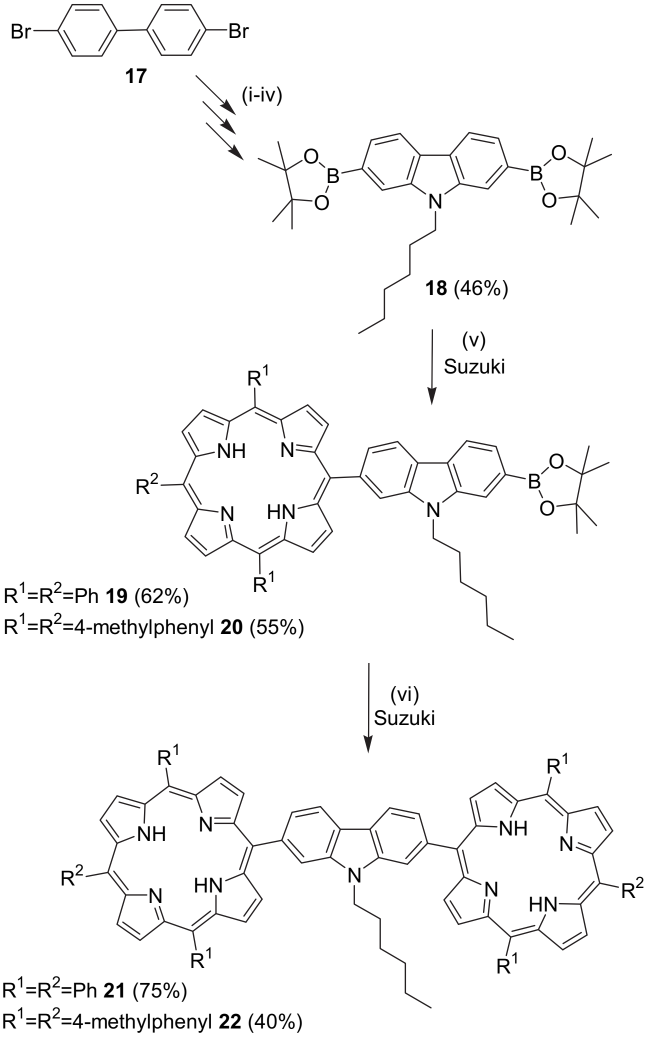
The initial step required generation of a borylated carbazole moiety. For the monomeric targets we chose the monoborylated carbazole **3**, which was synthesized via a procedure developed by Tavasli et al.[24] from 1,4-dibromo-3-nitro-phenyl **1** and phenyl boronic acid **2**, using Suzuki coupling conditions, to give a bromo nitro biphenyl (Scheme 1). Subsequent intramolecular cyclization using triethyl phosphite,[25] N-protection using a bromohexyl group and borylation using organolithium conditions yielded the borylated carbazole **3**. Suzuki coupling[22c] of **3** with either the monobrominated porphyrins **4**, **5**, and **7** or the dibrominated porphyrin **6** yielded the desired monomeric carbazole porphyrin compounds **8**, **10**, **14** and **16** in good coupling yields of 75–85%.



Scheme 1. Synthesis of carbazole porphyrin monomers. (i) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$, toluene, 90 °C, 6 h; (ii) P(EtO)$_3$, 160 °C, 18 h; (iii) a) ^{t}BuOK, DMF, rt, (b) bromohexane, 130 °C; (iv) (a) *n*-BuLi, THF, −78 °C (b) borolane, rt, 18 h; (v) (a) K$_3$PO$_4$, Pd(PPh$_3$)$_4$, THF, 80 °C, 18 h (b) Zinc: Zn(OAc)$_2$, CHCl$_3$, 70 °C; Palladium: Pd(OAc)$_2$, toluene, 110 °C; indium chloride: InCl$_3$, acetic acid, 110 °C.

Different metals were introduced to the porphyrin core, namely zinc,[26a] palladium[26b] and indium chloride[26c] to improve the optical properties via known procedures. This gave the metalated porphyrins **9**, **11**, **12**, **13** and **15** in moderate to good yields ranging from 59 to 89%.

Access to carbazole linked porphyrin dimers required the diborylated carbazole **18**. This was synthesized following a procedure by Tang et al.[27] from dibromo-biphenyl **17** as starting material (Scheme 2). Using a synthetic strategy similar to the one employed for **3**, intramolecular cyclization, N-protection and subsequent diborylation gave the desired diborylated carbazole **18** in a yield of 62%.



Scheme 2. Synthesis of carbazole linked porphyrin dimers. (i) HNO$_3$, AcOH, 110 °C. (ii) P(EtO)$_3$, 160 °C, 18 h (iii) bromohexane, K$_2$CO$_3$, DMF, 80 °C. (iv) (a) *n*-BuLi, THF, −78 °C (b) borolane, rt, 18 h (v) **4** or **5**, K$_3$PO$_4$, Pd(PPh$_3$)$_4$, THF, 80 °C, 18 h (vi) **4** or **5**, K$_3$PO$_4$, Pd(PPh$_3$)$_4$, THF, 80 °C, 18 h.

For the synthesis of carbazole linked porphyrin dimers a two-step approach was adopted. The first Suzuki coupling was carried out to attach the borylated carbazole **18** with the desired bromoporphyrin to form the porphyrin carbazoles **19** and **20** in yields of 62% and 55%, respectively. A second Suzuki coupling of **19** and **20** with the bromoporphyrins **4** or **5** yielded the desired dimers **21** and **22** in yields of 75% and 40%, respectively. We found this two-step Suzuki coupling approach to be more successful than a one-step approach where only trace amounts of dimer was formed, although Therien et al.[22c] reported good yields for this one-step method for other species. The main products from this approach were the deborylated porphyrin–carbazoles **8** and **10**.

