# Anthracenylporphyrins

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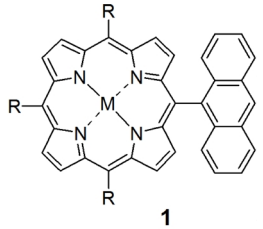
We report the synthesis and characterization of meso-anthracenylporphyrins with zinc and nickel metal centers. A variety of novel aryl and alkyl meso-substituted anthracenylporphyrins were synthesized *via* step-wise Suzuki cross-coupling reactions using anthracenyl boronates. This method was compared to standard syntheses based on condensation reactions to yield anthracenylporphyrins of the $A_2B_2$- and $A_3B$-type. The work was complemented by the synthesis of a number of the functionalized anthracene derivatives *via* Suzuki couplings. Selected systems were subjected to single-crystal X-ray analysis which revealed an unusual close packing for nickel(II) anthracenylporphyrins.

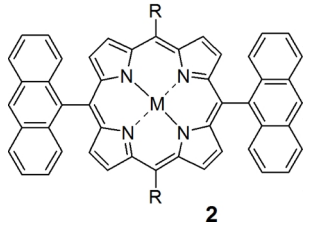
*Key words:* Porphyrins, Conformational Analysis, Anthracenylporphyrins, Tetrapyrroles, Suzuki Coupling

## Introduction

Porphyrins with meso-anthracenyl residues such as **1** or **2** are currently under study for a variety of applications ranging from photodynamic therapy [1], two-photon absorption [2], nonlinear optics [3 – 6], and organic semiconductors [7] to photovoltaics [8 – 10]. This is related to the ability of anthracene moieties to allow and control reversible multiple electron-transfer processes [11] and to their potential to yield systems with extended $\pi$ conjugation. Such expanded porphyrin systems also show interesting structural and functional features and possess unique metal coordination properties [12]. In addition, these chromophors offer potential in photodynamic cancer therapy due to the red shift observed which is associated with the extension of the $\pi$ conjugation of the macrocycle. This red shift overcomes potential problems associated with absorption and light scattering by the tissue, thus increasing penetration and enabling treatment to a wider variety to tumors [1, 13]. Even more intriguing are methods of extending the $\pi$ conjugation of a porphyrin macrocycle by triply fusing anthracenylporphyrins *via* oxidative intramolecular ring closure. Indeed, Anderson and coworkers have recently shown that the synthesis of fused bis-anthracene porphyrin monomers and dimers can thus be achieved [14]. These advances clearly indicate the potential of anthracenylporphyrins and require the development of appropriate methods for their synthesis. Here, we explore the synthesis of these porphyrins and compare the efficiency of two different preparative methods.




**1**




**2**

One method we envisaged to be successful was a standard 2+2 condensation reaction [15]. This method involves the acid-catalyzed condensation of dipyrromethane or dipyrromethane derivatives with an aldehyde to form the porphyrinogen. Subsequent oxidation with 2,3-dichloro-5,6-dicyanoquinone (DDQ) yields the corresponding porphyrin. This has been proven to be an effective method for $A_2B_2$-type porphyrins in previous studies [16], and thus was applied to the synthesis of $A_2B_2$-type anthracenylporphyrins. The design of the substitution pattern is only limited by the synthesis of the pyrrole derivatives and by the pos-

sibility of scrambling [17]. However, the scrambling products can easily be removed by column chromatography.

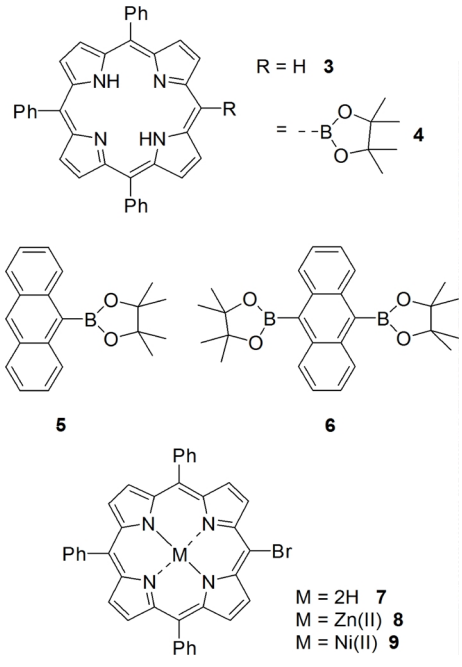
The other method used in the synthesis of anthracenylporphyrins was the palladium-catalyzed Suzuki cross-coupling [18]. This appeared to be the most straightforward method, and it was thought that it would result in higher yields than the condensation reaction. This reaction is widely used in porphyrin chemistry and has shown its potential for the synthesis of a wide variety of both $A_xB_y$-type porphyrins [19].

## Results and Discussion

*Anthracenylporphyrins via Suzuki cross coupling*

Palladium-mediated cross-coupling reactions have evolved into versatile methods for carbon-carbon bond formation [20, 21]. This so-called Suzuki cross-coupling reaction has proven particularly useful for the coupling of aryl halides and aryl boronic acids [18], thus it seemed the most straightforward synthetic route for the synthesis of anthracenylporphyrins. Initially, 5,10,15-triphenylporphyrin **3** was borylated to give **4**, and it was attempted to couple it to 9-bromoanthracene. A variety of reaction conditions, catalysts, cocatalysts and bases were tested. Using $Pd(PPh_3)_4$ or $Pd(dppe)_2$ no conversion was observed. Both $Pd_2(dba)_3$ and $PdCl_2(PPh_3)_2$ with $AsPh_3$ as cocatalyst gave the desired product in about 50 % yield. Using 3,5-di(*tert*-butyl)phenyl-substituted porphyrins which have a better solubility, gave similar results. However, control of the reaction was difficult. Often deborylated starting material and a polar green compound which did not appear to be worth pursuing were observed in an $^1H$ NMR analysis as the only products. Similarly, treatment with 1-bromonaphthalene or bromobenzonitrile under the same conditions gave the deborylated starting material as the only product. Anderson and coworkers found that use of $Pd_2(dba)_2$ [dba = dibenzylideneacetone], KOH and SPhos in *m*-xylene with the respective zinc(II) porphyrins gave conversion to the desired product in about 40 % yield [14].

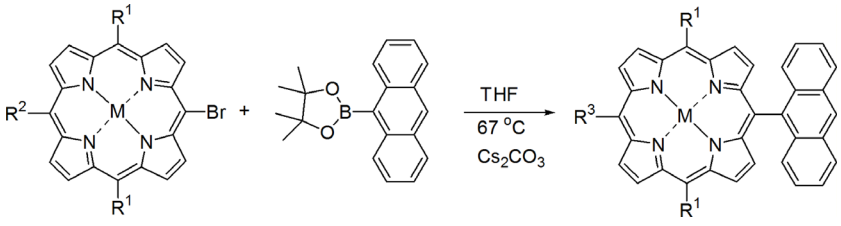
From our findings, we decided to reverse the functional groups of the porphyrin and the anthracene. A method adapted from a procedure by Therien *et al.* [22] yielded the borylanthracenes **5** and **6** in moderate yields, and these compounds were reacted with 5-bromo-10,15,20-triphenylporphyrin **7** [23] to optimize the reaction. A variety of conditions were attempted on a series of porphyrins in an attempt to obtain an array




of mono- and dianthracenylporphyrins. The success of this reaction was found to be dependent on a number of factors: the position of the functional group, the palladium catalyst and the metal in the center of the porphyrin.

A screening of the reaction conditions for reaction of **5** and **7** showed that use of $Pd(PPh_3)_4$ gave only moderate conversion (15 – 25 %) in THF with $K_3PO_4$ or $Cs_2CO_3$. $PdCl_2(PPh_3)_2$ proved to be a better catalyst in conjunction with $AsPh_3$ and gave moderate conversion in DMF ($\sim$ 30 %) and acceptable results in THF ($\sim$ 40 %). DME/water and DMF/toluene were also found to be unsuitable solvents. Use of the zinc(II) derivative **8** gave a significantly lower yield ($\sim$ 15 %) while the nickel(II) derivative **9** proved to be superior ($\sim$ 80 % yield). Likewise, $Pd_2(dba)_3/AsPh_3$ with $Cs_2CO_3$ as base in THF proved to be a good combination and converted **7** into the desired anthracene derivative in about 60 % yield. These results are in agreement with the observed high activity of some of these catalysts [24] and the applicabitity of the palladium complex $Pd_2(dba)_3$ in the presence of a tertiary phosphine ligand and a base [24, 25].

