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Anthracenylporphyrins.
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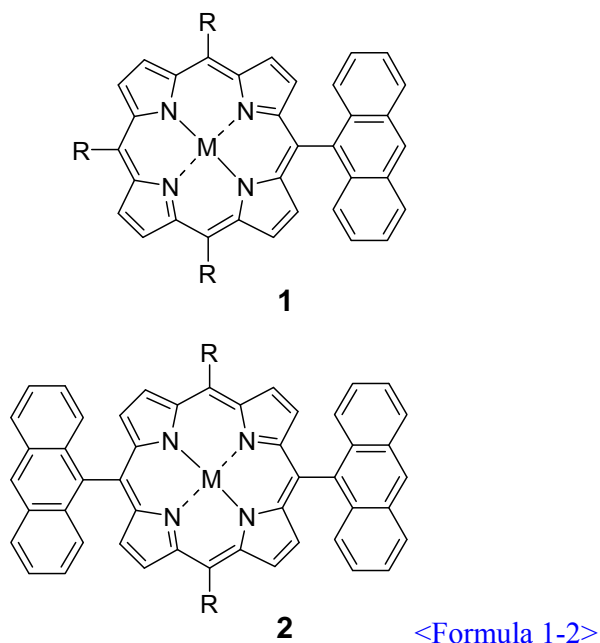
We report the synthesis and characterization of meso-anthracenylporphyrins with zinc and nickel metal centers. A variety of novel aryl and alky meso substituted anthracenylporphyrins were synthesized *via* step-wise Suzuki cross-coupling reactions using anthracenyl boronates. This method was compared to standard syntheses based on condensation reactions to yield anthracenylporphyrins of the A₂B₂- and A₃B-type. This was complemented by the synthesis of a number of the functionalized anthracene derivatives via Suzuki couplings for use in porphyrin functionalization. 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], organic semiconductors [7] to photovoltaics [8-10]. This is related to

the ability of anthracene moieties to enable and control reversible multiple electron-transfer processes [11] and on their potential to yield systems with extended π -conjugation. Such expanded porphyrin systems also show interesting structural and functional features and possess unique metal coordination properties [12]. In addition, these chromophores offer potential in photodynamic cancer therapy due to the red shift observed which is associated with the extension of the π -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 of tumors [1, 13]. Even more intriguing, a method of extending the π -conjugation of a porphyrin macrocycle is by triply fusing anthracenylporphyrins *via* oxidative intramolecular ring closure. Indeed, Anderson and coworkers have recently shown that the synthesis of fused bis-anthracene porphyrins monomers and dimers can be achieved by such means [14]. These advances clearly indicate the potential of anthracenylporphyrins and require the development of appropriate methods for the synthesis of a variety of anthracenylporphyrins. Here, we explore the synthesis of these porphyrins and compare the efficiency of two different preparative methods.



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 A₂B₂-type porphyrins in previous studies [16], and thus was applied to the synthesis of A₂B₂-type anthracenylporphyrins. The design of the substitution pattern is only limited by the synthesis of the pyrrole derivatives and by the possibility of scrambling [17]. However, the scrambling products can easily be removed by column chromatography.

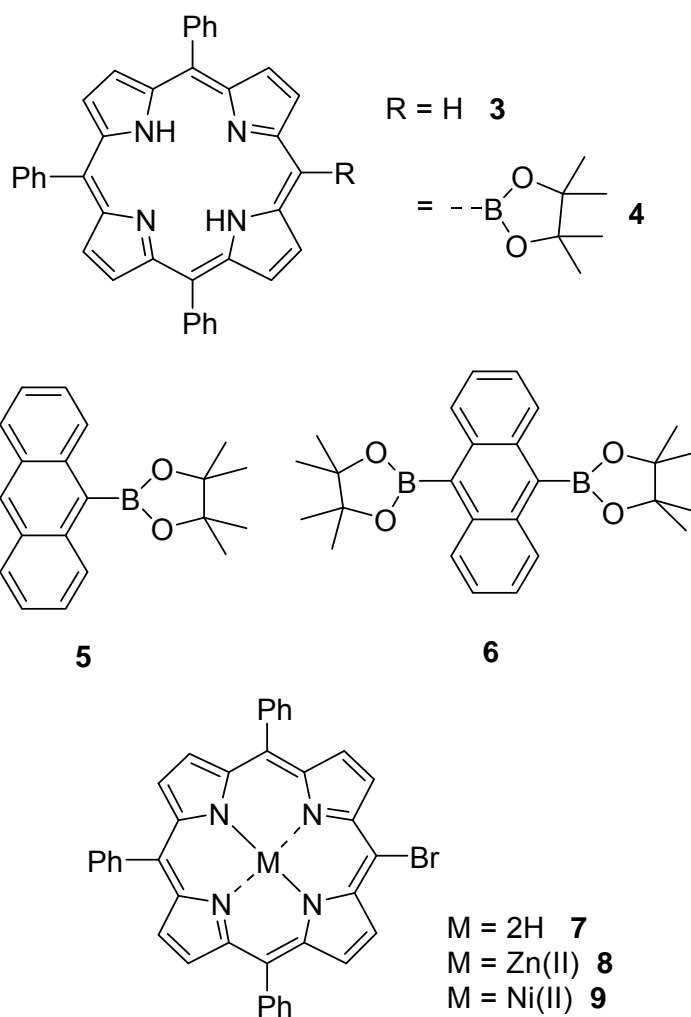
The other method used in the synthesis of anthracenylporphyrins was palladium-catalyzed Suzuki cross-coupling [18], as this appeared to be the most straightforward method and it was thought that it would result in higher yields than the condensation reaction. This reaction is widely used in porphyrin 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(PPh₃)₄ or Pd(dppe)₂ no conversion was observed. Both Pd₂(dba)₃ and PdCl₂(PPh₃)₂ with AsPh₃ as cocatalyst gave the desired product in about 50 % yield. Using