2.2. Photophysical studies

Photophysical studies were carried out on all porphyrin–carbazole monomers and dimers and for comparative purposes on the bromoporphyrin precursors. The dimeric porphyrins **21** and **22** exhibit almost identical UV absorption and emission spectra with regard to their monomeric counterparts. Dimer **22** shows a slight red shift in the Soret and Q band absorptions of 6 and 9 nm, respectively, compared to that of the monomer **10**. Dimer **21** does not display any bathochromic shift. Both dimers exhibit deep-red emission at 659 and 719 nm for **21** and 682 and 722 nm for **22**.

This deep-red emission is similar to that of other porphyrins developed as OLEDs, e.g., porphyrin–fluorene derivatives.[21]

2.3. OLED studies

The dicarbazole porphyrins **14** and **15** show improved stability and performance when compared to porphyrins with only one carbazole attached (e.g., **8** and **9**). The OLED results for porphyrin **15** are shown in Fig. 1. The electroluminescence spectrum shows a red emission cantered at 656 nm at a current density of 1.3 mA mm^{-2}.

The current–voltage plot shows poor rectification but emission was achieved with a low turn-on voltage of 4 V. The chemical structure and a photo of a working device are also inset. Stable emission across the full active area is shown and an estimate of the quantum efficiency was calculated to be 0.02% for this single layer device.

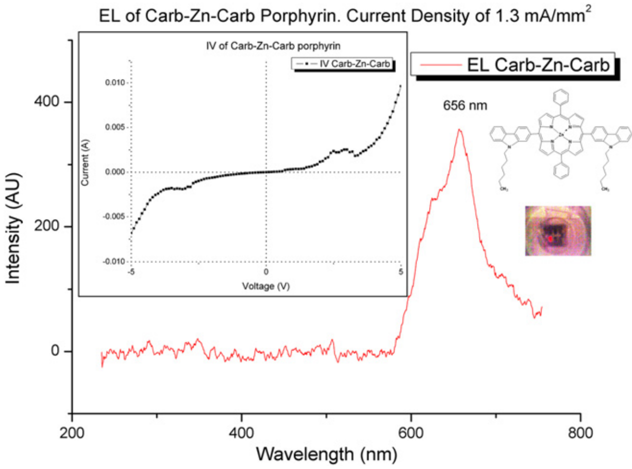


Fig. 1. Electroluminescence spectrum of **15** with current–voltage plot and working device photo (inset). Current density was 1.3 mA mm^{-2}.

The dimers **21** and **22** were also investigated for their optical properties. Fig. 2 shows the electroluminescence for dimer **22**, similar to that of **15**, with a red-emission cantered at 659 nm, blue-shifted from that of its monomer **10**, which emitted at 677 nm. Unfortunately, the dimers did not exhibit an increase in emission intensity in comparison to the monomers. This is most likely due to the aggregation quenching effect of the neighboring porphyrin unit. The current–voltage plot inset shows an ohmic dominated response with poor rectification but electroluminescence is observed at as low as 3 V with 1.6 mA mm^{-2}. Turn-on voltages for the metalated porphyrins **11**, **12** and **13** were 6 V, 3 V and 4 V, respectively, showing the effect of metal substitution. The free-base porphyrin **10** had a turn-on voltage of 6 V.

3. Conclusions

We have synthesized a range of porphyrin–carbazole derivatives, both monomeric and dimeric, and their metalated counterparts in good coupling yields via a novel synthetic strategy. These compounds all exhibit enhanced photoluminescence, with respect to the unsubstituted porphyrins. These carbazole porphyrins produced OLED devices emitting in the red, with greater emission intensity and stable emission than the bromo substituted porphyrin precursors. The dicarbazole porphyrin shows better results when compared to the single carbazole group demonstrating its enhancement of the emission. The dimer did not show significant enhancement of the emission when compared to the monomer as was thought. This may be due to an aggregation quenching effect from the close proximity of the second porphyrin unit, extra defect sites in the thin film or energy transfer away from the radiative paths. Despite this problem, the dimers exhibit low turn-on voltage and thus good potential for use in OLEDs. Further work on the development of polymeric porphyrin–carbazoles via a similar synthetic strategy should eliminate this aggregation defect and enhance the emissive properties.

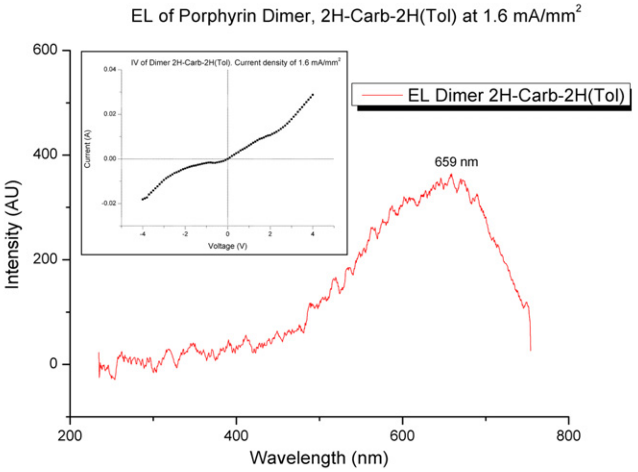


Fig. 2. Electroluminescence spectrum of **22** with current–voltage plot and working device photo (inset). Current density was 1.6 mA mm^{-2}.

4. Experimental section

4.1. General information

General experimental conditions for the synthesis and characterization of the compounds were as described before.[28] Infrared spectra were obtained using a Perkin–Elmer Spectrum One NTS FT-IR with a diamond ATR (Attenuated Total Reflectance) sampling accessory. Photophysical measurements were performed in THF, CH_2Cl_2 and toluene. Fluorescence spectra were recorded on Perkin–Elmer Precisely LS-55 spectrometer. UV–vis absorption measurements were performed with a Shimadzu MultiSpec-1501. Electrical characterization (current/voltage) was carried out using a Keithley 2400 source meter. Electroluminescence spectra were obtained using an Andor Solis intensified CCD camera coupled with an Oreil Spectrometer.