Using the optimized conditions, a number of anthracenylporphyrins were prepared and characterized (Scheme 1). Overall Ni(II) porphyrins were found to be much better coupling partners to the anthracene for meso-arylporphyrins than either free base or zinc(II)

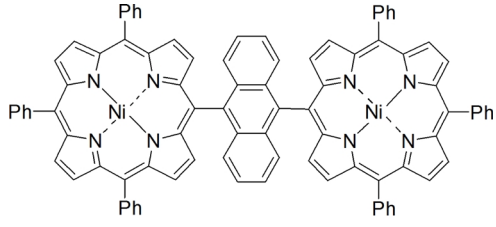



| $R^1$ | $R^2$ | M | Catalyst | $R^3$ | Compound | Yield (%) |
|---|---|---|---|---|---|---|
| 3,5-Di-*tert*-butyl-phenyl | Phenyl | 2H | $Pd_2(dba)_3/AsPh_3$ | Phenyl | **10** | 54 |
| 3,5-Di-*tert*-butyl-phenyl | Phenyl | Ni(II) | $PdCl_2(PPh_3)_2/AsPh_3$ | Phenyl | **11** | 12 |
| 3,5-Di-*tert*-butyl-phenyl | Br | 2H | $PdCl_2(PPh_3)_2/AsPh_3$ | Br | **12** | 25 |
| 3,5-Di-*tert*-butyl-phenyl | Br | Ni(II) | $PdCl_2(PPh_3)_2/AsPh_3$ | Br | **13** | 78 |
| Hexyl | Hexyl | 2H | $PdCl_2(PPh_3)_2/AsPh_3$ | Hexyl | **14** | 40 |
| Hexyl | Hexyl | Zn(II) | $PdCl_2(PPh_3)_2/AsPh_3$ | Hexyl | **15** | 57 |
| Hexyl | Hexyl | Ni(II) | $PdCl_2(PPh_3)_2/AsPh_3$ | Hexyl | **16** | 6 |
| Hexyl | Br | 2H | $PdCl_2(PPh_3)_2/AsPh_3$ | Br | **17** | 40 |
| Phenyl | Br | 2H | $PdCl_2(PPh_3)_2/AsPh_3$ | Anthracenyl | **18** | 35 |
| Phenyl | Br | Ni(II) | $PdCl_2(PPh_3)_2/AsPh_3$ | Anthracenyl | **19** | 84 |

Scheme 1. Selected reaction conditions for the synthesis of mono- and dianthracenylporphyrins.

porphyrins. When coupling was attempted using Zn(II) porphyrins, for the most part only starting material remained, and anthracenylporphyrins were isolated in low yield. Possibly this is due to the more ruffled conformation of Ni(II) meso-arylporphyrins [26], which gives the bulky anthracenyl residue easier access to the meso position [27]. For meso-alkylporphyrins the situation was reversed with both the free base and the zinc(II) complex giving good yields (*e. g.* compounds **14** and **15**). Using these conditions, dibrominated porphyrin precursors could be converted easily into the monobromo monoanthracenyl derivatives (**12**, **13**, **17**) opening the way for the preparation of functionalized anthracenylporphyrins *via* subsequent modification of the remaining bromo group. Note that Sooambar *et al.* used successfully the coupling of zinc(II) diiodoporphyrins in the presence of $Pd(PPh_3)_4$ and $Cs_2CO_3$ in their recent study on 5,15-bisanthracenylporphyrins [11].

The synthesis of meso-dianthracenylporphyrins *via* coupling reactions required longer reaction times. When the free base 5,15-dibromo-10,20-dihexylporphyrin was coupled with **3** for 12 h, only 50 % of the mono-substituted anthracenylporphyrin **17** was obtained with no debrominated or dianthracenylporphyrin isolated. The remaining porphyrin fraction which was isolated was recovered starting material. Reaction of (5,15-dibromo-10,20-dihexylporphyrinato)nickel(II) for 72 h yielded the dianthracenylporphyrin **19** in good yield accompanied by 5 % of the monoanthracenylporphyrin. However, attempts to



**20**

prepare 5,15-dialkyl-10,20-di(9-anthracenyl)porphyrins using this method failed. Nevertheless, an anthracenyl-linked bisporphyrin could be prepared as well. Coupling of the nickel(II) porphyrin **9** with 9,10-dibromoanthracene gave the respective dinuclear porphyrin **20** in 31 % yield. No product formation was observed with either the respective free base or zinc(II) porphyrin.

*RLi reactions*

Another alternative for the synthesis of the anthracenylporphyrins is the substitution of porphyrins with a free meso position using an anthracenyl lithium derivative. This method has worked well with many other RLi reagents [28] and could be applied for the preparation of anthracenyl-2,3,7,8,12,13,17,18-octaethylporphyrins [29]. Thus, $S_NAr$ reactions on the porphyrin using anthryl lithium was also attempted. Using the standard methodology established by us [28], the anthryl lithium was prepared *in situ* from bromoanthracene and butyl lithium. However, addition of porphyrin **3** to the dark-red solution did not, upon hydrol-

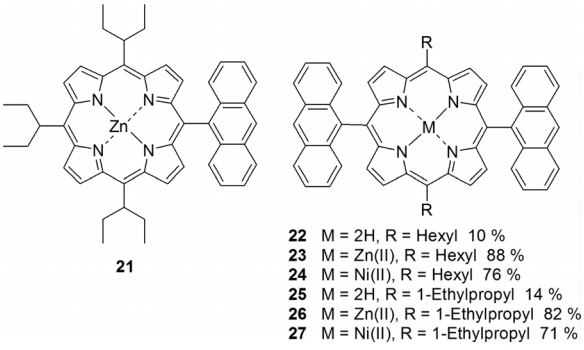
ysis, result in the expected color change to green. Repeated attempts failed as well, most likely due to the poor formation of anthryl lithium (at 0 °C for 1 h). As no butylporphyrin was isolated as a generic side product, the organolithium reagent may have formed and subsequently decomposed.

*Condensation reactions*

Physical chemists prefer using simpler condensation methods as opposed to the more elaborate synthetic routes. Thus, we investigated the synthesis of anthracenylporphyrins using condensation methods as well. The symmetric 5,10,15,20-tetra(9-anthracenyl)-porphyrin was first reported by Volz and Schäffer [30] followed by an improved synthesis by Tohara and Sato [31].

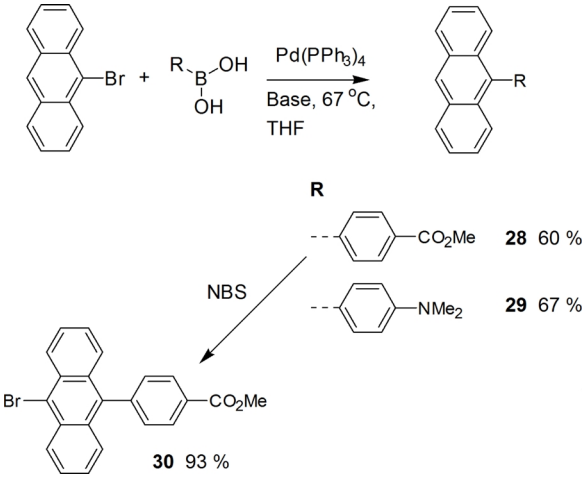
We focused on the preparation of anthracenylporphyrins with meso-alkyl residues that where not accessible using the methods described above. A one-pot condensation reaction for the synthesis of 5,15-dihexyl-10,20-dianthracenylporphyrin (**22**) first required the synthesis of 5-hexyldipyrromethane [32], which was isolated in a reasonable yield of 54 %. This compound was used in a condensation reaction with benzaldehyde using TEA, TFA and DDQ. The major product isolated from this reaction was **22** (10 %) accompanied by 5-anthracenyl-10,15,20-trihexylporphyrin (**14**) (2.5 %). Isolation of **14** from this mixture proved to be difficult, and therefore the relevant fraction was metalated with Zn(II)(acac)$_2$ and purified using preparative TLC to yield **15** and **23**. Compound **22** was also converted into the nickel(II) derivative for comparative analyses.

The condensation reaction was also used with 5-(1-ethylpropyl)dipyrromethane and 9-anthracenecarbaldehyde. Here, chromatography was much easier due to decreased scrambling and less side product formation. The scrambling product **21** was formed in less than 1 % yield and was not further characterized. Overall, this reaction gave a good yield of 14 % for compound **25**. Again, the free base was converted into the respective zinc(II) (**26**) and nickel(II) (**27**) complexes. The alternative combination of 5-(anthracen-9-yl)dipyrromethane and hexanal worked as well. However, the yields were lower, and thus this approach was not explored any further.




*Substituted anthracenes*

Lastly we performed some exploratory syntheses on the functionalization of anthracene using Suzuki couplings. The reaction of boronic acid derivatives with brominated anthracenes required optimization as well. Use of standard conditions gave only debrominated starting material. As a result of this the conditions and




Scheme 2. Synthesis of anthracene derivatives *via* Suzuki coupling reactions.