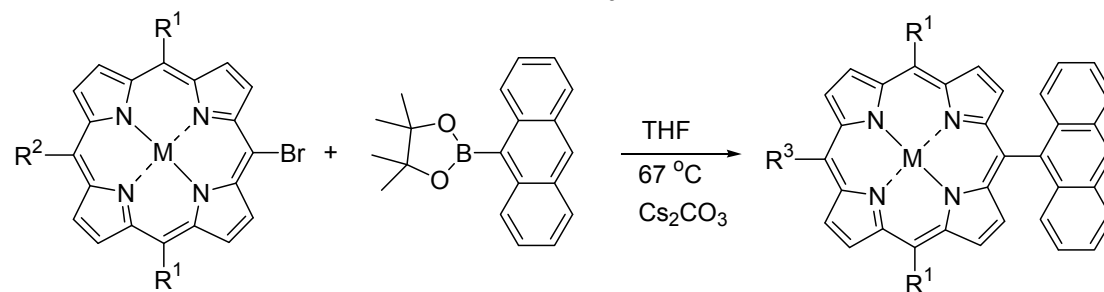
3,5-di(*tert*-butyl)phenyl substituted porphyrins which have a better solubility, gave similar results. However, control of the reaction was difficult. Often deborylated starting material and a polar green compound which did not appear to be worth pursuing from ^1H NMR analysis were observed as the only 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 $\text{Pd}_2(\text{dba})_2$ [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].



<Formula 3-9>

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 yield 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(PPh₃)₄ only gave moderate conversion (15-25 %) in THF with K₃PO₄ or Cs₂CO₃. PdCl₂(PPh₃)₂ proved to be a better catalyst in conjunction with AsPh₃ and gave moderate conversion in DMF (~30 %) and acceptable results in THF (~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 (~15 %) while the nickel(II) derivative **9** proved to be superior (~80 % yield). Likewise, Pd₂(dba)₃/AsPh₃ with Cs₂CO₃ 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 utility of using the palladium complex Pd₂(dba)₃ in the presence of a tertiary phosphine ligand and a base [24, 25].



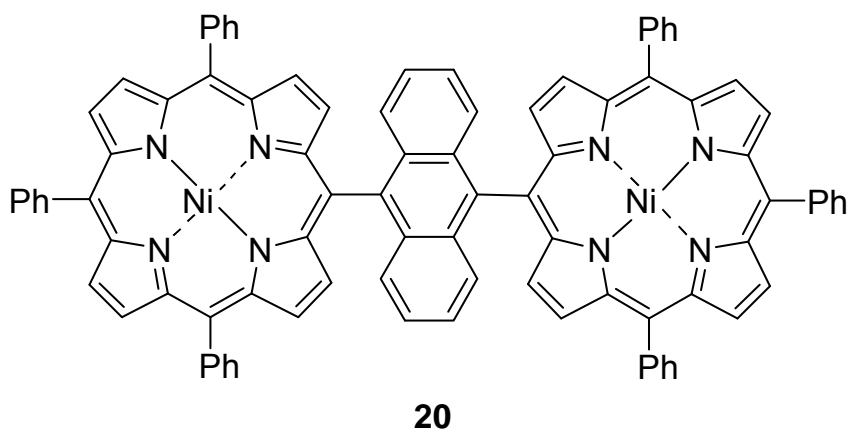
R ¹	R ²	M	Catalyst	R ³	Compound	Yield
3,5-Di- <i>tert</i> -butyl-phenyl	Phenyl	2H	Pd ₂ (dba) ₃ /AsPh ₃	Phenyl	10	54 %
3,5-Di- <i>tert</i> -butyl-phenyl	Phenyl	Ni(II)	PdCl ₂ (PPh ₃) ₂ /AsPh ₃	Phenyl	11	12 %
3,5-Di- <i>tert</i> -butyl-phenyl	Br	2H	PdCl ₂ (PPh ₃) ₂ /AsPh ₃	Br	12	25 %
3,5-Di- <i>tert</i> -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.

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) porphyrins. When coupling was attempted using Zn(II) porphyrins, only starting material for the most part remained and anthracenylporphyrins were isolated in low yield. Possibly this is due to the more ruffled conformation in 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 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(PPh₃)₄, Cs₂CO₃ 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 hours, only 50 % of the mono-substituted anthracenylporphyrin **17** was isolated 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 hours yielded the dianthracenylporphyrin **19** in good yield accompanied by 5 % of the monoanthracenylporphyrin. However, attempts to 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 porphyrin dimer **20** in 31 % yield. No product formation was observed with either the respective free base or zinc(II) porphyrin.



<Formula 20>

RLi reactions

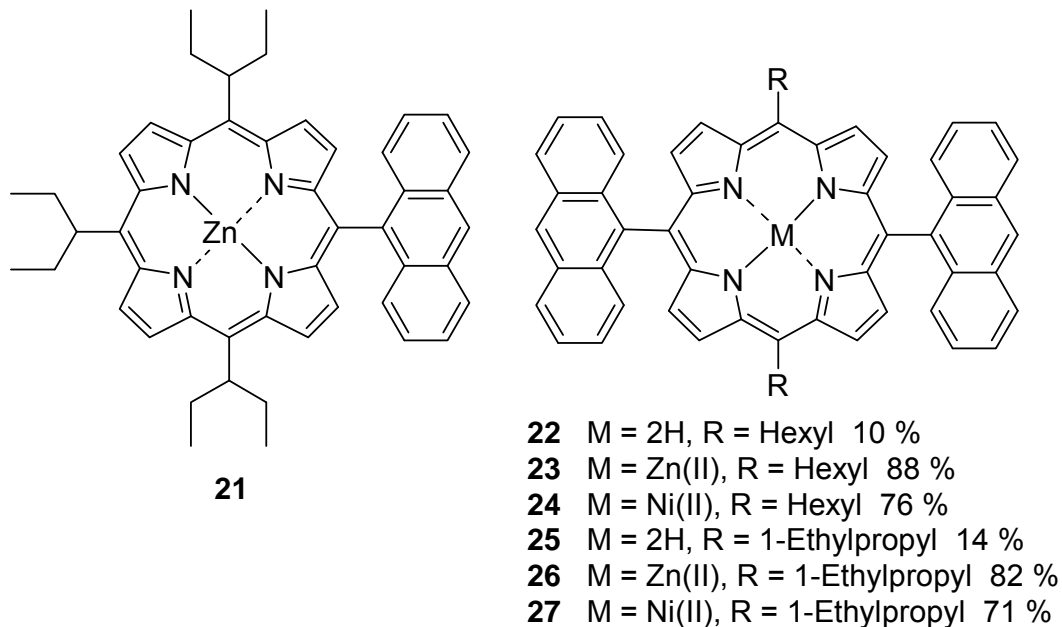
Another alternative for the synthesis of the anthracenylporphyrins is the substitution of porphyrins with a free meso position using an anthracenyl lithium derivative. This method has worked well with many other RLi reagents [28] and could be applied for the preparation of anthracenyl-2,3,7,8,12,13,17,18-octaethylporphyrins [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 hydrolysis, result in the expected color change to green. Repeated attempts failed as well, most likely due to the bad 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 were not accessible using the methods described above. For example, applying 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 thus 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.