4.2. Syntheses

*4.2.1. 9-Hexylcarbazol-6-[4′,4′,5′,5′-tetramethyl(1′,3′,2′)dioxaborolan-2-yl] (**3**).* *n*-BuLi (2.5 M in hexanes, 1.9 mL, 4.6 mmol) was added drop-wise to a solution of 2-bromo-9-hexylcarbazole (1.3 g, 3.8 mmol) in dry THF (25 mL) at −78 °C over 0.5 h. The reaction was stirred at −78 °C for 2 h, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.5 mmol, 1.5 mL) was added and the reaction was allowed stir at rt for 18 h. The milky solution was then poured onto iced H_2O and extracted using diethylether. The organic layer was then washed with saturated NaCl and dried over Na_2SO_4. Solvents were removed in vacuo and the yellow oily residue was recrystallized from ethanol to give white crystals (1.01 g, 71%, 2.7 mmol). Mp=86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.92 (t, $^3J_{H-H}$=13.8 Hz, 3H, C*H*$_3$), 1.31–1.34 (m, 6H, C*H*$_2$), 1.45 (s, 12H, C*H*$_3$), 1.86–1.92 (m, 2H, C*H*$_2$), 4.37 (t, $^3J_{H-H}$=14.6 Hz, 2H, C*H*$_2$), 7.25 (t, $^3J_{H-H}$=14.5 Hz, 1H, carbazole–*H*), 7.45 (d, $^3J_{H-H}$=8.2 Hz, 1H, carbazole–*H*), 7.51 (t, $^3J_{H-H}$=15.1 Hz, 1H, carbazole–*H*), 7.72 (d, 1H, $^3J_{H-H}$=7.8 Hz, 1H, carbazole–*H*), 7.93 (s, 1H, carbazole–*H*), 8.13 (d, $^3J_{H-H}$=3.0 Hz, 1H, carbazole–*H*), 8.15 (d, $^3J_{H-H}$=3.0 Hz, 1H, carbazole−*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=13.6, 22.1, 24.5, 26.5, 28.6, 31.2, 42.5, 83.3, 108.4, 114.6, 118.2, 119.2, 120.1, 124.5, 125.7, 139.5, 140.5 ppm; FT-IR (ATR): ν=2961, 2928, 2859, 1624, 1560, 1497, 1477, 1436, 1363, 1334, 1270, 1255, 1236, 1141, 1081, 966, 927, 854, 748, 732, 687 cm^{-1}; HRMS (ESI$^+$) [$C_{24}H_{32}NO_2$+H]: calcd 378.2604, found 378.2606.

*4.2.2. 3-(5′,10′,15′-Triphenylporphyrin-20′-yl)-9-hexyl-carbazole (**8**).* Porphyrin **4** (50 mg, 0.08 mmol), borylated carbazole **3** (61 mg, 0.16 mmol), and K_3PO_4 (210 mg, 0.97 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (9 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents removed in vacuo, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O. Organic layers dried over $MgSO_4$ and solvents removed in vacuo. Residue subjected to column chromatography (CH_2Cl_2/hexane 1:1) to yield purple product **8** (49 mg, 75%, 0.06 mmol). Mp=201 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H =−2.68 (s, 2H, N*H*), 0.78 (t, $^3J_{H-H}$=14.0 Hz, 3H, CH_3), 0.88−0.93 (m, 2H, CH_2), 1.24−1.29 (m, 2H, CH_2), 1.41−1.46 (m, 2H, CH_2), 1.96−2.00 (m, 2H, CH_2), 4.45 (t, $^3J_{H-H}$=14.0 Hz, 2H, CH_2), 7.42 (t, $^3J_{H-H}$=14.6 Hz, 1H, carbazole−*H*), 7.59−7.63 (m, 2H, carbazole−*H*), 7.77−7.82 (m, 9H, Ph−*H*), 8.16 (d, $^3J_{H-H}$=9.4 Hz, 1H, carbazole−*H*), 8.26 (d, $^3J_{H--H}$=15.2 Hz, 6H, Ph−*H*), 8.38 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole−*H*), 8.44 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole−*H*), 8.86−8.88 (m, 6H, β-*H*), 8.93 (d, $^3J_{H-H}$=4.7 Hz, 2H, β-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=13.9, 22.5, 26.9, 29.1, 31.5, 43.3, 109.1, 115.7, 117.9, 119.2, 120.1, 127.7, 131.2, 134.5, 139.3, 139.7, 141.2, 142.2 ppm; FT-IR (ATR): ν=3314, 3055, 2910, 2873, 1590, 1487, 1440, 1354, 1176, 1070, 1005, 776, 747, 700, 669 cm^{-1}; UV−vis (CH_2Cl_2): λ_{max} (log ε)= 422 (5,40), 517 (4.43), 522 (4.31) 591 (4.28), 646 nm (4.23); HRMS (MALDI LD$^+$) [$C_{56}H_{45}N_5$]: calcd 787.3675, found 787.3652.

*4.2.3. 3-(5′,10′,15′-Triphenylporphyrinato(zinc)(II)-20′-yl)-9-hexyl-carbazole (**9**).* Porphyrin **8** (27 mg, 0.03 mmol) was dissolved in $CHCl_3$ (10 mL) and heated to 70 °C. $Zn(OAc)_2$ (26 mg, 0.34 mmol) in MeOH (0.5 mL) was added and the reaction stirred for 30 min. Solvents removed and the residue redissolved in CH_2Cl_2 and filtered through a plug of silica. Solvents removed in vacuo to yield a bright purple solid **10** (24 mg, 74%, 0.03 mmol). Mp=182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.80 (t, $^3J_{H-H}$=14.0 Hz, 3H, CH_3), 1.25−1.30 (m, 4H, CH_2), 1.40−1.47 (m, 2H, CH_2), 1.94−2.00 (m, 2H, CH_2), 4.44 (t, $^3J_{H-H}$=14.6 Hz, 2H, CH_2), 7.40 (t, $^3J_{H-H}$=12.8 Hz, 1H, carbazole−*H*), 7.57−7.63 (m, 2H, carbazole−*H*), 7.76−7.83 (m, 9H, Ph−*H*), 8.18 (d, $^3J_{H-H}$=6.4 Hz, 1H, carbazole−*H*), 8.27−8.31 (m, 6H, Ph−*H*), 8.37 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole−*H*), 8.45 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole−*H*), 8.95−9.00 (m, 6H, β-*H*), 9.06 (d, $^3J_{H-H}$=4.7 Hz, 2H, β-*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=13.9, 22.6, 27.1, 29.2, 31.6, 43.3, 109.1, 115.6, 117.9, 119.2, 120.7, 121.1, 121.2, 122.1, 122.9, 125.9, 126.5, 126.6, 127.5, 131.9, 132.3, 134.4, 139.2, 140.3, 141.2, 142.8, 150.2, 150.6 ppm; FT-IR (ATR): ν=3052, 2926, 2870, 1596, 1486, 1438, 1326, 1239, 1174, 1067, 1001, 767, 727, 699, 665 cm^{-1}; UV−vis (CH_2Cl_2): λ_{max} (log ε)=423 (5.42), 549 (4.45), 587 nm (4.28); HRMS (MALDI LD$^+$) [$C_{56}H_{43}N_5Zn$]: calcd 849.2810, found 849.2801.