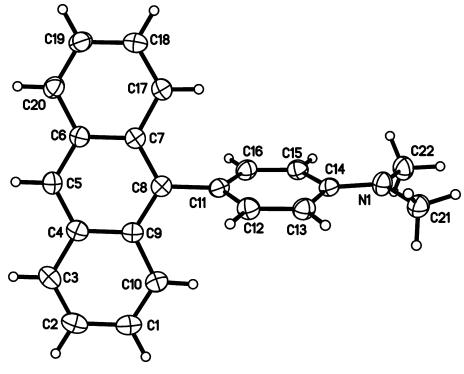


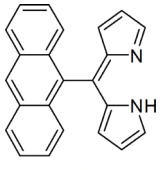

Fig. 1. View of the molecular structure of **29** in the crystal. Displacement ellipsoids are drawn at the 50 % probability level.

reagents were varied. As shown in Scheme 2, a few anthracene derivatives with different electronic properties could be synthesized successfully. While compounds such as **28** or **29** (for the structure of **29** see Fig. 1) could be obtained in good yields, the preparation of difunctionalized derivatives is still unsatisfactory. When the same boronic acid derivatives were coupled to 10-bromoanthracene-9-boronic acid under the same conditions, compounds **28** and **29** were isolated in a lower yield instead of the desired boronic acid derivatives. An example for an entry into compounds suitable for porphyrin modification is the conversion of **28** into **3** using NBS.

*Structural studies*

Crystallization of the 5-(anthracenyl)-dipyrromethane under aerobic conditions gave crystals of the respective dipyrromethane **31**. As shown in Fig. 2, the dipyrrolic unit is planar, clearly indicating the dipyrromethane character. The anthracene unit is planar as well and forms a dihedral angle of 80.8° with the dipyrromethane unit. In contrast to the respective dipyrromethanes [33] this compound does not form intermolecular hydrogen bonds in the crystal.

Compound **19** (Fig. 3) crystallized in a monoclinic space group on an inversion center and exhibits a more or less planar conformation. The Δ24 value (deviation of the 24 macrocycle atoms from their least-squares-plane) is 0.03 Å, and only minor *wav* and *ruf* contributions (*e. g.*, $C_m$ displacements of 0.04 – 0.1 Å) were found. The average Ni–N bond length is 1.964(3) Å, indicative of an almost planar porphyrin. The anthracenyl units are orthogonal to the 4N-plane (87.6°) while the phenyl rings are slightly tilted to the 4N-plane (108.7°). The porphyrin molecules form a very closely packed lattice in the crystal. Two hydrogen atoms from the phenyl residue are in a bifurcated close contact to a neighboring nickel atom (Ni···H20F = 2.838 Å, Ni···H20G = 3.152 Å) (Fig. 4). As a result, the meso substituents are tilted slightly upwards and downwards from the macrocycle. *E. g.*, the *ipso* carbons of the phenyl and anthracenyl residues are displaced from the 4N-plane by 0.13 and 0.19 Å, respectively.




**31**

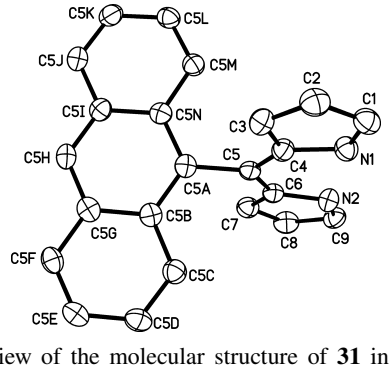



Fig. 2. View of the molecular structure of **31** in the crystal. Hydrogen atoms have been removed for clarity; displacement ellipsoids are drawn at the 50 % probability level.

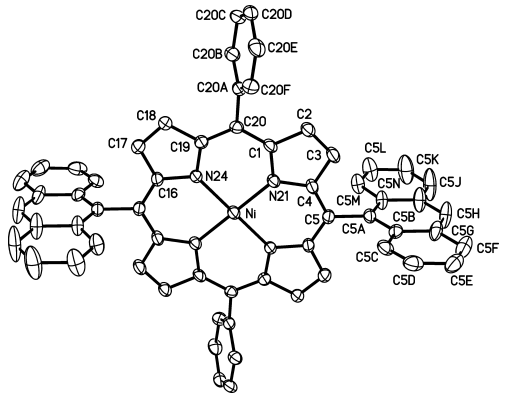



Fig. 3. View of the molecular structure of **19** in the crystal. Hydrogen atoms have been removed for clarity; displacement ellipsoids are drawn at the 50 % probability level.

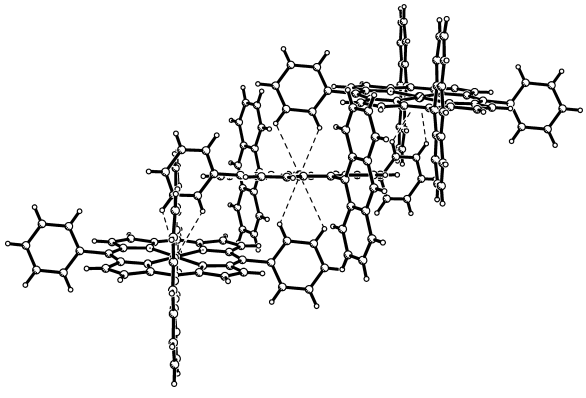


Fig. 4. View of the molecular packing of the porphyrin molecules of **19** in the crystal. Dashed lines indicate close H···Ni contacts.

The molecular structure of **11** is shown in Fig. 5. The porphyrin exhibits the classic *ruf* distortion with alternating up and down $C_m$ displacements of 0.54

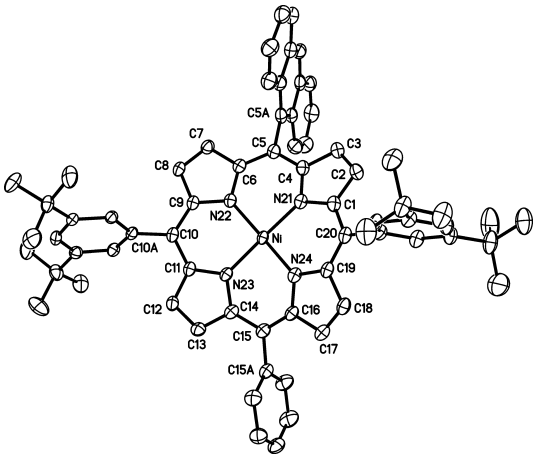



Fig. 5. View of the molecular structure of **11** in the crystal. Hydrogen atoms have been removed for clarity, displacement ellipsoids are drawn at the 50 % probability level.

to 0.61 Å [34]. The overall Δ24 displacement is 0.29 Å. These displacements are similar to those of other meso-tetraaryl-Ni(II)porphyrins, and the nonplanar character is also evidenced by the average Ni–N bond length of 1.919(3) Å [35, 36]. Likewise, the meso-aryl residues are almost orthogonal to the 4N-plane of the macrocycle. The relevant dihedral angles for the residues at C5, C10, C15, and C20 are 97.3, 105.3, 81.6, and 94.2°, respectively. The crystal structure is rather similar to that of **14**. Again, the meso-phenyl ring of one molecule is rather close to the Ni center of a neighboring porphyrin. However, here the "coordination" is "monodentate" with the closest contact being Ni···H15E (2.731 Å).

The molecular structure of **16** also exhibits a planar macrocycle [37]. This is indicated by a Δ24 of 0.01 Å and an average Ni–N bond length of 1.960(2) Å. The anthracenyl residues are almost orthogonal to the plane of the four nitrogen atoms (96.2°). In the crystal packing there are no close contacts. The anthracene residues prevent $\pi$ stacking of the porphyrins, and the hexyl side chains are oriented between neighboring anthracenyl substituents and hinder $\pi$ stacking as well. The observation of both planar and nonplanar Ni(II) porphyrins in this series indicates the conformational flexibility of these systems [35 – 38].

## Conclusion

We report the synthesis of mono- and disubstituted anthracenylporphyrins *via* Suzuki cross-coupling and condensation reactions. Ni(II) porphyrins are favored for the synthesis of meso-aryl-substituted anthracenylporphyrins and anthracene-linked porphyrin dimers. When comparing the two synthetic methods for the synthesis of disubstituted anthracenylporphyrins, the condensation reaction has many advantages over the Suzuki cross-coupling reaction. The condensation is a more cost-efficient method, requiring less analysis, time and waste resulting thus in greener chemistry. Furthermore, it is a synthetic pathway to access dianthracenylporphyrins poorly formed or not at all in attempted syntheses *via* Suzuki cross-coupling reactions. The anthracenylporphyrins reported herein provide a scaffold for further synthesis of elaborate anthracenylporphyrins. Future work will focus on extending the $\pi$ conjugation of these mono- and dinuclear anthracenylporphyrins *via* oxidative fusion. These extended porphyrin systems' anticancer properties will then be determined through biological testing.