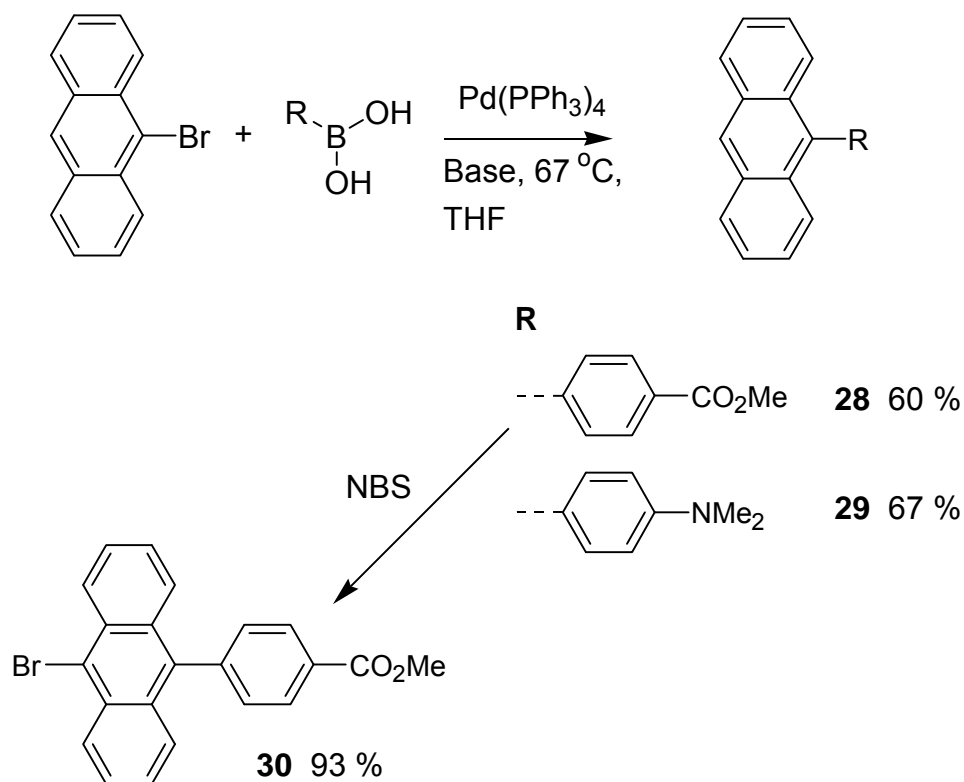
<Formula 21-27>

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. Thus, the scrambling product **21** was formed in less than 1 % yield and 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 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** (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.



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

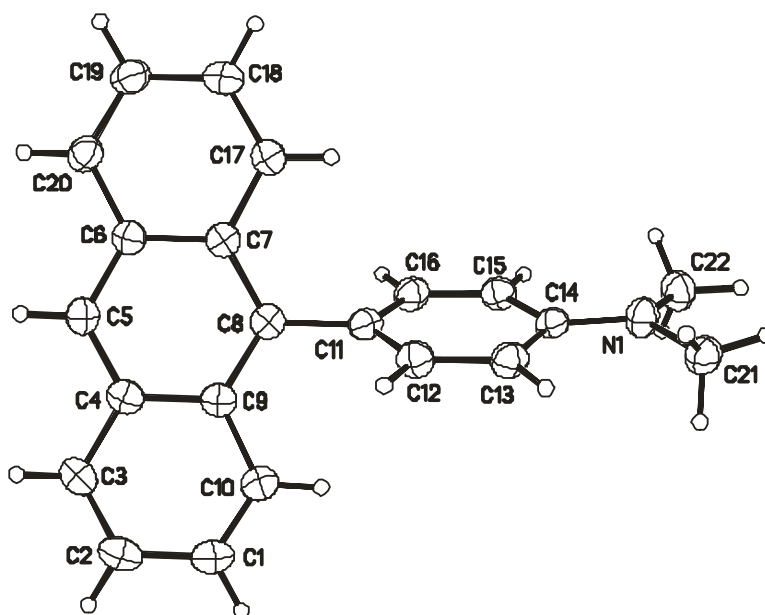
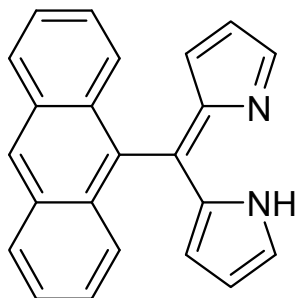


Fig. 1. View of the molecular structure of **29** in the crystal. Displacement ellipsoids are drawn at the 50 % probability level.

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.