*4.2.4. 3-(5,10,15-Tris(4-methylphenyl)porphyrin-20-yl)-9-hexyl-carbazole (**10**).* Porphyrin **5** (50 mg, 0.08 mmol), borylated carbazole **3** (60 mg, 0.16 mmol), and K_3PO_4 (194 mg, 0.91 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (9 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents removed in vacuo, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O. Organic layers dried over $MgSO_4$ and solvents removed in vacuo. Residue subjected to column chromatography (CH_2Cl_2/hexane 1:1) to yield purple product **10** (54 mg, 86%, 0.07 mmol). Mp=184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=−2.66 (s, 2H, N*H*), 0.76 (t, $^3J_{H-H}$=12.9 Hz, 3H, CH_3), 0.87−0.92 (m, 2H, CH_2), 1.23−1.27 (m, 2H, CH_2), 1.39−1.43 (m, 2H, CH_2), 1.92−1.99 (m, 2H, CH_2), 2.73 (s, 6H, tolyl−CH_3), 2.75 (s, 3H, tolyl−CH_3), 4.44 (t, $^3J_{H-H}$=14.0 Hz, 2H, CH_2), 7.43 (t, $^3J_{H-H}$=14.0 Hz, 1H, carbazole−*H*), 7.57−7.61 (m, 6H, tolyl−*H*), 7.60−7.62 (m, 2H, carbazole−*H*), 8.14 (d, $^3J_{H-H}$=7.0 Hz, 6H, tolyl−*H*), 8.29 (s, 1H, carbazole−*H*), 8.38 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole−*H*), 8.44 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole−*H*), 8.88−8.92 (m, 8H, β-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=11.0, 13.9, 14.1, 21.6, 22.6, 29.1, 30.4, 38.7, 43.3, 68.2, 109.1, 115.8, 117.9, 119.2, 125.9, 127.4, 128.8, 130.9, 134.5, 137.3, 139.3, 139.4 ppm; FT-IR (ATR): ν=3319, 2924, 2856, 1723, 1458, 1325, 1271, 1121, 1071, 971, 793, 725 cm^{-1}; UV−vis (CH_2Cl_2): λ_{max} (log ε)=423 (5.50), 518 (4.61), 554 (4.50), 591 (4.41), 650 nm (4.39); HRMS (MALDI LD$^+$) [$C_{59}H_{51}N_5$]: calcd 828.4144, found 829.4121.

*4.2.5. 3-(5,10,15-Tris(4-methylphenyl)porphyrinato(zinc)(II)-20-yl)-9-hexyl-carbazole (**11**).* Porphyrin **10** (50 mg, 0.06 mmol) was dissolved in $CHCl_3$ (10 mL) and heated to 70 °C. $Zn(OAc)_2$ (54 mg, 0.30 mmol) in MeOH (0.5 mL) was added and the reaction stirred for 30 min. Solvents removed and the residue redissolved in CH_2Cl_2 and filtered through a plug of silica. Solvents removed in vacuo to yield a bright purple solid **11** (43 mg, 81%, 0.05 mmol). Mp=144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.78 (t, $^3J_{H-H}$=9.3 Hz, 3H, CH_3), 0.87−0.92 (m, 4H, CH_2), 1.29−1.33 (m, 2H, CH_2), 1.96−1.99 (m, 2H, CH_2), 2.74 (s, 6H, tolyl−CH_3), 2.75 (s, 3H, tolyl−CH_3), 4.44 (t, $^3J_{H-H}$=6.0 Hz, 2H, CH_2), 7.41 (t, $^3J_{H-H}$=9.3 Hz, 1H, carbazole−*H*), 7.57−7.62 (m, 6H, Ph−*H*), 7.60 (m, 2H, carbazole−*H*), 8.14−8.17 (m, 6H, Ph−*H*), 8.29 (s, 2H, carbazole−*H*), 8.38 (d, $^3J_{H-H}$=4.9 Hz, 1H, carbazole−*H*), 8.44 (d, $^3J_{H-H}$=4.9 Hz, 1H, carbazole−*H*), 8.98−9.01 (m, 8H, β-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=13.9, 21.5, 21.9, 22.7, 27.1, 31.6, 53.4, 77.2, 109.0, 115.6, 117.8, 119.2, 120.6, 125.9, 127.3, 127.4, 131.9, 132.1, 134.3, 134.4, 134.5, 147.9 ppm; FT-IR (ATR): ν=2921, 1598, 1492, 1437, 1324, 1180, 1068, 998, 850, 794, 743, 720 cm^{-1}; UV−vis (CH_2Cl_2): λ_{max} (log ε)=422 (5.52), 547 (4.63), 588 nm (4.40); HRMS (MALDI LD$^+$) [$C_{59}H_{49}N_5Zn$]: calcd 891.3279, found 891.3237.