## Experimental Section

$^1$H NMR spectra were recorded on a Bruker DPX 400 (400 MHz for $^1$H NMR). High-resolution mass spectrometry was carried out on a Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray source. Low-resolution mass spectra were recorded on a Micromass/Waters Corp. Quattro *micro*™ LC-MS/MS instrument. UV/Vis measurements were performed using a Shimadzu MultiSpec-1501 instrument. Melting points were determined using a Stuart SMP10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 $F_{254}$ (Merck) precoated aluminum sheets. Column chromatography was performed using a forced flow of the indicated solvent system on Fluka silica gel 60 (230 – 400 mesh) or aluminum oxide. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone under argon. *n*-Butyl lithium, 1-bromonaphthalene, 2-bromonaphthalene, 1,4-dibromobenzene, and 3-bromobenzotrifluoride were purchased from Aldrich Chem. Co., 1-bromo-4-pentylbenzene was supplied from Maybridge, 9-bromophenanthrene, 3-bromoanisole and 9-bromoanthracene from Acros, and 4-bromodimethylaniline from Fluka. All named chemicals were used without further purification. All known compounds (dipyrromethane [39], substituted dipyrromethane [19], $A_2$ porphyrins [40] and $A_3$ porphyrins [41]) were synthesized according to literature procedures. The handling of all air-/water-sensitive materials was carried out using standard high-vacuum techniques. Freeze-thaw degassing was effected by freezing under argon, pumping under vacuum, thawing in the absence of gases, and then re-freezing and pumping under vacuum. This process was repeated three

times, and on the final cycle, the flask was purged with argon.

*Suzuki cross-coupling approach for anthracenylporphyrins*

To a stirred slurry of $Cs_2CO_3$ (5 eq.) in anhydrous THF, (0.1 mmol, 1 eq.) bromoporphyrin [23] (304 mg, 1 mmol, 10 eq.), borylanthracene [22] and $PdCl_2(PPh_3)_2$/$AsPh_3$ or $Pd_2(dba)_2$ (0.2 eq.) were added. The reaction mixture was heated to 67 °C, shielded from light and stirred overnight. The reaction was monitored by TLC using DCM/*n*-hexane (1 : 2, v/v) as the mobile phase. This mixture was washed with $NaHCO_3$-saturated, water and dried over $Na_2SO_4$. The organic solvent was evaporated, and the crude mixture was dry-loaded onto a silica column. The anthracenylporphyrin was isolated using dichloromethane/*n*-hexane (1 : 2, v/v) as the mobile phase. The solvent was removed, and the anthracenylporphyrins were further purified by recrystallization from dichloromethane/MeOH.

*Condensation approach for anthracenylporphyrins* [15]

9-anthracenylaldehyde (206 mg, 1 mmol, 4 eq.) was dissolved in 1 L of dry DCM, and 1 mmol (4 eq.) of a substituted dipyrromethane derivative [26, 30] was added. The mixture was degassed by bubbling a stream of argon through the mixture for 30 min. Trifluoroacetic acid (1 eq.) was added drop wise to the mixture *via* a syringe. The reaction was shielded from light and allowed to stir for 4 h under argon at r. t. DDQ (13 eq.) was added to the mixture and was allowed to stir for a further 30 min. Triethylamine (15 mL) was added, and the mixture was allowed to stir for a further hour. The solvent was reduced to 500 mL, and the mixture was passed through a large silica plug, using DCM as the eluent. The porphyrin-containing fractions were collected and purified further by column chromatography using DCM/*n*-hexane (1 : 2, v/v) as the mobile phase. The desired product fraction was recrystallized from DCM and MeOH.

*5-Anthracenyl-10,20-bis(3,5-di-tert-butylphenyl)-15-phenylporphyrin (**10**)*

Prepared *via* Suzuki cross-coupling approach to yield 51 mg (0.054 mmol, 54 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.92. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 422 (6.67), 519 (5.47), 533 (5.32), 597 nm (5.10). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.67 (s, 2H, N*H*), 1.46 (s, 36H, C$H_3$), 7.08 (t, $J$ = 6.75 Hz, 2H, 7,2-anthracenyl-*H*), 7.15 (d, $J$ = 9.38 Hz, 2H, 1,8-anthracenyl-*H*), 7.47 (m, 5H, phenyl-*H*), 7.72 (m, 6H, *tert*-butylphenyl-*H*), 8.22 (d, $J$ = 5.63, 2H, $\beta$-*H* ), 8.25 (d, $J$ = 8.65 Hz, 2H, 6,3-anthracenyl-*H*), 8.68 (d, $J$ = 5.47 Hz, 2H, $\beta$-*H*), 8.8 (dd, 4H, 5,4 anthracenyl-*H*), 8.9 (s, 1H, 10-anthracenyl-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 29.6, 31.57, 34.90, 119.03, 120.19, 125.04, 125.60, 126.67, 127.63, 128.01, 128.34, 128.58, 128.71, 129.71, 130.82, 131.91, 132.03, 132.34, 132.91, 133.52, 134.38, 139.71, 141.42, 142.34, 142.63, 143.02, 143.64, 148.61, 148.80. – HRMS ((+)-ESI): $m/z$ = 938.5317 (calcd. 938.5287 for $C_{68}H_{66}BrN_4$, $[M+H]^+$).

*{5-Anthracenyl-10,20-bis(3,5-di-tert-butylphenyl)-15-phenylporphyrinato}nickel(II) (**11**)*

Prepared *via* Suzuki cross-coupling approach to yield 12 mg (0.012 mmol, 12 %) of orange crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.95. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 420 (4.66), 528 (0.056), 654 nm (0.08). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.46 (s, 36H, C$H_3$) 7.15 (t, $J$ = 8.67 Hz, 2H, 7,2-anthracenyl-*H*), 7.22 (d, $J$ = 8.32 Hz, 2H, 8,1-anthracenyl-*H*), 7.53 (m, 5H, phenyl-*H*), 7.82 (m, 6H, *tert*-butylphenyl-*H*), 8.28 (d, $J$ = 8.63 Hz, 2H, 6,3-anthracenyl-*H*), 8.36 (d, $J$ = 4.68 Hz, 2H, $\beta$-*H*), 8.49 (s, 2H, 5,4-anthracenyl-*H*), 8.83 (d, $J$ = 5.20 Hz, 2H, $\beta$-*H*), 8.89 (s, 1H, 10 anthracenyl-*H*), 8.95 (dd, 4H, $\beta$-*H*). – HRMS ((+)-ESI): $m/z$ = 994.4729 (calcd. 994.4484 for $C_{58}H_{48}N_4Ni$, $[M+H]^+$).

*5-Anthracenyl-15-bromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrin (**12**)*

Prepared *via* Suzuki cross-coupling approach to yield 24 mg (0.025 mmol, 25 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.5. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 424 (4.38), 527 (3.15), 556 (3.03), 599 (2.77), 653 nm (2.46). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.40 (s, 2H, NH), 1.54 (s, 36H, C$H_3$), 7.05 (t, $J$ = 7.18 Hz, 2H, 7,2-anthracenyl-*H*), 7.13 (d, $J$ = 9.43 Hz, 2H, 1,8-anthracenyl-*H*), 7.81 (m, 4H, phenyl-$H_p$ and 6,3-anthracenyl-*H*), 8.10 (s, 4H, phenyl-$H_o$), 8.24 (d, $J$ = 4.50 Hz, 2H, $\beta$-*H*), 8.31 (d, $J$ = 8.98 Hz, 2H, 4,5-anthracenyl-*H*), 8.70 (d, $J$ = 4.94 Hz, 2H, $\beta$-*H*), 8.94 (s, 1H, 10-anthracenyl-*H*), 8.99 (d, $J$ = 4.5 Hz, 2H, $\beta$-*H*), 9.75 (d, $J$ = 4.04 Hz, 2H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 29.6, 31.57, 34.90, 103.24, 115.60, 121.07, 125.00, 125.23, 125.69, 126.14, 127.10, 127.74, 127.89, 128.03, 128.14, 128.50, 129.73, 130.71, 131.52, 133.41, 134.01, 135.01, 135.63, 140.49, 148.78. – HRMS ((+)-ESI): $m/z$ = 940.4106 (calcd. 940.4080 for $C_{62}H_{61}BrN_4$, $[M+H]^+$).

*{5-Anthracenyl-15-bromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrinato}nickel(II) (**13**)*

Prepared *via* Suzuki cross-coupling approach to yield 78 mg (0.078 mmol, 78 %) of orange crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.94. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 418 (4.00), 529 (0.03), 654 nm (0.021). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.12 (t, $J$ = 7.64 Hz, 2H, 7,2-anthracenyl-*H*), 7.16 (d, $J$ = 9.21 Hz, 2H, 8,1-anthracenyl-*H*),

7.45 (m, 4H, phenyl-$H_p$ and 6,3-anthracenyl-*H*), 7.73 (m, 2H, phenyl-$H_o$), 7.86, (d, 2H, $J$ = 1.86 Hz, phenyl-$H_o$), 8.18 (d, 2H, $J$ = 4.92 Hz, $\beta$-*H*), 8.26 (d, 2H, $J$ = 8.69 Hz, 5,4-anthracenyl-*H*), 8.62 (d, 2H, $J$ = 4.89 Hz, $\beta$-*H*), 8.86 (m, 3H, $\beta$-*H*, 10-anthracenyl-*H*), 9.58 (d, $J$ = 5.55 Hz, 2H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 31.48, 34.82, 114.6, 120.74, 121.14, 124.93, 125.66, 127.85, 128.04, 128.14, 128.63, 130.73, 132.35, 132.89, 133.31, 133.45, 134.3, 139.33, 142.12, 142.79, 143.53, 144, 148.88. – HRMS ((+)-ESI): $m/z$ = 996.3287 (calcd. 996.3277 or $C_{46}H_{29}BrN_4Ni$, $[M+H]^+$).