**31**

<Formula 31>

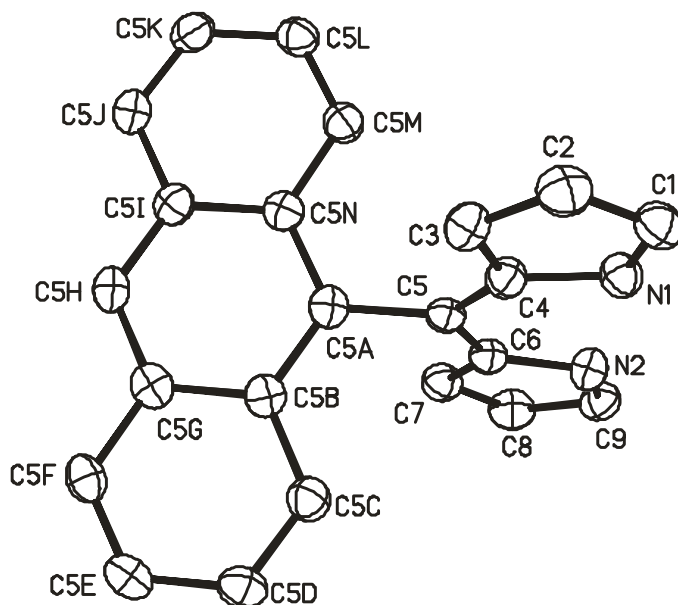


Fig. 2. View of the molecular structure of **31** in the crystal. Hydrogen atoms have been removed for clarity, displacement ellipsoids are drawn at the 50 % probability level.

Compound **19** (Fig. 3) crystallized in a monoclinic space group on an inversion center and exhibits a more or less planar conformation. The Δ_{24} 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 for an almost planar porphyrin. The anthracenyl residue is orthogonal to the 4N-plane (87.6°) while the phenyl ring is 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 ($\text{Ni}\cdots\text{H20F} = 2.838 \text{ \AA}$, $\text{Ni}\cdots\text{H20G} = 3.152 \text{ \AA}$) (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 \AA , respectively.

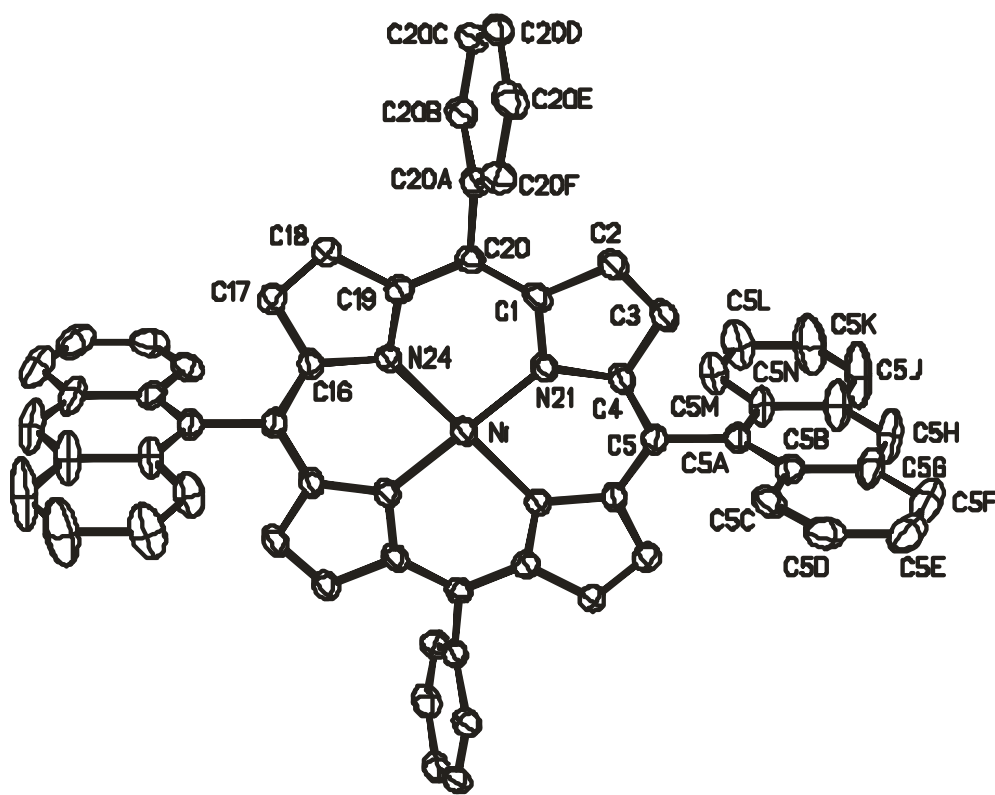


Fig. 3. View of the molecular structure of **19** in the crystal. Hydrogen atoms have been removed for clarity, displacement ellipsoids are drawn at the 50 % probability level.