*4.2.6. 3-(5,10,15-Tris(4-methylphenyl)porphyrinato(palladium)(II)-20-yl)-9-hexyl-carbazole (**12**).* Porphyrin **10** (30 mg, 0.04 mmol), $Pd(OAc)_2$ (24 mg, 0.11 mmol), and toluene (20 mL) were placed in a two-necked round bottomed flask and heated to 110 °C. Upon reaction completion, the solvent was removed in vacuo and the residue was redissolved in CH_2Cl_2. The crude product was filtered through a plug of silica, solvents were removed in vacuo to yield a red colored solid **12** (30 mg, 89%, 0.03 mmol). Mp=130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.79 (t, $^3J_{H-H}$=13.4 Hz, 3H, CH_3), 1.25−1.31 (m, 2H, CH_2), 1.59−1.64 (m, 2H, CH_2), 1.93−1.99 (m, 2H, CH_2), 2.71(s, 6H, tolyl−CH_3), 2.73 (s, 3H, tolyl−CH_3), 4.42 (t, $^3J_{H-H}$=14.2 Hz, 2H, CH_2), 7.39−7.42 (m, 1H, carbazole−*H*), 7.48 (d, $^3J_{H-H}$=5.9 Hz, 1H, carbazole−*H*), 7.56−7.61 (m, 6H, tolyl−*H*), 8.08 (d, $^3J_{H-H}$=7.8 Hz, 6H, tolyl−*H*), 8.24 (s, 1H, carbazole−*H*), 8.37 (d, $^3J_{H-H}$=7.8 Hz, 1H, carbazole−*H*), 8.43 (d, $^3J_{H-H}$=7.8 Hz, 1H, carbazole−*H*), 8.84−8.89 (m, 8H, β-*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=13.9, 21.6, 22.6, 24.9, 27.1, 29.1, 29.6, 31.6, 34.2, 43.3, 66.7, 109.1, 115.3, 118.1, 119.2, 120.6, 121.8, 122.2, 122.5, 125.9, 126.1, 127.4, 128.2, 128.6, 129.7, 130.9, 131.1, 134.1, 137.4, 138.9, 139.3, 139.4, 141.2, 141.7, 141.9 ppm;; FT-IR (ATR): ν=2933, 1580, 1490, 1422, 1313, 1188, 1072, 1001, 844, 774, 735 cm^{-1}; UV−vis (CH_2Cl_2): λ_{max} (log ε)=421 (4.42), 526 nm (3.53); HRMS (MALDI LD$^+$) [$C_{59}H_{49}N_5Pd$]: calcd 933.3023, found 933.3058.

*4.2.7. 3-[Chloro{5,10,15-tris(4-methylphenyl)porphyrinato}indium(III)-20-yl]-9-hexyl-carbazole (**13**).* Porphyrin **10** (33 mg, 0.04 mmol), $InCl_3$ (88 mg, 0.40 mmol), CH_3COONa (298 mg, 4.25 mmol), and glacial acetic acid (15 mL) were placed in a round bottomed flask and heated to 110 °C and left stir for 18 h. Upon reaction completion, the solvent was removed in vacuo and the residue was redissolved in CH_2Cl_2. The crude product was extracted from saturated $NaHCO_3$, organic phases washed with brine and dried over $MgSO_4$. Solvents were removed in vacuo to yield a purple-green colored solid **13** (23 mg, 59%, 0.02 mmol). Mp=141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=0.83 (t, $^3J_{H-H}$=12.9 Hz, 3H, CH_3), 0.89–0.93 (m, 2H, CH_2), 1.24–1.31 (m, 4H, CH_2), 1.43–1.48 (m, 2H, CH_2), 1.97–2.01 (m, 2H, CH_2), 2.74 (s, 6H, tolyl–CH_3), 2.75 (s, 3H, tolyl–CH_3), 4.47 (t, $^3J_{H-H}$=13.8 Hz, 2H, CH_2), 7.42 (t, $^3J_{H-H}$=14.0 Hz, 1H, carbazole–*H*), 7.54–7.59 (m, 4H, tolyl–*H*), 7.63–7.65 (m, 2H, carbazole–*H*), 8.04 (d, $^3J_{H-H}$=7.6 Hz, 4H, tolyl–*H*), 8.28 (d, $^3J_{H-H}$=7.6 Hz, 4H, tolyl–*H*), 8.38 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole–*H*), 8.44 (s, 2H, carbazole–*H*), 8.50 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole–*H*), 9.11–9.17 (m, 8H, β-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=13.8, 21.4, 22.4, 24.8, 26.9, 28.9, 31.4, 43.4, 109.0, 115.3, 116.4, 117.9, 118.0, 119.2, 120.5, 121.7, 122.3, 126.2, 127.4, 127.5, 132.5, 134.1, 134.8, 137.6, 138.8, 139.1, 141.2, 149.5, 149.7 ppm;; FT-IR (ATR): ν=3021, 2922, 2854, 1736, 1598, 1477, 1325, 1260, 1181, 1069, 1008, 796, 745, 722 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=431 (5.45), 562 (4.47), 603 nm (4.32); HRMS (MALDI LD$^+$) [$C_{59}H_{49}N_5InCl$]: calcd 977.2671, found 977.2705.