*5-Anthracenyl-10,15,20-trihexylporphyrin (**14**)*

Prepared *via* Suzuki cross-coupling approach to yield 29 mg (0.04 mmol, 40 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.69. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 421 (2.19), 519 (1.00), 551 (0.79), 600 (0.55), 660 nm (0.53). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.31 (s, 2H, N*H*), 0.95 (t, $J$ = 7.40 Hz, 9H, $C_5H_{10}CH_3$), 1.50 (m, 12H, $C_3H_6CH_2CH_2CH_3$), 2.57 (m, 6H, $CH_2CH_2C_3H_8CH_3$), 4.94 (t, $J$ = 7.99 Hz, 4H, $CH_2CH_2C_3H_6CH_3$), 5.08 (t, $J$ = 8.19 Hz, 2H, $CH_2C_4H_8CH_3$), 7.04 (t, $J$ = 6.55 Hz, 2H, 2,7-anthracenyl-*H*), 7.14 (d, $J$ = 9.01 Hz, 2H, 1,8-anthracenyl-*H*), 7.50 (t, $J$ = 7.37 Hz, 2H, 6,3-anthracenyl-*H*), 8.25 (d, $J$ = 4.71 Hz, 2H, 4,5-anthracenyl-*H*), 8.35 (d, $J$ = 9.01 Hz, 2H, $\beta$-*H*), 8.90 (s, 1H, 10-anthracenyl-*H*), 9.25 (d, $J$ = 5.12 Hz, 2H, $\beta$-*H*), 9.55 (d, $J$ = 4.91 Hz, 2H, $\beta$-*H*), 9.61 (d, $J$ = 4.71 Hz, 2H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.76, 22.34, 29.89, 31.50, 34.97, 35.50, 38.25, 38.44, 112.43, 118.80, 119.67, 124.59, 125.21, 127.33, 127.80, 128.34, 130.51, 134.84, 136.00, 162.05. – HRMS ((+)-ESI): $m/z$ = 738.4639 (calcd. 738.4661 for $C_{52}H_{58}N_4$, $[M+H]^+$).

*(5-Anthracenyl-10,15,20-trihexylporphyrinato)zinc(II) (**15**)*

Prepared *via* Suzuki cross-coupling approach to yield 46 mg (0.057 mmol, 57 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.6. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 450 (2.11), 519 (0.51), 671 nm (1.12). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.715 (m, 9H, $C_5H_{10}$,$CH_3$), 1.43 (m, 6H, $C_4H_8CH_2CH_3$), 1.51 (m, 6H, $C_3H_6CH_2CH_2CH_3$), 1.75 (m, 6H, $C_2H_6CH_2C_2H_4CH_3$), 2.34 (m, 6H, $CH_2CH_2C_3H_6CH_3$), 5.15 (t, $J$ = 8.99 Hz, 4H, $CH_2C_4H_8CH_3$), 5.37 (t, $J$ = 8.27 Hz, 2H, $CH_2C_4H_8CH_3$), 7.21 (t, $J$ = 6.64 Hz, 2H, 2,7-anthracenyl-*H*), 7.40 (d, $J$ = 7.16 Hz, 2H, 1,8-anthracenyl-*H*), 7.85 (t, $J$ = 6.94 Hz, 2H, 6,3-anthracenyl-*H*), 8.36 (m, 4H, 4,5-anthracenyl-*H* and $\beta$-*H*), 8.71 (s, 1H, 10-anthracenyl-*H*), 9.14 (d, $J$ = 4.63 Hz, 2H, $\beta$-*H*), 9.33 (d, $J$ = 5.14 Hz, 2H, $\beta$-*H*), 9.47 (d, $J$ = 5.12 Hz, 2H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 10.98, 23.00, 23.74, 28.94, 23.74, 28.937, 29.73, 30.96, 31.96, 38.73, 46.10, 68.169, 128.82, 130.91, 132.45, 167.80. – HRMS ((+)-ESI): $m/z$ = 800.3818 (calcd. 800.3796 for $C_{52}H_{56}N_4Zn$, $[M+H]^+$).

*(5-Anthracenyl-10,15,20-trihexylporphyrinato)nickel(II) (**16**)*

Prepared *via* Suzuki cross-coupling approach to yield 5 mg (0.006 mmol, 6 %) of orange crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.75. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 421 (1.66), 522 (0.67), 554 (0.59), 651 nm (0.363). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.759 (m, 9H, $C_5H_{10}$,$CH_3$), 1.47 (m, 6H, $C_4H_8CH_2CH_3$), 1.58 (m, 6H, $C_3H_6CH_2CH_2CH_3$), 1.87 (m, 6H, $C_2H_6CH_2C_2H_4CH_3$), 2.27 (m, 6H, $CH_2CH_2C_3H_6CH_3$), 4.45 (t, $J$ = 8.49 Hz, 4H, $CH_2C_4H_8CH_3$), 4.57 (t, $J$ = 8.49 Hz, 2H, $CH_2C_4H_8CH_3$), 6.99 (t, $J$ = 8.23 Hz, 2H, 2,7-anthracenyl-*H*), 7.40 (d, $J$ = 7.68 Hz, 2H, 1,8-anthracenyl-*H*), 7.65 (t, $J$ = 8.20 Hz, 2H, 6,3-anthracenyl-*H*), 8.08 (d, $J$ = 5.40 Hz, 2H, $\beta$-*H*), 8.2 (d, $J$ = 9.61 Hz, 2H, 4,5-anthracenyl-*H*), 8.80 (s, 1H, 10-anthracenyl-*H*), 9.01 (d, $J$ = 5.40 Hz, 2H, $\beta$-*H*), 9.30 (d, $J$ = 5.40 Hz, 2H, $\beta$-*H*), 9.38 (d, $J$ = 5.40 Hz, 2H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.55, 22.18, 23.23, 28.43, 28.76, 28.88, 29.19, 30.45, 31.27, 32.55, 38.22, 43.03, 52.98, 53.33, 62.72, 67.72, 128.24, 130.40, 131.88, 163.59, 167.30. – HRMS ((+)-ESI): $m/z$ = 794.3893 (calcd. 794.3858 for $C_{52}H_{56}N_4Ni$, $[M+H]^+$).

*5-Anthracenyl-15-bromo-10,20-dihexylporphyrin (**17**)*

Prepared *via* Suzuki cross-coupling approach to yield 29.3 mg (0.04 mmol, 40 %) of purple crystals. M. p.: $\geq$ 300 °C. – $R_f$ = 0.57. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 420 (2.92), 517 (1.79), 551 (1.46), 592 (1.30), 651 nm (1.046). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.33 (s, 2H, N*H*), 0.93 (t, $J$ = 7.23 Hz, 6H, $C_5H_{10}CH_3$), 1.40 (m, 4H, $C_4H_8CH_2CH_3$), 1.51 (m, 4H, $C_3H_6CH_2CH_2CH_3$), 1.81 (m, 4H, $C_2H_4CH_2C_2H_4CH_3$), 2.51 (m, 4H, $CH_2CH_2C_3H_6CH_3$), 4.90 (t, $J$ = 8.13 Hz, 4H, $CH_2C_4H_8CH_3$), 7.03 (t, $J$ = 6.02 Hz, 2H, 2,7-anthracenyl-*H*), 7.09 (d, $J$ = 8.74 Hz, 2H, 1,8-anthracenyl-*H*), 7.49 (t, $J$ = 7.53 Hz, 2H, 6,3-anthracenyl-*H*), 8.26 (d, $J$ = 4.52 Hz, 2H, 4,5-anthracenyl-*H*), 8.33 (d, $J$ = 8.74 Hz, 2H, $\beta$-*H*), 8.97 (s, 1H, 10-anthracenyl-*H*), 9.21 (d, $J$ = 4.22 Hz, 2H, $\beta$-*H*), 9.51 (d, $J$ = 5.52 Hz, 2H, $\beta$-*H*), 9.80 (d, $J$ = 5.12 Hz, 2H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.96, 22.54, 30.08, 31.71, 35.13, 38.56, 102.68, 114.75, 120.52, 124.90, 125.65, 127.87, 128.10, 128.48, 130.74, 135.04, 141.8, 142.0, 142.8. – HRMS ((+)-ESI): $m/z$ = 732.9862 (calcd. 732.2828 for $C_{46}H_{45}BrN_4$, $[M+H]^+$).