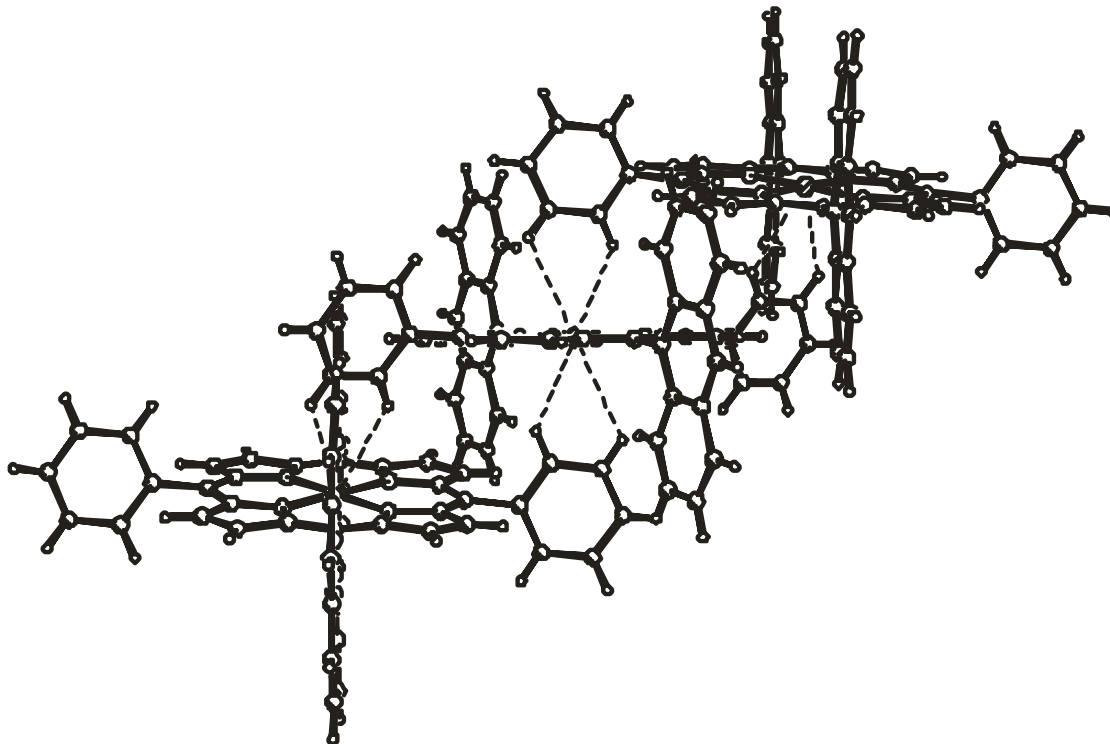


Fig. 4. View of the molecular packing of the porphyrin molecules of **19** in the crystal.

Dashed lines indicate close H \cdots 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 to 0.61 Å [34]. The overall Δ_{24} displacement is 0.29 Å. These displacements are similar to 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 \cdots H15E (2.731 Å).

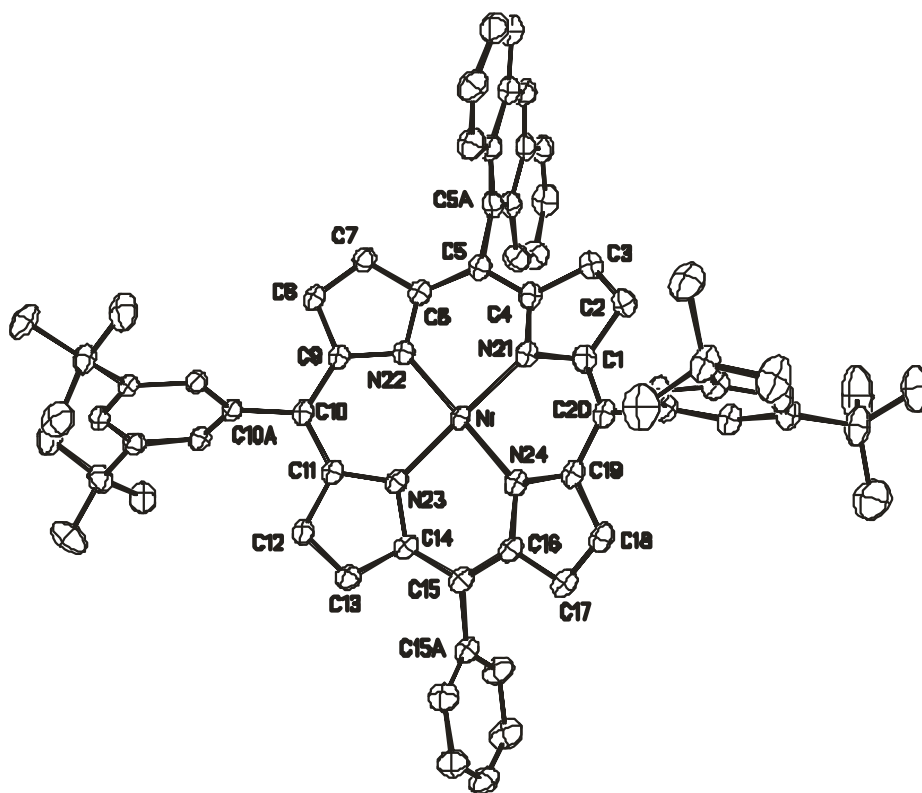


Fig. 5. View of the molecular structure of **11** in the crystal. Hydrogen atoms have been removed for clarity, displacement ellipsoids are drawn at the 50 % probability level.

The molecular structure of **16** exhibits a planar macrocycle as well [37]. This is indicated by a Δ_{24} 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 π -stacking of the porphyrins, and the hexyl side chains are oriented between neighboring anthracenyl substituents and hinder π -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, waste and thus results in greener chemistry. Furthermore, it is a synthetic pathway to access dianthracenylporphyrins which gave little or no yield when attempted synthesis was carried out *via* Suzuki cross-coupling reactions. The anthracenylporphyrins reported here in provide a scaffold for further synthesis of elaborate anthracenylporphyrins. Further work will focus on extending the π -conjugation of these anthracenylporphyrin monomers and dimers *via* oxidative fusion. These extended porphyrin systems' anticancer properties will then be determined through biological testing.

Experimental Section

^1H NMR spectra were recorded on a Bruker DPX 400 (400 MHz for ^1H NMR). High resolution mass spectrometry was carried out on a Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with electrospray source. Low resolution mass spectra were recorded on a Micromass/Waters Corp. Quattro *micro*TM 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 F₂₅₄ (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-bromo-dimethylaniline from Fluka. All named chemicals were used without further purification. All known compounds (dipyrromethane [39], substituted dipyrromethane [19], A₂ porphyrins [40] and A₃ 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 affected by freezing under Argon, pumping under vacuum, thawing in the absence of gases 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 Cs₂CO₃ (5 eq.) in anhydrous THF, (0.1 mmol, 1 eq.) bromoporphyrin [23], (304 mg, 1mmol, 10 eq.) borylanthracene [22] and PdCl₂(PPh₃)₂/AsPh₃ or Pd₂(dba)₂ (0.2 eq) were added. The reaction was heated to 67 °C, shielded from light and allowed to stir overnight. The reaction was monitored by TLC using DCM/*n*-hexane (1:2, v/v) as the mobile phase. This mixture was washed with saturated NaHCO₃, H₂O and dried over Na₂SO₄. The organic solvent was evaporated and the crude mixture was dry-loaded onto a silica column, and the desired 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 room temperature. 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. ≥ 300 °C. $R_f = 0.92$. – UV/Vis (CH₂Cl₂): $\lambda_{\max}(\lg \epsilon_{\max}) = 422 (6.67)$, 519 (5.47), 533 (5.32), 597 nm (5.10). – ¹H NMR (400 MHz, CDCl₃): $\delta = -2.67$ (s, 2H, NH), 1.46 (s, 36H, CH₃), 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, β -*H*), 8.25 (d, $J = 8.65$ Hz, 2H, 6,3-anthracenyl-*H*), 8.68 (d, $J =$