*4.2.8. Bis(3,3′-{5′,15′-diphenyl)porphyrin-10′,20′-yl}-9-hexyl-carbazole (**14**).* Porphyrin **6** (50 mg, 0.08 mmol), borylated carbazole 3 (303 mg, 0.81 mmol), and K_3PO_4 (345 mg, 1.62 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (9.4 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents removed in vacuo, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine, and H_2O. Organic layers dried over $MgSO_4$ and solvents removed in vacuo. Crude product redissolved and filtered through a plug of silica gel using CH_2Cl_2 as eluent. Solvent removed and purple solid recrystallized from CH_2Cl_2/MeOH to yield purple crystals **14** (58 mg, 76%, 0.06 mmol). Mp=283 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ_H=−2.61 (s, 2H, N*H*), 0.79 (t, $^3J_{H-H}$=13.4 Hz, 6H, CH_3), 0.89–0.92 (m, 4H, CH_2), 1.25–1.29 (m, 4H, CH_2), 1.97–2.02 (m, 4H, CH_2), 4.46 (t, $^3J_{H-H}$=14.0 Hz, 4H, CH_2), 7.41–7.45 (m, 2H, carbazole–*H*), 7.59–7.64 (m, 4H, carbazole–*H*), 7.77–7.81 (m, 6H, Ph–*H*), 8.18 (d, $^3J_{H-H}$=7.6 Hz, 2H, carbazole–*H*), 8.26 (d, $^3J_{H--H}$=7.6 Hz, 4H, Ph–*H*), 8.30 (d, $^3J_{H-H}$=1.8 Hz, 2H, carbazole–*H*), 8.39 (d, $^3J_{H-H}$=7.6 Hz, 2H, carbazole–*H*), 8.45 (d, $^3J_{H-H}$=8.2 Hz, 2H, carbazole–*H*), 8.87 (d, $^3J_{H-H}$=4.7 Hz, 4H, β-*H*), 8.94 (d, $^3J_{H-H}$=4.7 Hz, 4H, β-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=13.8, 22.4, 24.8, 26.9, 28.9, 31.4, 4.2, 108.9, 115.6, 117.8, 119.1, 120.0, 120.5, 120.9, 122.1, 122.7, 125.8, 126.5, 127.5, 134.4, 139.2, 139.6, 141.1, 142.1 ppm; FT-IR (ATR): ν=3313, 2925, 1598, 1456, 1438, 1324, 1240, 1175, 1000, 970, 927, 798, 724, 700, 687, 663 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=426 (5.49), 518 (4.47), 554 (4.36), 592 (4.30), 648 nm (4.29); HRMS (MALDI LD$^+$) [$C_{68}H_{60}N_6$]: calcd 960.4879, found 960.4841.

*4.2.9. Bis(3,3′-{5′,15′-diphenyl)porphyrinato(zinc)II-10′,20′-yl}-9-hexyl-carbazole (**15**).* Porphyrin **14** (50 mg, 0.05 mmol) was dissolved in $CHCl_3$ (10 mL) and heated to 70 °C. $Zn(OAc)_2$ (56 mg, 0.26 mmol) in MeOH (0.5 mL) was added and the reaction stirred for 30 min. Solvents removed and the residue redissolved in CH_2Cl_2 and filtered through a plug of silica. Solvents removed in vacuo to yield a bright purple solid **15** (42 mg, 81%, 0.04 mmol). Mp=251 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ_H=0.79 (t, $^3J_{H-H}$=13.2 Hz, 3H, CH_3), 1.25–1.28 (m, 8H, CH_2), 1.41–1.45 (m, 4H, CH_2), 1.96–2.00 (m, 4H, CH_2), 4.45 (t, $^3J_{H-H}$=13.9 Hz, 2H, CH_2), 7.41 (t, $^3J_{H-H}$=13.9 Hz, 2H, carbazole–*H*), 7.59–7.64 (m, 4H, carbazole–*H*), 7.76–7.79 (m, 6H, Ph–*H*), 8.18 (d, $^3J_{H-H}$=7.3 Hz, 2H, carbazole–*H*), 8.27 (d, $^3J_{H-H}$=6.6 Hz, 4H, Ph–*H*), 8.31 (s, 2H, carbazole–*H*), 8.38 (d, $^3J_{H-H}$=7.4 Hz, 2H, carbazole–*H*), 8.45 (d, $^3J_{H-H}$=8.1 Hz, 2H, carbazole–*H*), 8.97 (d, $^3J_{H-H}$=4.4 Hz, 4H, β-*H*), 9.04 (d, $^3J_{H-H}$=4.4 Hz, 4H, β-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=13.8, 22.4, 26.9, 28.9, 31.4, 43.2, 108.9, 115.5, 117.7, 119.0, 120.5, 121.9, 122.8, 125.7, 126.4, 126.5, 127.4, 131.8, 132.1, 134.2, 139.1, 140.2, 141.1, 142.7, 150.1, 150.5 ppm; FT-IR (ATR): ν=2923, 1598, 1450, 1436, 1324, 1179, 1005, 970, 828, 744, 723 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=424 (5.52), 548 (4.51), 590 nm (4.38); HRMS (MALDI LD$^+$) [$C_{68}H_{58}N_6Zn$]: calcd 1022.4061, found 1022.4014.

*4.2.10. 3-(5′,15′-Diphenylporphyrin-10′-yl)-9-hexyl-carbazole (**16**).* Porphyrin **7** (50 mg, 0.09 mmol), borylated carbazole 3 (35 mg, 0.09 mmol), and K_3PO_4 (197 mg, 0.92 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (10.7 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents removed in vacuo, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine, and H_2O. Organic layers dried over $MgSO_4$ and solvents removed in vacuo. Residue subjected to column chromatography (CH_2Cl_2/hexane 1:1) and product recrystallized from CH_2Cl_2/MeOH to give purple crystals **16** (38 mg, 61%, 0.05 mmol). Mp=182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=−2.91 (s, 2H, N*H*), 0.77 (t, $^3J_{H-H}$=13.4 Hz, 3H, CH_3), 1.22–1.26 (m, 4H, CH_2), 1.39–1.45 (m, 2H, CH_2), 1.93–2.00 (m, 2H, CH_2), 4.43 (t, $^3J_{H-H}$=14.0 Hz, 2H, CH_2), 7.42 (t, $^3J_{H-H}$=12.8 Hz, 1H, carbazole–*H*), 7.58–7.65 (m, 2H, carbazole–*H*), 7.78–7.81 (m, 6H, Ph–*H*), 8.16 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole–*H*), 8.26–8.29 (m, 4H, Ph–*H*), 8.38 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole–*H*), 8.44 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole–*H*), 8.91 (d, $^3J_{H-H}$=4.6 Hz, 2H, β-*H*), 8.95 (d, $^3J_{H-H}$=4.6 Hz, 2H, β-*H*), 9.06 (d, $^3J_{H-H}$=4.6 Hz, 2H, β-*H*), 9.38 (d, $^3J_{H-H}$=4.7 Hz, 4H, β-*H*) 10.27 (s, 1H, *meso-H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=13.9, 22.5, 27.1, 29.1, 31.5, 43.3, 109.1, 115.8, 117.9, 119.2, 119.7, 120.7, 121.6, 122.2, 122.8, 125.9, 126.7, 126.8, 126.9, 127.7, 130.7, 131.3, 131.4, 131.8, 134.6, 134.7, 136.6, 139.2, 140.1, 141.2, 141.8, 147.5 ppm; FT-IR (ATR): ν=3307, 2925, 2825, 1596, 1456, 1404, 1324, 1001, 969, 932, 845, 796, 723, 699, 656 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=424 (5.43), 518 (4.48), 524 (4.33) 590 (4.30), 647 nm (4.26); HRMS (MALDI LD$^+$) [$C_{50}H_{41}N_5$]: calcd 711.3362, found 711.3362.