*5,15-Dianthracenyl-10,20-diphenylporphyrin (**18**)*

Prepared *via* Suzuki cross-coupling approach to yield 28 mg (0.035 mmol, 35 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.6. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 423 (3.05), 521 (1.85), 555 (1.65), 598 (1.45), 654 nm (1.40). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.18 (s, 2H, N*H*), 7.06 (t, $J$ = 7.34 Hz, 4H, 7,2-anthracenyl-*H*), 7.16 (d,

*J* = 8.07 Hz, 4H, 1,8-anthracenyl-*H*), 7.50 (t, *J* = 8.07 Hz, 4H, 6,3-anthracenyl-*H*), 7.70 (m, 10H, phenyl-*H*), 8.20 (d, *J* = 6.34 Hz, 2H, *β*-*H*), 8.32 (m, 6H, 4,5-anthracenyl-*H* and *β*-*H*), 8.71 (d, *J* = 4.96 Hz, 4H, *β*-*H*), 8.96 (s, 2H, 10-anthracenyl-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 29.6, 115.58, 120.03, 124.87, 125.61, 126.53, 127.64, 127.90, 128.11,128.54, 130.81, 134.30, 135.24, 135.78, 141.60. – HRMS ((+)-ESI): $m/z$ = 814.3137 (calcd. 814.3096 for $C_{60}H_{38}N_4$, $[M+H]^+$).

*(5,15-Dianthracenyl-10,20-diphenylporphyrinato)nickel(II) (**19**)*

Prepared *via* Suzuki cross-coupling approach to yield 73 mg (0.084 mmol, 84 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.9. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 420 (2.57), 529 (1.55), 656 nm (0.16). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.12 (m, 6H, 7,2-anthracenyl-*H* and phenyl-$H_p$), 7.49 (t, *J* = 7.00 Hz, 4H, 8,1-anthracenyl-*H*), 7.63 (m, 8H, 6,3-anthracenyl-*H* and phenyl-$H_m$), 8.03 (dd, 4H, phenyl-$H_o$), 8.25 (d, *J* = 4.85 Hz, 4H, *β*-*H*), 8.28 (d, *J* = 8.73 Hz, 4H, 5,4-anthracenyl-*H*), 8.63 (d, *J* = 5.09 Hz, 4H, *β*-*H*), 8.90 (s, 2H, 10-anthracenyl-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 124.96, 125.67, 126.62, 127.57, 127.84, 128.05, 128.24, 130.77, 132.23, 132.61, 133.48, 134.44, 140.62, 142.71, 143.75. – HRMS ((+)-ESI): $m/z$ = 870.2302 (calcd. 870.2293 for $C_{60}H_{36}N_4Ni$, $[M+H]^+$).

*9,10-Di{(10,15,20-Triphenylporphyrin-5-ylato)nickel(II)}-anthracene (**20**)*

To a stirred slurry of $Cs_2CO_3$ (5 eq.) in anhydrous THF, 26 mg (0.4 mmol, 2 eq.) of {5-bromo-10,15,20-triphenylporphyrinato}nickel(II) (**9**), 268 mg (0.2 mmol, 1 eq.) of 9,10-bisborylanthracene [22] and $PdCl_2(PPh_3)_2$/$AsPh_3$ or $Pd_2(dba)_2$ (0.2 eq.) were added. The reaction mixture was heated to 67 °C, shielded from light and stirred for 48 h. The reaction was monitored by TLC using DCM/*n*-hexane (1 : 2, v/v) as the mobile phase. This mixture was washed with $NaHCO_3$-saturated, water and dried over $NaSO_4$. The organic solvent was evaporated, and the crude mixture was dry loaded onto a silica column. The anthracenylporphyrin dimer **6** was isolated using dichloromethane/*n*-hexane (1 : 2, v/v) as the mobile phase. The solvent was removed, and the anthracenylporphyrin was further purified by recrystallization from dichloromethane/MeOH yielding 82 mg (0.06 mmol, 31 %). M. p. $\geq$ 300 °C. – $R_f$ = 0.88. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 404 (2.32), 500 (1.00), 532 (1.07), 577 nm (0.58). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.20 (d, *J* = 7.99 Hz, 2H, 7,2 anthracenyl-*H*), 7.38 (t, *J* = 7.52 Hz, 2H, 8,1-anthracenyl-*H*), 7.47 (m, 8H, phenyl-$H_p$ and 6,3-anthracenyl-*H*), 7.56 (m, 12H, phenyl-$H_m$), 7.63 (d, *J* = 7.52 Hz, 2H, 5,4-anthracenyl-*H*), 7.77 (m, 12H, phenyl-$H_o$), 8.11 (m, 4H, *β*-*H*), 8.61 (d, *J* = 5.17 Hz, 4H, *β*-*H*), 8.80 (d, *J* = 4.70 Hz, 4H, *β*-*H*), 8.84 (m, 4H, *β*-*H*). – HRMS ((+)-ESI): $m/z$ = 1362.3221 (calcd. 1362.3178 for $C_{90}H_{54}N_8Ni_2$, $[M+H]^+$).

*5,15-Dianthracenyl-10,20-dihexylporphyrin (**22**)*

Prepared *via* condensation approach to yield 83 mg (0.1 mmol, 10 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.7. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 423 (4.60), 534 (3.61), 580 (2.78), 653 nm (2.92). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.05 (s, 2H, N*H*), 0.95 (m, 6H, $C_5H_{10}CH_3$), 1.46 (m, 8H, $C_3H_6CH_2CH_2CH_3$), 2.50 (m, 4H, $CH_2CH_2C_3H_8CH_3$), 4.88 (t, *J* = 8.50 Hz, 4H $CH_2CH_2C_3H_6CH_3$), 7.06 (t, *J* = 6.50 Hz, 4H, 2,7-anthracenyl-*H*), 7.15 (d, *J* = 8.67 Hz, 4H, 1,8-anthracenyl-*H*), 7.51 (t, *J* = 8.05 Hz, 4H, 6,3-anthracenyl-*H*), 8.32 (d, *J* = 4.64 Hz, 4H, *β*-*H*) 8.35 (d, *J* = 9.60 Hz, 4H, 4,5-anthracenyl-*H*), 8.99 (s, 2H, 10-anthracenyl-*H*), 9.26 (d, *J* = 4.33 Hz, 4H, *β*-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.93, 22.53, 29.58, 31.72, 35.06, 38.49, 114.32, 119.82, 124.90, 125.59, 127.73, 128.11, 128.61, 130.78, 135.18, 136.35. – HRMS ((+)-ESI): $m/z$ = 830.4315 (calcd. 830.4348 for $C_{60}H_{54}N_4$, $[M+H]^+$).

*(5,15-Dianthracenyl-10,20-dihexylporphyrinato)zinc(II) (**23**)*

Porphyrin **22** (41 mg, 0.05 mmol, 1 eq.) was isolated *via* condensation approach and placed in a 100 mL flask with $Zn(acac)_2$ (21 mg, 0.008 mmol, 1.5 eq.). Toluene (50 mL) was added, and the mixture was refluxed for 3 h. The progress of the reaction was monitored by TLC using DCM/*n*-hexane (1 : 2, v/v). Upon completion of the reaction, the solvent was removed in vacuum, and the product was isolated after passage through a plug of silica gel using DCM as the eluent. Recrystallization of the product using DCM/ MeOH yielded 39 mg (0.044 mmol, 88 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.6. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 424 (2.94), 460 (1.95), 522 (1.82), 560 (1.68), 603 nm (1.30). –$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.75 (t, *J* = 8.95 Hz, 6H, $C_5H_{10}CH_3$), 1.62 (m, 8H, $C_3H_6CH_2CH_2CH_3$), 2.35 (m, 4H, $CH_2CH_2C_3H_8CH_3$), 4.94 (t, *J* = 7.19 Hz, 4H $CH_2CH_2C_3H_6CH_3$), 7.02 (t, *J* = 8.29 Hz, 4H, 2,7-anthracenyl-*H*), 7.11 (d, *J* = 8.63 Hz, 4H, 1,8-anthracenyl-*H*), 7.49 (t, *J* = 7.25 Hz, 4H, 6,3-anthracenyl-*H*), 7.82 (d, *J* = 5.19 Hz, 4H, *β*-*H*), 8.34 (d, *J* = 8.64 Hz, 4H, 4,5-anthracenyl-*H*), 8.37 (d, *J* = 4.84 Hz, 2H, *β*-*H*), 8.96 (s, 2H, 10-anthracenyl-*H*), 9.34 (d, *J* = 4.84 Hz, 2H, *β*-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 8.59, 10.93, 11.16, 14.00, 22.65, 22.95, 23.74, 28.91, 29.32, 29.68, 30.34, 31.89, 38.75, 42.21, 45.88, 53.36, 68.12, 128.77, 130.82, 132.44, 167.76. – HRMS ((+)-ESI): $m/z$ = 892.3529 (calcd. 892.3483 for $C_{60}H_{52}N_4Zn$, $[M+H]^+$).