5.47 Hz, 2H, β -H), 8.8 (dd, 4H, 5,4 anthracenyl-H), 8.9 (s, 1H, 10-anthracenyl-H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 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 $\text{C}_{68}\text{H}_{66}\text{BrN}_4$, $[\text{M}+\text{H}]^+$).

{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. ≥ 300 °C. R_f = 0.95. – UV/Vis (CH_2Cl_2): λ_{max} ($\lg \epsilon_{\text{max}}$) = 420 (4.66), 528 (0.056), 654nm (0.08). – ^1H NMR (400 MHz, CDCl_3): δ =1.46 (s, 36H, CH_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, β -H), 8.49 (s, 2H, 5,4-anthracenyl-H), 8.83 (d, J = 5.20 Hz, 2H, β -H), 8.89 (s, 1H, 10 anthracenyl-H), 8.95 (dd, 4H, β -H). – HRMS ((+)-ESI): m/z = 994.4729 (calcd. 994.4484 for $\text{C}_{58}\text{H}_{48}\text{N}_4\text{Ni}$, $[\text{M}+\text{H}]^+$).

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. ≥ 300 °C. R_f = 0.5. – UV/Vis (CH_2Cl_2): λ_{max} ($\lg \epsilon_{\text{max}}$) = 424 (4.38), 527 (3.15), 556 (3.03), 599 (2.77), 653 nm (2.46). – ^1H NMR (400 MHz, CDCl_3): δ = - 2.40 (s, 2H, NH), 1.54 (s, 36H, CH_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, β -H), 8.31 (d, J = 8.98 Hz, 2H, 4,5-

anthracenyl-*H*), 8.70 (d, $J = 4.94$ Hz, 2H, β -*H*), 8.94 (s, 1H, 10-anthracenyl-*H*), 8.99 (d, $J = 4.5$ Hz, 2H, β -*H*), 9.75 (d, $J = 4.04$ Hz, 2H, β -*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 $\text{C}_{62}\text{H}_{61}\text{BrN}_4, [\text{M}+\text{H}]^+$).

{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. ≥ 300 °C. $R_f = 0.94$. – UV/Vis (CH_2Cl_2): λ_{max} (lg ϵ_{max}) = 418 (4.00), 529 (0.03), 654 nm (0.021). – ^1H 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, β -*H*), 8.26 (d, 2H, $J = 8.69$ Hz, 5,4-anthracenyl-*H*), 8.62 (d, 2H, $J = 4.89$ Hz, β -*H*), 8.86 (m, 3H, β -*H*, 10-anthracenyl-*H*), 9.58 (d, $J = 5.55$ Hz, 2H, β -*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 $\text{C}_{46}\text{H}_{29}\text{BrN}_4\text{Ni}, [\text{M}+\text{H}]^+$).

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. ≥ 300 °C. $R_f = 0.69$. – UV/Vis (CH_2Cl_2): λ_{max} (lg ϵ_{max}) = 421

(2.19), 519 (1.00), 551 (0.79), 600 (0.55), 660 nm (0.53). – ^1H NMR (400 MHz, CDCl_3): $\delta = -2.31$ (s, 2H, NH), 0.95 (t, $J = 7.40$ Hz, 9H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 1.50 (m, 12H, $\text{C}_3\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_3$), 2.57 (m, 6H, $\text{CH}_2\text{CH}_2\text{C}_3\text{H}_8\text{CH}_3$), 4.94 (t, $J = 7.99$ Hz, 4H, $\text{CH}_2\text{CH}_2\text{C}_3\text{H}_6\text{CH}_3$), 5.08 (t, $J = 8.19$ Hz, 2H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 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, β -*H*), 8.90 (s, 1H, 10-anthracenyl-*H*), 9.25 (d, $J = 5.12$ Hz, 2H, β -*H*), 9.55 (d, $J = 4.91$ Hz, 2H, β -*H*), 9.61 (d, $J = 4.71$ Hz, 2H, β -*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 $\text{C}_{52}\text{H}_{58}\text{N}_4$, $[\text{M}+\text{H}]^+$).

(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. ≥ 300 °C. $R_f = 0.6$. – UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} (\lg \varepsilon_{\text{max}}) = 450$ (2.11), 519 (0.51), 671 nm (1.12). – ^1H NMR (400 MHz, CDCl_3): $\delta = 0.715$ (m, 9H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 1.43 (m, 6H, $\text{C}_4\text{H}_8\text{CH}_2\text{CH}_3$), 1.51 (m, 6H, $\text{C}_3\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_3$), 1.75 (m, 6H, $\text{C}_2\text{H}_6\text{CH}_2\text{C}_2\text{H}_4\text{CH}_3$), 2.34 (m, 6H, $\text{CH}_2\text{CH}_2\text{C}_3\text{H}_6\text{CH}_3$), 5.15 (t, $J = 8.99$ Hz, 4H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 5.37 (t, $J = 8.27$ Hz, 2H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 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 β -*H*), 8.71 (s, 1H, 10-anthracenyl-*H*), 9.14 (d, $J = 4.63$ Hz, 2H, β -*H*), 9.33 (d, $J = 5.14$ Hz, 2H, β -*H*), 9.47 (d, $J = 5.12$ Hz, 2H, β -*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. ≥ 300 °C. $R_f = 0.75$. – UV/Vis (CH_2Cl_2): λ_{max} ($\lg \epsilon_{max}$) = 421 (1.66), 522 (0.67), 554 (0.59), 651 nm (0.363). – 1H 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, β -*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, β -*H*), 9.30 (d, $J = 5.40$ Hz, 2H, β -*H*), 9.38 (d, $J = 5.40$ Hz, 2H, β -*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 (0.04mmol, 40 %) of purple crystals. M. p. ≥ 300 °C. $R_f = 0.57$. – UV/Vis (CH_2Cl_2): λ_{max} ($\lg \epsilon_{max}$) = 420 (2.92), 517 (1.79), 551 (1.46), 592 (1.30), 651 nm (1.046). – 1H NMR (400 MHz, $CDCl_3$): $\delta = -2.33$ (s, 2H, *NH*), 0.93 (t, $J = 7.23$ Hz, 6H, $C_5H_{10}CH_3$), 1.40 (m, 4H,