*4.2.11. 3-(5′,10′,15′-Triphenylporphyrin-20-yl)-6-[4′,4′,5′,5′-tetramethyl(1′,3′,2′)dioxaborolan-2′-yl]-9-hexyl-carbazole (**19**).* Porphyrin **4** (50 mg, 0.08 mmol), borylated carbazole **18** (90 mg, 0.18 mmol), and K_3PO_4 (343 mg, 1.62 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (9.4 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents removed in vacuo, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine, and H_2O. Organic layers dried over $MgSO_4$ and solvents removed in vacuo. Residue subjected to column chromatography (CH_2Cl_2/hexane 1:1) to yield purple product, which was recrystallized from CH_2Cl_2/MeOH to give purple crystals **19** (46 mg, 62%, 0.05 mmol). Mp=231 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ_H=−2.65 (s, 2H, N*H*), 0.78 (t, $^3J_{H-H}$=13.6 Hz, 3H, CH_3), 0.88–0.92 (m, 2H, CH_2), 1.23–1.28 (m, 2H, CH_2), 1.56 (s, 12H, CH_3), 1.97–2.02 (m, 4H, CH_2), 4.47–4.50 (m, 2H, CH_2), 7.63 (d, $^3J_{H-H}$=8.3 Hz, 1H, carbazole–*H*), 7.76–7.80 (m, 9H, Ph–*H*), 7.87 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole–*H*), 8.16 (d, $^3J_{H-H}$=7.9 Hz, 2H, carbazole–*H*), 8.26 (d, $^3J_{H-H}$=7.6 Hz, 6H, Ph–*H*), 8.38 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole–*H*), 8.45 (d, $^3J_{H-H}$=7.6 Hz, 1H, carbazole–*H*), 8.86–8.88 (m, 6H, β-*H*), 8.93 (d, $^3J_{H-H}$=3.8 Hz, 2H, β-*H*) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=13.9, 22.4, 24.8, 26.8, 29.0, 31.4, 43.1, 83.7, 107.7, 114.9, 115.3, 115.8, 118.3, 118.9, 119.5, 120.0, 120.9, 121.7, 121.8, 125.0, 125.3, 126.5, 127.5, 131.1, 134.4, 139.7, 140.1, 140.6, 140.7, 142.1 ppm; FT-IR (ATR): ν=3311, 3053, 2927, 2855, 1624, 1597, 1560, 1430, 1332, 1243, 1143, 1078, 964, 797, 727, 699, 686 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=422 (5.13), 515 (4.22), 552 (4.17), 592 (4.15), 655 nm (4.09); HRMS (MALDI LD$^+$) [$C_{62}H_{57}N_5O_2B$+H]: calcd 914.4605, found 914.4604.

*4.2.12. 3-(5′,10′,15′-Tris(4-methylphenyl)-20′-yl)-6-[4′,4′,5′,5′-tetramethyl(1′,3′,2′)dioxaborolan-2′-yl]-9-hexyl-carbazole (**20**).* Porphyrin **5** (50 mg, 0.08 mmol), borylated carbazole **18** (190 mg, 0.38 mmol), and K_3PO_4 (322 mg, 1.52 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (8.8 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents removed in vacuo, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O. Organic layers dried over $MgSO_4$ and solvents removed in vacuo. Residue filtered through a plug of silica using CH_2Cl_2/hexane (1:1) and CH_2Cl_2 as eluent to give three fractions. Solvents removed to yield purple product 20 (40 mg, 55%, 0.04 mmol). Mp=220 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=−2.67 (s, 2H, N*H*), 0.78 (t, $^3J_{H-H}$=14.2 Hz, 3H, C*H*$_3$), 0.87–0.92 (m, 2H, C*H*$_2$), 1.25–1.30 (m, 4H, C*H*$_2$), 1.49 (s, 12H, C*H*$_3$), 1.96–2.02 (m, 2H, C*H*$_2$), 2.73 (s, 6H, tolyl–C*H*$_3$), 2.75 (s, 3H, tolyl–C*H*$_3$), 4.49 (t, $^3J_{H-H}$=14.2 Hz, 2H, C*H*$_2$), 7.56–7.60 (m, 6H, tolyl–*H*), 7.87 (d, $^3J_{H-H}$=7.8 Hz, 1H, carbazole–*H*), 8.07 (s, 1H, carbazole–*H*), 8.14 (d, $^3J_{H-H}$=8.3 Hz, 6H, tolyl–*H*), 8.29 (s, 1H, carbazole–*H*), 8.38 (d, $^3J_{H-H}$=7.8 Hz, 1H, carbazole–*H*), 8.45 (d, $^3J_{H-H}$=7.8 Hz, 1H, carbazole–*H*), 8.87–8.92 (m, 8H, β-*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=13.9, 21.6, 22.6, 25.0, 27.1, 29.7, 31.6, 43.2, 83.9, 115.6, 115.9, 118.4, 119.9, 120.2, 120.8, 121.9, 125.4, 126.7, 127.4, 130.9, 134.5, 137.3, 139.3, 139.9, 130.4, 140.7 ppm; FT-IR (ATR): ν=3316, 2922, 2853, 1725, 1625, 1560, 1451, 1333, 1259, 1143, 1080, 965, 798, 733, 687 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=424 (5.60), 518 (4.49), 553 (4.36), 592 (4.27), 649 nm (4.26); HRMS (ESI) [$C_{65}H_{63}N_5O_2B$+H]: calcd 956.5075, found 956.5072.