*(5,15-Dianthracenyl-10,20-dihexylporphyrinato)nickel(II) (**24**)*

Porphyrin **22** (41 mg, 0.05 mmol, 1 eq.) was isolated *via* condensation approach and placed in a 100 mL flask with $Ni(acac)_2$ (21 mg, 0.008 mmol, 1.5 eq.). Toluene (50 mL) was added, and the mixture was refluxed for 3 h. The progress of the reaction was monitored by TLC using DCM/*n*-hexane (1 : 2, v/v). Upon completion of the reaction, the solvent was removed in vacuum, and the product was isolated after passage through a plug of silica gel using DCM as the eluent. Recrystallization of the product using DCM/ MeOH yielded 34 mg (0.038 mol, 76 %) of orange crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.94. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 420 (2.27), 534 nm (1.07). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.88 (t, $J$ = 7.45 Hz, 6H, $C_5H_{10}CH_3$), 1.43 (m, 8H, $C_3H_6CH_2CH_2CH_3$), 2.36 (m, 4H, $CH_2CH_2C_3H_8CH_3$), 4.52 (t, $J$ = 8.24 Hz, 4H $CH_2CH_2C_3H_6CH_3$), 7.12 (t, $J$ = 6.47 Hz, 4H, 2,7-anthracenyl-*H*), 7.15 (d, $J$ = 8.83 Hz, 4H, 1,8-anthracenyl-*H*), 7.50 (t, $J$ = 7.23 Hz, 4H, 6,3-anthracenyl-*H*), 8.25 (d, $J$ = 4.98 Hz, 4H, $\beta$-*H*), 8.28 (d, $J$ = 8.63 Hz, 4H, 5,4-anthracenyl-*H*), 8.90 (s, 2H, 10-anthracenyl-*H*), 9.14 (d, $J$ = 5.05 Hz, 4H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.88, 22.46, 30.01, 31.56, 34.19, 37.47, 113.53, 118.26, 125.00, 125.56, 127.71, 128.00, 128.04, 129.71, 130.80, 132.50, 134.42, 134.63, 142.37, 142.62. – HRMS ((+)-ESI): $m/z$ = 886.3546 (calcd. 886.3545 for $C_{60}H_{52}N_4Ni$, $[M+H]^+$).

*5,15-Dianthracenyl-10,20-bis(1-ethylpropyl)porphyrin (**25**)*

Prepared *via* condensation approach to yield 112 mg (0.14 mmol, 14 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.73. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 422 (4.38), 522 (3.21), 558 (2.92), 600 (2.79), 654 nm (2.81). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.22 (s, 2H, N*H*) 0.97, (t, $J$ = 7.11 Hz, 12H, $CHCH_2CH_3$), 2.74 (m, 8H, $CHCH_2CH_3$), 2.74 (m, 2H, $CHCH_2CH_3$), 7.14 (t, $J$= 7.13 Hz, 4H, 7,2-anthracenyl-*H*), 7.32 (t, $J$ = 8.11 Hz, 4H, 8,1-anthracenyl-H), 7.48 (t, $J$ = 8.12 Hz, 4H, 6,3-anthracenyl-*H*), 7.74 (d, $J$ = 6.55 Hz, 2H, $\beta$-*H*), 8.27 (m, 4H, 5,4-anthracenyl-*H*), 8.32 (d, $J$ = 8.74 Hz, 2H, $\beta$-*H*), 8.80 (s, 1H, 10-anthracenyl-*H*), 8.95 (s, 1H, 10-anthracenyl-*H*), 9.32 (d, $J$ = 5.11 Hz, 4H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.14, 34.54, 51.15, 124.84, 125.01, 125.45, 125.81, 126.96, 127.20, 127.55, 128.00, 128.49, 128.76, 130.74, 131.54, 132.72, 135.03. – HRMS ((+)-ESI): $m/z$ = 802.4035 (calcd. 802.4035 for $C_{58}H_{50}N_4$, $[M+H]^+$).

*{5,15-Dianthracenyl-10,20-bis(1-ethylpropyl)porphyrinato}zinc(II) (**26**)*

Porphyrin **25** (56 mg, 0.07 mmol, 1 eq.) was isolated *via* condensation approach and placed in a 100 mL flask with $Zn(acac)_2$ (31 mg, 0.12 mmol, 1.5 eq.). Toluene (50 mL) was added, and the mixture was refluxed for 3 h. The progress of the reaction was monitored by TLC using DCM/*n*-hexane (1 : 2, v/v). Upon completion of the reaction, the solvent was removed in vacuum, and the product was isolated after passage through a plug of silica gel using DCM as the eluent. Recrystallization of the product using DCM/ MeOH yielded 54 mg (0.06 mmol, 82 %) of purple crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.56. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 424 (2.61), 540 (1.61), 589 (1.18), 665 nm (0.75). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.035 (s, 12H, $C_3H_5CH_3$), 2.76 (m, 8H, $CHCH_2CH_3$), 5.03 (m, 2H, $CHC_3H_5$), 7.01 (t, $J$ = 8.13 Hz, 4H, 2,7-anthracenyl-*H*), 7.12 (t, $J$ = 9.04 Hz, 4H, 1,8-anthracenyl-*H*), 7.44 (t, $J$ = 7.68 Hz, 4H, 6,3-anthracenyl-*H*), 8.27 (d, $J$ = 6.73 Hz, 4H, $\beta$-*H*), 8.35 (d, $J$ = 8.00 Hz, 4H, $\beta$-*H*), 8.89 (s, 2H, 10-anthracenyl-*H*), 8.98 (d, $J$ = 8.22 Hz, 4H, 4,5-anthracenyl-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 0.86, 14.24, 20.87, 34.55, 60.22, 124.13, 124.77, 125.335, 127.42, 128.02, 128.74, 130.74, 135.06. – HRMS ((+)-ESI): $m/z$ = 864.3173 (calcd. 864.3170 for $C_{58}H_{48}N_4Zn$, $[M+H]^+$).

*{5,15-Dianthracenyl-10,20-bis(1-ethylpropyl)-porphyrinato}nickel(II) (**27**)*

Porphyrin **25** (56 mg, 0.07 mmol, 1 eq.) was isolated *via* condensation approach and placed in a 100 mL flask with $Ni(acac)_2$ (31 mg, 0.12 mmol, 1.5 eq.). Toluene (50 mL) was added, and the mixture was refluxed for 3 h. The progress of the reaction was monitored by TLC using DCM/*n*-hexane (1 : 2, v/v). Upon completion of the reaction, the solvent was removed in vacuum, and the product was isolated after passage through a plug of silica gel using DCM as the eluent. Recrystallization of the product using DCM/ MeOH yielded 44 mg (0.05 mmol, 71 %) of orange crystals. M. p. $\geq$ 300 °C. – $R_f$ = 0.94. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 424 (2.61), 540 (1.61), 589 (1.18), 665 nm (0.75). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.027 (t, 12H, $C_3H_5$,$CH_3$), 2.38 (m, 8H, $CHCH_2CH_3$), 3.13 (m, 2H, $CHC_3H_5$), 7.08 (t, $J$ = 6.39 Hz, 4H, 2,7-anthracenyl-*H*), 7.19 (t, $J$ = 7.45 Hz, 4H, 1,8-anthracenyl-*H*), 7.46 (t, $J$ = 7.45 Hz, 4H, 6,3-anthracenyl-*H*), 8.06 (d, $J$ = 4.36 Hz, 2H, $\beta$-*H*), 8.22 (d, $J$ = 8.00 Hz, 2H, 4,5-anthracenyl-*H*), 8.82 (s, 2H, 10-anthracenyl-*H*), 9.07 (d, $J$ = 4.36 Hz, 2H, $\beta$-*H*), 9.35 (d, $J$ = 4.36 Hz, 2H, $\beta$-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.88, 37.27, 60.24, 124.79, 125.36, 127.44, 128.01, 128.72, 130.74, 135.00. – HRMS ((+)-ESI): $m/z$ = 858.3196 (calcd. 858.3232 for $C_{58}H_{48}N_4Ni$, $[M+H]^+$).