C₄H₈CH₂CH₃), 1.51 (m, 4H, C₃H₆CH₂CH₂CH₃), 1.81 (m, 4H, C₂H₄CH₂C₂H₄CH₃), 2.51 (m, 4H, CH₂CH₂C₃H₆CH₃), 4.90 (t, *J* = 8.13 Hz, 4H, CH₂C₄H₈CH₃), 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, *β*-*H*), 8.97 (s, 1H, 10-anthracenyl-*H*), 9.21 (d, *J* = 4.22 Hz, 2H, *β*-*H*), 9.51 (d, *J* = 5.52 Hz, 2H, *β*-*H*), 9.80 (d, *J* = 5.12 Hz, 2H, *β*-*H*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₄₆H₄₅BrN₄, [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. ≥ 300 °C. *R_f* = 0.6. – UV/Vis (CH₂Cl₂): λ_{max} (lg ε_{max}) = 423 (3.05), 521 (1.85), 555 (1.65), 598 (1.45), 654 nm (1.40) – ¹H NMR (400 MHz, CDCl₃): δ = 2.18 (s, 2H, *NH*), 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*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₆₀H₃₈N₄, [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. ≥ 300 °C. $R_f = 0.9$. – UV/Vis (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 420 (2.57), 529 (1.55), 656 nm (0.16). – ¹H NMR (400 MHz, CDCl₃): δ = 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*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₆₀H₃₆N₄Ni, [M+H]⁺).

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

To a stirred slurry of Cs₂CO₃ (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 PdCl₂(PPh₃)₂/AsPh₃ or Pd₂(dba)₂ (0.2 eq.) were added. The reaction was heated to 67 °C, shielded from light and allowed to stir 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 saturated NaHCO₃, H₂O and dried over NaSO₄. The organic solvent was evaporated, and the crude mixture was dry loaded onto a silica column. The desired anthracenylporphyrin dimer **6** 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 yielding 82 mg (0.06 mmol, 31 %). M. p. ≥ 300 °C. $R_f = 0.88$. – UV/Vis (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 404 (2.32), 500 (1.00), 532 (1.07), 577 nm (0.58). – ¹H NMR (400 MHz, CDCl₃): δ = 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. ≥ 300 °C. $R_f = 0.7$. – UV/Vis (CH_2Cl_2): λ_{max} ($\lg \epsilon_{max}$) = 423 (4.60), 534 (3.61), 580 (2.78), 653 nm (2.92). – 1H NMR (400 MHz, $CDCl_3$): $\delta = -2.05$ (s, 2H, NH), 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 $CH_2CH_2C_3H_8CH_3$), 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 from the 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 (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 424 (2.94), 460 (1.95), 522 (1.82), 560 (1.68), 603 nm (1.30). – ¹H NMR (400 MHz, CDCl₃): δ = 0.75 (t, $J = 8.95$ Hz, 6H, C₅H₁₀CH₃), 1.62 (m, 8H, C₃H₆CH₂CH₂CH₃), 2.35 (m, 4H, CH₂CH₂C₃H₈CH₃), 4.94 (t, $J = 7.19$ Hz, 4H CH₂CH₂C₃H₆CH₃), 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*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₆₀H₅₂N₄Zn, [M+H]⁺).

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

Porphyrin **22** (41 mg, 0.05 mmol, 1 eq.) was isolated from the 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 (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 420 (2.27), 534 nm (1.07). – ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, J = 7.45 Hz, 6H, C₅H₁₀CH₃), 1.43 (m, 8H, C₃H₆CH₂CH₂CH₃), 2.36 (m, 4H, CH₂CH₂C₃H₈CH₃), 4.52 (t, J = 8.24 Hz, 4H CH₂CH₂C₃H₆CH₃), 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, β -*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, β -*H*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₆₀H₅₂N₄Ni, [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 (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 422 (4.38), 522 (3.21), 558 (2.92), 600 (2.79), 654 nm (2.81). – ¹H NMR (400 MHz, CDCl₃): δ = -2.22 (s, 2H, NH) 0.97, (t, J = 7.11 Hz, 12H, CHCH₂CH₃), 2.74 (m, 8H, CHCH₂CH₃), 2.74 (m, 2H, CHCH₂CH₃), 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, β -*H*), 8.27 (m, 4H, 5,4-anthracenyl-*H*), 8.32 (d, J = 8.74 Hz, 2H, β -*H*), 8.80 (s, 1H, 10-anthracenyl-*H*), 8.95 (s, 1H, 10-anthracenyl-*H*), 9.32 (d, J = 5.11 Hz, 4H, β -*H*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₅₈H₅₀N₄, [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 from the 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 (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 424 (2.61), 540 (1.61), 589 (1.18), 665 nm (0.75). – ¹H NMR (400 MHz, CDCl₃): δ = 0.035 (s, 12H, C₃H₅CH₃), 2.76 (m, 8H, CHCH₂CH₃), 5.03 (m, 2H, CHC₃H₅), 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, β -*H*), 8.35 (d, $J = 8.00$ Hz, 4H, β -*H*), 8.89 (s, 2H, 10-anthracenyl-*H*), 8.98 (d, $J = 8.22$ Hz, 4H, 4,5-anthracenyl-*H*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₅₈H₄₈N₄Zn, [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 from the 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. ≥ 300 °C. $R_f = 0.94$. – UV/Vis (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 424 (2.61), 540 (1.61), 589 (1.18), 665 nm (0.75). – ¹H NMR (400 MHz, CDCl₃): δ = 0.027 (t, 12H, C₃H₅, CH₃), 2.38 (m, 8H, CHCH₂CH₃), 3.13 (m, 2H, CHC₃H₅), 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, β -*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, β -*H*), 9.35 (d, $J = 4.36$ Hz, 2H, β -*H*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 C₅₈H₄₈N₄Ni, [M+H]⁺).