*4.2.13. 3,6-Bis[5′,10′,15′-triphenylporphyrin-20′-yl]-9-hexyl-carbazole (**21**).* Porphyrin **19** (20 mg, 0.02 mmol), bromoporphyrin **4** (14 mg, 0.02 mmol), and K_3PO_4 (37 mg, 0.18 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (5 mg, 0.04 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents removed in vacuo, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine and H_2O. Organic layers dried over $MgSO_4$ and solvents removed in vacuo. Residue subjected to column chromatography (CH_2Cl_2/hexane 2:1), giving 3 fractions, the first of which was debrominated porphyrin 4 and the second of which was the desired product 22 as a purple solid (22 mg, 75%, 0.02 mmol). Mp >310°C; ^{1}H NMR (600 MHz, $CDCl_3$): δ_H=−2.55 (s, 2H, N*H*), 0.70 (t, $^3J_{H-H}$=13.9 Hz, 3H, C*H*$_3$), 0.91–0.95 (m, 2H, C*H*$_2$), 1.18–1.24 (m, 4H, C*H*$_2$), 2.06–2.10 (m, 2H, C*H*$_2$), 4.55–4.57 (m, 2H, C*H*$_2$), 7.81–7.85 (m, 18H, Ph–*H*), 7.90 (d, $^3J_{H-H}$=5.9 Hz, 1H, carbazole–*H*), 8.24 (d, $^3J_{H-H}$=7.9 Hz, 2H, carbazole–*H*), 8.31–8.34 (m, 12H, Ph–*H*), 8.51 (d, $^3J_{H-H}$=10.6 Hz, 1H, carbazole–*H*), 8.67 (d, $^3J_{H-H}$=7.5 Hz, 2H, carbazole–*H*), 8.93–8.95 (m, 8H, *β-H*), 8.97 (d, $^3J_{H-H}$=4.1 Hz, 4H, β-*H*), 9.08 (d, $^3J_{H-H}$=4.5 Hz, 4H, β-*H*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=13.7, 22.4, 27.1, 29.6, 31.4, 43.5, 108.0, 116.0, 118.2, 120.1, 120.9, 122.1, 126.6, 127.0, 127.6, 131.1, 134.5, 139.9, 140.0, 142.1 ppm; FT-IR (ATR): ν=3317, 2956, 2924, 2867, 1644, 1598, 1454, 1440, 1350, 1244, 1155, 1056, 1001, 965, 795, 723, 698 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)= 423 (5.60), 517 (4.61), 554 (4.43), 592 (4.38), 647 nm (4.37); HRMS (MALDI LD$^+$) [$C_{94}H_{69}N_9$]: calcd 1323.5676, found 1323.5653.

*4.2.14. 3,6-Bis[5′,10′,15′-tri(4-methylphenyl)porphyrin-20′-yl]-9-hexyl-carbazole (**22**).* Porphyrin **20** (30 mg, 0.03 mmol), bromoporphyrin **5** (21 mg, 0.03 mmol), and K_3PO_4 (53 mg, 0.25 mmol) were charged to a 50 mL Schlenk tube and dried under high vacuum for 20 min. THF (10 mL) was added and the solution was degassed via three freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (11 mg, 0.01 mmol) was added, the reaction heated to 80 °C under argon and left to stir at this temperature for 18 h. Solvents removed in vacuo, the residue dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, brine, and H_2O. Organic layers dried over $MgSO_4$ and solvents removed in vacuo. Residue subjected to column chromatography (CH_2Cl_2/hexane 1:1) to yield purple product 22 (17 mg, 40%, 0.01 mmol). Mp >310 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=−2.63 (s, 2H, N*H*), 0.68 (t, $^3J_{H-H}$=14.0 Hz, 3H, C*H*$_3$), 0.88–0.93 (m, 2H, C*H*$_2$), 1.18–1.23 (m, 2H, C*H*$_2$), 1.42–1.45 (m, 2H, C*H*$_2$), 2.02–2.06 (m, 2H, C*H*$_2$), 2.75 (s, 18H, tolyl–C*H*$_3$), 4.52 (t, $^3J_{H-H}$=14.1 Hz, 2H, CH_2), 7.61 (d, $^3J_{H-H}$=5.8 Hz, 12H, tolyl–*H*), 8.17 (d, $^3J_{H-H}$=6.4 Hz, 12H, tolyl–*H*), 8.31 (d, $^3J_{H-H}$=8.2 Hz, 2H, carbazole–*H*), 8.44 (s, 2H, carbazole–*H*), 8.69 (d, $^3J_{H-H}$=8.2 Hz, 2H, carbazole–*H*), 8.92–8.95 (m, 12H, β-*H*), 9.02 (d, $^3J_{H-H}$=4.1 Hz, 4H, β-*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C=13.9, 21.5, 22.9, 29.7, 31.6, 43.2, 115.6, 120.6, 123.8, 124.7, 127.7, 129.1, 135.0, 139.8, 142.4, 143.6, 149.3, 150.3, 155,8, 156.6 ppm; FT-IR (ATR): ν=3317, 2920, 2852, 1603, 1559, 1507, 1453, 1321, 1219, 1181, 1109, 965, 840, 797, 731, 708 cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=428 (5.47), 518 (4.32), 556 (4.25), 594 (4.07), 649 nm (4.07); HRMS (MALDI LD$^+$) [$C_{100}H_{81}N_9$]: calcd 1407.6615, found 1407.6569.

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