*Methyl 4-(anthracen-9-yl)benzoate (**28**)*

To a stirred slurry of $K_3PO_4$ (1 g, 4.7 mmol, 5 eq.) in anhydrous THF, 128 mg (0.5 mmol, 1 eq.) of 9-bromoanthracene, 4-methoxycarbonylphenylboronic acid (450 mg,

Table 1. Summary of crystal data, data collection and refinement for the crystal structure determinations.

| | **11** | **19** | **29** | **31** |
|---|---|---|---|---|
| Chemical formula | $C_{68}H_{64}N_4Ni \cdot CH_2Cl_2$ | $C_{60}H_{36}N_4Ni \cdot 2CH_4O$ | $C_{22}H_{19}N$ | $C_{23}H_{16}N_2$ |
| $M_r$ | 1080.87 | 935.72 | 297.38 | 320.38 |
| Crystallization | $CH_2Cl_2/CH_3OH$ | $CH_2Cl_2/CH_3OH$ | $CH_2Cl_2/CH_3OH$ | $CH_2Cl_2/CH_3OH$ |
| Color, habit | red block | red prism | colorless prism | brown prism |
| Crystal size, mm$^3$ | $0.4 \times 0.3 \times 0.2$ | $0.2 \times 0.1 \times 0.03$ | $0.4 \times 0.3 \times 0.15$ | $0.5 \times 0.3 \times 0.1$ |
| Lattice type | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $C2/c$ | $C2/c$ | $P2_1/c$ |
| $a$, Å | 13.1239(18) | 20.44(2) | 16.483(10) | 12.273(7) |
| $b$, Å | 15.1433(17) | 18.237(16) | 8.655(5) | 8.155(5) |
| $c$, Å | 16.1923(18) | 15.538(17) | 22.315(13) | 16.787(10) |
| $\alpha$, deg | 62.810(5) | 90 | 90 | 90 |
| $\beta$, deg | 76.940(7) | 129.764(12) | 98.611(6) | 103.554(8) |
| $\gamma$, deg | 77.389(6) | 90 | 90 | 90 |
| $V$, Å$^3$ | 2763.7(6) | 4452(8) | 3148(3) | 1633.4(17) |
| $Z$ | 2 | 4 | 8 | 4 |
| $d_{calc}$, Mg m$^{-3}$ | 1.30 | 1.40 | 1.26 | 1.30 |
| $\mu$, mm$^{-1}$ | 0.5 | 0.5 | 0.1 | 0.1 |
| $T$, K | 102 | 108 | 118 | 118 |
| $\theta_{max}$, deg | 25 | 31.19 | 25 | 25 |
| Refl. coll. / indep. / $R_{int}$ | 64416 / 9714 / 0.0601 | 17190 / 3908 / 0.0415 | 12454 / 2753 / 0.051 | 11956 / 2863 / 0.0633 |
| Refl. with $F \geq 4.0\ \sigma(F)$ | 9431 | 3707 | 2173 | 2443 |
| No. of ref. parameters | 698 | 313 | 210 | 226 |
| $R1/wR2$ [$F \geq 4.0\ \sigma(F)$] | 0.0723 / 0.1831 | 0.0738 / 0.1986 | 0.0479 / 0.1250 | 0.0657 / 0.1878 |
| $R1/wR2$ (all data) | 0.0744 / 0.1846 | 0.0775 / 0.2025 | 0.0668 / 0.1410 | 0.0820 / 0.2054 |
| $S$ | 1.093 | 1.079 | 1.060 | 1.003 |
| $\Delta\rho_{max}$, e Å$^{-3}$ | 1.377 | 1.089 | 0.215 | 0.339 |

2.5 mmol, 5 eq.) and $Pd(PPh_3)_4$ (0.2 eq.) were added. The reaction mixture was heated to 67 °C, shielded from light and stirred overnight. The reaction was monitored by TLC using EtOAc/*n*-hexane (5 : 95, v/v) as the mobile phase. This mixture was washed with $NaHCO_3$-saturated, water and dried over $NaSO_4$. The organic solvent was evaporated, and the crude mixture was dry loaded onto a silica column, and the anthracenylporphyrin was isolated using EtOAc/*n*-hexane (5 : 95, v/v) as the mobile phase. Recrystallization of the product using DCM/ MeOH yielded 19 mg (0.03 mmol, 60 %) of yellow crystals. M. p. 172 – 174 °C. – $R_f$ = 0.47. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 343 (5.54), 360 (5.80), 380 (5.58), 401 (5.60), 427 nm (5.63). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.99 (s, 3H, C*H*$_3$), 7.38 (t, $J$ = 7.51 Hz, 2H, 8,1-anthracenyl-*H*), 7.50 (t, $J$ = 7.51 Hz, 2H, 7,2-anthracenyl-*H*), 7.58 (t, $J$ = 8.40 Hz, 4H, phenyl-*H*), 8.12 (d, $J$ = 7.51 Hz, 2H, 6,3-anthracenyl-*H*), 8.29 (d, $J$ = 7.51 Hz, 2H, 5,4-anthracenyl-*H*), 8.62 (s, 1H, 10-anthracenyl-*H*). – $^{13}$ C NMR (100.6 MHz, $CDCl_3$): $\delta$ = 52.13, 123.07, 125.05, 125.56, 126.20, 126.96, 127.39, 127.62, 127.95, 128.30, 129.57, 130.01, 131.32, 137.51, 138.0, 143.86, 166.56, 167.02, 171.68. – HRMS ((+)-ESI): $m/z$ = 313.1229 (calcd. 313.1219 for $C_{22}H_{16}O_2$, $[M+H]^+$).

*9-(4-(N,N-Dimethylamino)phenyl)anthracene (**29**)*

Prepared using a method adapted from the procedure of Bonifazi *et al.* [19a] to yield 9 mg (0.7 mmol, 67 %) of yellow crystals. M. p. 262 – 264 °C. – $R_f$ = 0.52. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 337 (5.57), 354 (5.55), 372 (5.57), 384 (5.58), 422 nm (5.62). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.12 (s, 6H, C*H*$_3$), 6.99 (d, $J$ = 9.05 Hz, 2H, 5,4-anthracenyl-*H*), 7.32 (t, $J$ = 9.05 Hz, 2H, 6,3-anthracenyl-*H*), 7.39 (t, $J$ = 8.4 Hz, 2H, phenyl-$H_o$), 7.50 (t, $J$ = 7.98 Hz, 2H, phenyl-$H_m$), 8.09 (d, $J$ = 9.05 Hz, 2H, 7,2-anthracenyl-*H*), 8.09 (d, $J$ = 9.05 Hz, 2H, 8,1-anthracenyl-*H*), 8.51 (s, 1H, 10-anthracenyl-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 0.6, 40.24, 112.02, 124.83, 125.64, 125.80, 126.93, 128.04, 130.52, 131.38, 131.71, 137.59, 149.90.

*Methyl 4-(10-bromoanthracen-9-yl)benzoate (**30**)*

To a solution of **28** (19 mg, 0.03 mmol, 1 eq.) in chloroform (250 mL) and pyridine (75 $\mu$L), *N*-bromosuccinimide (8 mg, 0.045 mmol, 1.5 eq.) was added, and the mixture was stirred at r. t. for 2 h. The progress of the reaction was monitored by TLC at five minute intervals using EtOAc/*n*-hexane (5 : 95, v/v) as the eluent. The reaction was quenched with acetone (25 mL) and the solvent reduced and passed through a plug of silica using DCM. Recrystallization of the product using DCM/ MeOH yielded 12 mg (0.03 mmol, 93 %) of yellow crystals. M. p. 105 – 107 °C. – $R_f$ = 0.31. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 333 (5.52), 350 (5.54), 367 (5.56), 387 (5.59), 419 nm (5.62). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.05 (s, 3H, C*H*$_3$), 7.42 (t, $J$ = 7.56 Hz, 2H, 8,1-anthracenyl-*H*), 7.53 (t, $J$ = 8.48 Hz, 2H, 7,2-anthracen-

yl-*H*), 7.62 (m, 4H, phenyl-*H*), 8.30 (d, $J$ = 7.51 Hz, 2H, 6,3-anthracenyl-*H*), 8.65 (d, $J$ = 8.89 Hz, 2H, 5,4-anthracenyl-*H*). – $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 52.35, 126.90, 127.11, 128.05, 129.77, 130.18, 130.34, 131.35, 136.39, 143.56, 173.1, 76.92. – HRMS ((+)-ESI): $m/z$ = 390.2925 (calcd. 390.2925 for $C_{22}H_{16}BrO_2$, $[M+H]^+$).

*X-Ray structure determinations*

Growth and handling of crystals followed the concept developed by Hope [42]. Intensity data were collected with a Rigaku Saturn-724 system with Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) and a CCD detector. The intensities were corrected for Lorentz, polarization and extinction effects. The structures were solved with Direct Methods using the SHELXTL PLUS program system and refined against $|F^2|$ with the program XL from SHELX-97 using all data [43]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generally placed into geometrically calculated positions and refined using a ridging model. The N-H hydrogen atoms were located in difference maps and refined using the standard riding model. Crystal data and refinement parameters are compiled in Table 1.

*Refinements*: **11**: High vibrational movement was observed for some of the *tert*-butyl methyl groups. The methylene chloride of solvation was refined as 100 % but probably is only partially occupied. **19**: The porphyrin macrocycle is located on a special position. The compound crystallized with disordered methanol molecules of solvation. No hydrogen atoms were included in the refinement for these solvate molecules. **31**: The N-H hydrogen atoms were disordered over both positions and refined with 50 % occupancy each.

CCDC 789257 (**11**), 789258 (**29**), 789259 (**31**) and 789260 (**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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