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

To a stirred slurry of K₃PO₄ (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, 2.5 mmol, 5 eq.) and Pd(PPh₃)₄ (0.2 eq.) were added. The reaction was heated to 67 °C, shielded from light and allowed to stir overnight. The reaction was monitored by TLC using EtOAc/ *n*-hexane (5:95, v/v) as the mobile phase. This mixture was washed with saturated NaHCO₃, H₂O and dried over NaSO₄. The organic solvent was evaporated, and the crude mixture was dry loaded onto a silica column and the desired 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 (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 343 (5.54), 360 (5.80), 380 (5.58), 401 (5.60), 427 nm (5.63). – ¹H NMR (400 MHz,

CDCl₃): δ = 3.99 (s, 3H, CH₃), 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*). – ¹³C NMR (100.6 MHz, CDCl₃): δ = 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 C₂₂H₁₆O₂, [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 (CH₂Cl₂): λ_{\max} (lg ϵ_{\max}) = 337 (5.57), 354 (5.55), 372 (5.57), 384 (5.58), 422 nm (5.62). – ¹H NMR (400 MHz, CDCl₃): δ = 3.12 (s, 6H, CH₃), 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*). – ¹³C NMR (100 MHz, CDCl₃): δ = 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 μ L). *N*-bromosuccinimide (8 mg, 0.045 mmol, 1.5 eq.) was added, and the mixture was allowed to stir at room temperature 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): λ_{max} ($\lg \epsilon_{\text{max}}$) = 333 (5.52), 350 (5.54), 367 (5.56), 387 (5.59), 419 nm (5.62). – ^1H NMR (400 MHz, CDCl_3): δ = 4.05 (s, 3H, CH_3), 7.42 (t, $J = 7.56$ Hz, 2H, 8,1-anthracenyl- H), 7.53 (t, $J = 8.48$ Hz, 2H, 7,2-anthracenyl- 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): δ = 52.35, 126.90, 127.11, 128.05, 129.77, 130.18, 130.34, 131.35, 136.39, 143.56, 173.1, 176.92. – HRMS ((+)-ESI): m/z = 390.2925 (calcd. 390.2925 for $\text{C}_{22}\text{H}_{16}\text{BrO}_2$, $[\text{M}+\text{H}]^+$).

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

Compound	11	19	29	31
Chemical formula	C ₆₈ H ₆₄ N ₄ Ni• CH ₂ Cl ₂	C ₆₀ H ₃₆ N ₄ Ni• 2CH ₄ O	C ₂₂ H ₁₉ N	C ₂₃ H ₁₆ N ₂
<i>M_r</i>	1080.87	935.72	297.38	320.38
Crystallization	CH ₂ Cl ₂ /CH ₃ OH	CH ₂ Cl ₂ /CH ₃ OH	CH ₂ Cl ₂ /CH ₃ OH	CH ₂ Cl ₂ /CH ₃ OH
Color, habit	red block	red prism	colorless prism	brown prism
Crystal size, mm ³	0.4 × 0.3 × 0.2	0.2 × 0.1 × 0.03	0.4 × 0.3 × 0.15	0.5 × 0.3 × 0.1
Lattice type	triclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	13.1239(18)	20.44(2)	16.483(10)	12.273(7)
<i>b</i> , Å	15.1433(17)	18.237(16)	8.655(5)	8.155(5)
<i>c</i> , Å	16.1923(18)	15.538(17)	22.315(13)	16.787(10)
<i>α</i> , deg	62.810(5)	90	90	90
<i>β</i> , deg	76.940(7)	129.764(12)	98.611(6)	103.554(8)
<i>γ</i> , deg	77.389(6)	90	90	90
<i>V</i> , Å ³	2763.7(6)	4452(8)	3148(3)	1633.4(17)
<i>Z</i>	2	4	8	4
<i>d_{calc}</i> (Mg.m ⁻³)	1.30	1.40	1.26	1.30
<i>μ</i> , mm ⁻¹	0.5	0.5	0.1	0.1
<i>θ_{max}</i> , deg	25	31.19	25	25
<i>T</i> , K	102	108	118	118
Collec. refl.	64416	17190	12454	11956
Indep. refl.	9714	3908	2753	2863
Refl. with <i>F</i> ≥ 4.0σ(<i>F</i>)	9431	3707	2173	2443
<i>R_{int}</i>	0.0601	0.0415	0.051	0.0633
No. of parameters	698	313	210	226
<i>Δρ_{max}</i> , e Å ⁻³	1.377	1.089	0.215	0.339
<i>S</i>	1.093	1.079	1.060	1.003
<i>R</i> 1 [<i>F</i> ≥ 4.0σ(<i>F</i>)]	0.0723	0.0738	0.0479	0.0657
<i>wR</i> 2 [<i>F</i> > 4.0σ(<i>F</i>)]	0.1831	0.1986	0.1250	0.1878
<i>R</i> 1 (all data)	0.0744	0.0775	0.0668	0.0820
<i>wR</i> 2 (all data)	0.1846	0.2025	0.1410	0.2054

Figure Captions

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

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 for 50 % probability.

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

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

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

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

Figure for Content Section:

