Chapter IV

Azulene: In the Synthesis of Porphyrinoids
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AZULENE: IN THE SYNTHESIS OF PORPHYRINOIDS

4.1. Introduction

Modifications of a porphyrinoid core that involve the replacement of one or two of the nitrogen atoms by CH units have led to a new class of macrocycles known as carbaporphyrinoids, which have interesting properties both in terms of their aromaticity and their potential ability to bind metal ions. An extension of the mono- and dicarbaporphyrinoid concept to tri- and tetra-carbaporphyrinoids is a logical and long awaited development in the Carbaporphyrinoids field.

![Figure 4.1: Structure of porphyrin](image)

The aim of this approach was to treat porphyrins from the perspective of the annulene chemist, allows the incorporation of two CH\(_2\) and two -CH=CH- units, which act as inner and outer bridges, into the parent [18]annulene (1). This modification results in the bridged annulene, which corresponds to the aromatic tetracyclopentadienic hydrocarbon 2.
Compound 2 can be regarded as the parent structure of porphyrins or heteroporphyrins (Figure 4.2). This compound, which has been named quatyrin and its oxidized derivative dehydroquatyrin (3) have not been reported to date, although the importance of 2 to the fields of both annulenes and porphyrins has been highlighted. Consequently, the synthesis of quatyrin and any compound that contains a quatyrin-containing frame is a fascinating goal at the intersection of carbaporphyrinoid, annulene, and cyclophane carbocation chemistry.

4.2. Azulene

Azulene (12) is a special carbocycle where the five membered rings behave similarly to heterocycles and both α-positions are highly reactive towards electrophilic substitution. Azulene, with the same molecular formula and five conjugated double bonds like naphthalene, differ in having positive dipole moment of 1.08 D and blue color of the compound. The blue color of azulene is due to minor difference in the HOMO-LUMO gap originated from different perturbation of the location of the connecting bond in forming the bicyclic ring.17,18 Azulene exhibits relatively intense fluorescence from its S₂ state, while undergoing an ultrafast internal conversion from its S₁ to S₀ states via conical intersection.19

On the other hand the presence of heptatriene motif in the skeleton allows a formation of stable cations that have stimulated a broad interest in these, colorful compounds. A formal combination of two charged monocyclic sextet systems, viz. the cyclopentadienyl anion and the tropylium cation is encountered in the 10 π-electron system of azulene. The ultraviolet spectrum of azulene and its electron delocalization energy of ca. 35 kcal/mole indicate a state of bonding very similar to that in benzenoid systems.20
Introduction of an azulene moiety to the porphyrinoid framework is of particular interest because of the unusual electronic properties of this bicyclic system. Synthetic routes to azulene have long been of interest because of its unusual structure. In 1939 the first method was reported for the synthesis of azulene starting from indane and ethyl diazoacetate.\textsuperscript{21}

Carbaporphyrinoids are porphyrinoid analogues that possess at least one CH unit replacing pyrrolic nitrogen in the coordination core. This “internal” carbon atom normally belongs to a carbo- or heterocyclic ring substituting one of the pyrroles. Azulene was involved into the porphyrinoid skeleton first by N. Sprutta, eventually creating a big family of carbaporphyrins.\textsuperscript{22} The idea of employing azulene to porphyrins was based on the special properties of this surprising molecule.
Exploration of this concept led to the synthesis of azuliporphyrin and its heteroanalogues, which exhibit borderline macrocyclic aromaticity and unusual reactivity pathways.

### 4.3. Synthesis of 21-monoheteroatom substituted carbaporphyrins

Azuliporphyrin, one of the carbaporphyrins, was reported first time in 1997.\textsuperscript{23} Since then, various azuliporphyrin derivatives, such as *meso*-free,\textsuperscript{24} *meso*-aryl,\textsuperscript{25} core-modified,\textsuperscript{26,27} ring-expanded,\textsuperscript{28} and contracted\textsuperscript{29} azuliporphyrins, as well as their metal complexes,\textsuperscript{30,31} adj-diazuli, opp-di-azuliporphyrins\textsuperscript{32,33} and tetraazuliporphyrin tetracation\textsuperscript{34} have been reported.

#### 4.3.1. Synthesis of azuliporphyrin

There are two general methods for the synthesis of azuliporphyrin:

(i) 3+1 condensation

(ii) Direct synthesis or one-pot condensation

Most syntheses of these specific carbaporphyrins were relied upon 3+1 MacDonald condensation.\textsuperscript{35} This approach has been extraordinarily successful and has allowed the synthesis of diverse structures. However, the “3+1” methodology relies upon the availability of tripyrranes\textsuperscript{36} or related precursors.\textsuperscript{37,38}

![Scheme 4.2: [3+1] synthesis of azuliporphyrins](image)

Although an excellent route has been developed for synthesizing these crucial intermediates, this method involves multistep procedures which place severe limitations on the quantities of azuliporphyrin products that can be conveniently...
prepared. While applying the one pot direct condensation of azulene, pyrrole and aldehyde in the presence of acid, good to moderate yield of azuliporphyrin was obtained along with the formation of substantial amounts of meso-tetraarylporphyrins.39

4.4. Synthesis of 21,23-diheteroatom substituted carbaporphyrins: Oppdicarbaporphyrins

There is currently great deal of interest in synthesis of this type of modified carbaporphyrinoids, which are related to doubly N-confused porphyrins. The oppdicarbaporphyrins are prepared by the reaction of carbatripyrrane with modified diols of thiophene or furan or with 1,3-diformylazulene. Azulene favors electrophilic substitution at the 1 and 3 positions, which are analogous to the α-positions on the pyrrole nucleus and this characteristic allows the synthesis of novel tripyrrane analogues. This type of “carbatripyrrane” could act as a precursor to a series of porphyrin analogues with two modified subunits.

Scheme 4.3: [3+1] synthetic approach for the synthesis of dicarbaporphyrinoids

4.5. Synthesis of tetraazuliporphyrinogen

Synthesis of porphyrinoids are generally depends upon their regioselective reactivity of pyrrole toward electrophilic substitution at the α- positions,40 likewise azulene also favors electrophilic substitution at the 1,3-positions and therefore potentially has the
necessary chemical properties to allow the construction of macrocyclic systems. Azulene reacts with aldehyde in the presence of an acid catalyst to give calixazulenes possesses the same carbon skeleton as quatyrin (2).

\[
\text{R-CHO} + \left[ \text{H}^+ \right] \rightarrow \text{R-CHO}^+ + \text{H}_2\text{O}
\]

\[
\begin{array}{c}
\text{Scheme 4.4: Synthesis of tetraazuliporphyrinogen} \\
\end{array}
\]

4.6. Synthesis of hydride thiophene/furan and azulene macrocycles

Molecules containing extended π-electron chromophores are of interest because of their potential for applications in optoelectronics, electrochromic, or molecular conductivity.\cite{41,42} These applications necessitate systems with unique electronic features, such as near-infrared absorptions, high extinction coefficients, or small HOMO-LUMO gaps.\cite{43,44,45} To achieve these requested molecular properties, combinations of different structural motifs involving azulene are tested.\cite{46,47,48} Compound was synthesized by the of 2,5-bisdiol of thiophene/furan (18) with azulene (17) in presence of acid catalyst in dichloromethane.

\[
\begin{array}{c}
\text{Scheme 4.5: Synthesis of tetra-p-tolyl-dithia/dioxodiazuliporphyrinogen} \\
\end{array}
\]
Combination of the azulene $\pi$-system with the heteroporphyrin-like macrocyclic skeleton results in a three-state redox switchable chromophore with a potential for electrochromic (including a near-IR region) or molecular conductivity applications. This new systems can be linked into multielement conductive arrays using technologies developed for both azulenes$^{49,50,51,52}$ and porphyrins.$^{53,54}$

4.7. Synthesis of azulenylporphyrin

Azulene can serve as either an electron donor or an electron acceptor depending on the nature and connectivity of the substituent, as judged from the well-known electron-rich nature of the five membered ring and the electron-deficient nature of the seven membered ring. Chromophores for nonlinear optics applications are based on design concepts that include strength of the electron donor and electron acceptor, and conjugation extension.$^{55}$ Porphyrin can be modified by the selection of group attached covalently at meso-position for the achievement of better chromophoric properties. Covalent attachment of azulene to porphyrin provides a substantial impact to porphyrin chromophores.

Scheme 4.6: Synthesis of meso-azulenylporphyrin

4.8. Results and Discussion

Carbaporphyrinoid systems have attracted a considerable amount of interest in recent year due to their unique reactivity and spectroscopic properties$^{56,57,58}$. These compound compete with N-confused porphyrins and corroles in their ability to stabilize higher transition metal oxidation states and they often shows strong absorptions in the far red that make them potentially good candidates as photosensitizers for photodynamic therapy (PDT).

Calix[4]azulene was prepared by the reaction of azulene and paraformaldehyde in the presence of Florisil in dichloromethane. The formation of compound was confirmed by different spectroscopic data. $^1$H NMR spectrum of the compound shows a singlet at 4.71 ppm for the eight bridging methylene protons, a triplet at 6.69 ppm for $2^3, 7^3, 12^3, 17^3$ azulene CH-protons, another singlet at 7.08 ppm for four $21, 22, 23, 24$ inner azulene -CH protons. Triplet at 7.44 ppm was assigned for $2^2, 3^2, 7^2, 8^2, 12^2, 13^2, 17^2, 18^2$ azulene protons and most downfielded doublet at 8.27 ppm for $2^1, 3^1, 7^1, 8^1, 12^1, 13^1, 17^1, 18^1$ azulene protons. UV-Visible spectrum of compound 27 shows four bands at 244, 292, 502, 538 nm.

![Scheme 4.7: Synthesis of calix[4]azulene](image)

Figure 4.4: $^1$H NMR spectrum of calix[4]azulene

Azulene and p-tolualdehyde was added to the freshly distilled and dried dichloromethane in nitrogen atmosphere. The mixture was stirred for 15 min and after then acidic ionic liquid was added in catalytic amount to the solution. The reaction mixture was protected from light and stirred for 1 hour. The mixture was washed with distilled water and the organic layer was extracted with dichloromethane. Combined organic layer was treated over anhydrous sodium sulfate and solvent was evaporated under reduced pressure to give crude product. The compound was subjected to chromatography over basic alumina and the isomers were separated as αααα, ααββ and αααβ as 1st, 2nd and 3rd fraction respectively. The isolated compound was confirmed by different spectroscopic technique. 1H NMR spectrum of αααα-isomer of 5,10,15,20-tetratolyl calix[4]azulene showed doublet at 7.98 ppm for 2\(^1\),3\(^1\),7\(^1\),8\(^1\),12\(^1\),13\(^1\),17\(^1\),18\(^1\) protons of azulene ring and a triplet at 7.29 ppm for four protons of 2\(^3\),7\(^3\),12\(^3\),17\(^3\) azulene ring, another doublet at 6.92 ppm for eight ortho-protons of phenyl ring and doublet at 6.88 ppm for m-protons of phenyl ring. A singlet appeared at 6.71 ppm for inner four protons of four azulene ring and a most upfielded singlet at 2.16 ppm for twelve 4-tolylmethyl protons. Whereas 1H NMR spectrum of ααββ-isomer of 5,10,15,20-tetratolyl calix[4]azulene showed two doublets at 8.08 ppm and 8.02 ppm were assigned for eight 2\(^1\),3\(^1\), 12\(^1\),13\(^1\) and 7\(^1\),8\(^1\),17\(^1\),18\(^1\) protons of azulene ring respectively. Four triplets appeared at 7.46 ppm, 7.33 ppm, 6.94 ppm and 6.81 ppm for (2\(^3\), 12\(^3\)), (7\(^3\),17\(^3\)), (2\(^2\),3\(^2\),12\(^2\),13\(^2\)), and (7\(^2\),8\(^2\),17\(^2\),18\(^2\)) azulene ring protons respectively. The third isomer of compound shows one doublet at 8.41 ppm and another at 7.92 ppm for 2\(^1\), 3\(^1\) and 12\(^1\), 13\(^1\) azulene ring protons respectively. A doublet of doublet appears at 8.06 ppm for four 7\(^1\),8\(^1\), 17\(^1\),18\(^1\) azulene ring protons. Three different singlet at 7.15 ppm, 6.72 ppm and 6.52 ppm for inner azulene ring protons.

Figure 4.5: $^1$H NMR spectrum of $\alpha\alpha\alpha\beta$-isomer of 5,10,15,20-tetratolyl calix[4]azulene
Azulene and acetone was added to the freshly distilled and dried dichloromethane in nitrogen atmosphere. The mixture was stirred for 15 min and after then acidic ionic liquid was added in catalytic amount to the solution. The reaction mixture was protected from light and stirred for 1 hour. The mixture was washed with distilled water and the organic layer was extracted with dichloromethane. Combined organic layer was treated with anhydrous sodium sulfate and solvent was evaporated under reduced pressure to give crude product.


The crude product was purified by column chromatography over neutral alumina eluting with 0.5:9.5(CHCl₃:Hexane, v/v) afforded the pure compound 5,5,10,10,15,15,20,20-octamethyl calix[4]azulene in 92% yield. The applied method for the synthesis of 5,5,10,10,15,15,20,20-octamethyl calix[4]azulene relies on the known suitability of azulene as a substrate for Rothemund-type condensations. The structure of the compound was confirmed by different spectroscopic data. ¹H NMR spectrum of the compound showed a singlet at δ 1.27 ppm which was assigned for the twenty four meso methyl protons, another singlet appeared at δ 5.86 ppm was assigned for the inner protons of the azulene moiety. A doublet appeared at δ 8.45 ppm for 2¹,3¹, proton of the azulene moiety having coupling constant of 9.57 Hz and two triplets at δ 7.39 and 9.95 ppm for the outer azulene protons. In ¹³C NMR spectrum of said compound showed eight peaks at δ 139.4(4C, 21,22,23,24), 137.3 (4C; 2²,7²,12²,17²), 135.6 (8C; 2,3,7,8,12,13,17,18), 133.4 (8C; 2¹,3¹,7¹,8¹,12¹,13¹, 17¹,18¹), 132.2 (8C; 1,4,6,9,11,14,16,19), 121.5 (8C; 2²,3²,7²,8²,12²,13²,17²,18²), 45.6 (4C; 5,10,15,20), 27.1 (CH₃) carbons respectively.

Figure 4.6: $^1$H NMR spectrum of 5,5,10,10,15,15,20,20-octamethyl calix[4]azulene
4.9. Synthesis of azuliporphyrins

*meso*-5,10,15,20-Tetrakis(4-chlorophenyl)azuliporphyrin was synthesized by minor modification in the literature procedure, 1-(4-sulfopropyl)pyridinium trifluoromethylacetate was added to the stirred solution of azulene, 4-chlorobenzaldehyde and pyrrole in dry DCM under nitrogen atmosphere. The resulting solution was further stirred at room temperature for 16 to 20 hours. Reaction was monitored by TLC, after completion of the reaction, DDQ was added to the solution and the reaction mixture was allowed to stir for another 1 hour. After completion of the reaction, the reaction mixture was extracted with water, NaHCO₃ and chloroform. Organic phase was collected, dried over sodium sulfate and solvent was evaporated under reduced pressure. Crude product obtained was subjected to column chromatography over basic alumina eluting with 20:80 hexanes/CH₂Cl₂. Tetrakis(4-chlorophenyl)porphyrin eluted initially, followed by trace amounts of carbaporphyrins, and then a deep reddish-brown fraction corresponding to the azuliporphyrin product was collected. Further recrystallization of the product from chloroform/methanol gave desired azuliporphyrin as a lustrous green powder.

The ¹H-NMR spectrum of the compound gave two triplets at 7.06 and 7.56 ppm for the outer protons of azulene moiety and a doublet at 7.69 ppm with coupling constant 9.6 Hz of 6,7-protons of azulene. Singlet at 4.92 ppm appeared for the innermost azulene moiety. Two doublet at 7.92 ppm and 7.89 ppm appears for four aryl ortho and meta-protons. UV-Visible spectrum of the compound in 1% TFA/CHCl₃ gave prominent absorption peaks at 440.05 nm and 655.75 nm.

Scheme 4.10: Synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)azuliporphyrin
Figure 4.7: $^1$H NMR spectrum of 5,10,15,20-tetrakis(4-chlorophenyl) azuliporphyrin

Figure 4.8: UV/Visible spectrum of 5,10,15,20-tetrakis(4-tert-butylphenyl) azuliporphyrin in 1% TFA/CHCl$_3$
4.10. Synthesis of 2,5-[bis(4-tert-butyl-phenyl)hydroxymethyl]thiophene

2,5-[Bis(4-tert-butyl-phenyl)hydroxymethyl]thiophene was synthesized by the minor modification of literature procedure. Thiophene was added to a solution of n-BuLi and TMEDA in hexanes under nitrogen atmosphere. Then dilithiothiophene suspension was added dropwise to a solution of corresponding aldehyde in anhydrous THF at 0°C. After completion of the reaction, reaction mixture was extracted with ethyl acetate and dried over Na₂SO₄, and concentrated to give yellow oil. The crude product was precipitated by the slow addition of hexanes to give 2,5-[bis(4-tert-butyl-phenyl) hydroxymethyl] thiophene, as white amorphous powder. The structure of the compound was confirmed by different spectroscopic data. In ¹H NMR spectrum of compound 2,5-[bis(4-tert-butyl-phenyl)hydroxymethyl] thiophene (36d) showed two sharp singlets at δ 2.32 and 2.13 ppm which were assigned for eighteen methyl protons and two hydroxy group protons, two singlets at 5.90 and 6.67 ppm were assigned for one meso methyl protons and two thiophenic protons. Two doublets at 7.33 and 7.36 ppm with coupling constant 8.04 Hz were assigned for two aryl protons. ¹³C NMR spectrum of compound 2,5-[bis(4-tert-butyl-phenyl)hydroxymethyl]thiophene showed three peaks at 31.31, 34.55 and 72.44 ppm and were assigned for tert-butylmethyl carbon, tert-butyl carbon and meso carbon, peak at 124.31 ppm was assigned for β-thiophenic carbon, 125.44 and 125.99 ppm were assigned for aryl carbon and finally three peaks at 139.92, 148.11 and 150.95 ppm were assigned for α-thiophenic carbon and quartenary carbon respectively.

Scheme 4.11: Synthesis of 2,5-[bis(4-tert-butyl-phenyl)hydroxymethyl] thiophene
4.11. Synthesis of 5,10,15,20-tetra-(4-tert-butyl-phenyl)-22,24-dithia/dioxo diazuliporphyrinogen

Compound 5,10,15,20-tetra-(4-tert-butyl-phenyl)-22,24-dithia/dioxo diazuliporphyrinogen was synthesized by the reaction of equimolar ratio of 2,5-[bis(4-tert-butyl-phenyl)hydroxymethyl]thiophene and azulene in dry dichloromethane. The reaction mixture was stirred for 15 min under nitrogen atmosphere. After 15 minute Et₂OBF₃ (20µL) was added and the reaction mixture protected from light and stirred for the next 40 minutes. After completion of the reaction, the solvent was evaporated under reduced pressure and then subjected to column chromatography. The structure of the compound was confirmed by different spectroscopy. ¹H NMR spectrum of the compound showed a doublet at 8.21 ppm for the four azulene protons (2¹, 3¹, 12¹, 13¹) having coupling constant of 9.76 Hz, and a singlet appeared at 7.69 ppm for the inner azulene protons, a triplet at 7.32 ppm appeared for the 2³ and 12³ proton (J = 10.2 Hz) of azulene moiety another triplet appeared at 6.78 ppm (J =10.2 Hz) for the 2², 3², 12², 13², protons of azulene moiety. A multiplet appeared at 7.14 ppm for the aryl protons and a singlet 2.32 ppm for the tert-butyl group of aaaa-isomer of 5,10,15,20-tetra-(4-tert-butylphenyl)-22,24-dithiadiazuliporphyrinogen. UV-Visible spectrum of the compound showed three absorption peaks at 299nm, 356 nm and 375nm. Whereas ¹H NMR spectrum ααββ-isomer shows two doublets at δ 8.23 and 8.16 ppm for the
2¹, 3¹ and 12¹, 13¹ protons of azulene moiety, showing that both azulene moiety were present in different environments.

Scheme 4.12: Synthesis of 5,10,15,20-tetra-(4-tert-butylphenyl)-22,24-dithiadiazuliporphyrinogen

Figure 4.10: (a) ¹H NMR spectrum of ααββ-isomer of 5,10,15,20-tetra-(4-tert-butylphenyl)-22,24-dithiadiazuliporphyrinogen; (b) ¹H NMR spectrum of ααααα-isomer of 5,10,15,20-tetra-(4-tert-butylphenyl)-22,24-dithiadiazuliporphyrinogen

Oxidation of 5,10,15,20-tetra-(4-tert-butylphenyl)-22,24-dithiadiazuliporphyrinogen with varying amounts of DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone) leads to mixtures of the porphyrin analogue compound 37 and dication 39. These species constitute a multielectron redox system with no precedence in carbaporphyrinoid chemistry. Tetrathiaporphyrin and its oxacongener are the only other porphyrin analogues for which two different oxidation states (isophlorin and dication) could be isolated.\textsuperscript{59,60,61} 5,10,15,20-tetra-(4-tert-butylphenyl)-22,24-dithiadiazuliporphyrinogen and DDQ was dissolved in dry DCM and the solution was stirred for 10 mins and then the solvent was evaporated under reduced pressure. Product obtained from the reaction was then dissolved in freshly distilled THF and SnCl\textsubscript{2} during which the color of the solution changes from dark blue to red. The solvent of the reaction mixture was evaporated and the reaction mixture was subjected to chromatography to obtain the pure compound as a first violet fraction. The UV-Visible spectrum of the compound showed a soret band at 438.68 nm along with two other bands at 533.43 and 656.77 nm.


Bromine was added to the solution of porphyrin (38) in 50 mL of freshly distilled CH\textsubscript{2}Cl\textsubscript{2}. The color of the solution changed quickly from dark red to navy blue. The solid 5,10,15,20-tetra-(p-tert-butyl-phenyl)-22,24-dithiadiazuliporphyrin dication·2 [Br\textsubscript{3}] was precipitated by addition of n-pentane to the reaction mixture. The UV-Visible spectrum of the compound showed absorption bands at 441.34 nm, 561.19 nm\textsubscript{1} and at 663.27 nm.
Scheme 4.13: Synthesis of 5,10,15,20-tetra-\((p\text{-}\text{tert}-\text{butyl phenyl})\)-22,24-dithiadiazuliporphyrinogen and its dicationic species

Figure 4.11: UV-Visible absorption spectra (CH\(_2\)Cl\(_2\), 298 K) of 5,10,15,20-tetra-\((p\text{-}\text{tert}-\text{butyl-phenyl})\)-22,24-dithiadiazuliporphyrin (red) and 5,10,15,20-tetra-\((p\text{-}\text{tert}-\text{butyl-phenyl})\)-22,24-dithiadiazuliporphyrin dication (black)
4.12.2. UV-Visible titrations of 5,10,15,20-tetra-(p-tert-butyl-phenyl)-22,24-dithiadiazuliporphyrinogen with mercuric perchlorate

The complexation studies of compound 5,10,15,20-tetra-(p-tert-butyl-phenyl)-22,24-dithiadiazuliporphyrinogen was carried out with UV-Visible spectroscopy in DMSO at room temperature. Titrations were performed by adding aliquots of 20 µl of stock solutions (5.0 X 10^{-5} M) of cationic guests (mercuric perchlorate) to the investigated host (5.0 X 10^{-5} M). The UV-Visible spectrum of compound showed an absorption maximum at 299.01 nm. With the addition of mercuric perchlorate to the guest solution the absorption peak gradually increases in intensity giving rise to new peak at 254.10 nm.

Figure 4.12: The absorption spectra of 5,10,15,20-tetra-(p-tert-butyl-phenyl)-22,24-dithiadiazuliporphyrinogen (5 × 10^{-5} M) in DMSO solution upon the addition of 20 µl stock solution (5 × 10^{-5} M) of mercuric perchlorate

4.13. Synthesis of 2,7-dimethyl-octa-3,5-diyne-2,7-diol

CuCl₂ was added to a solution of 2-methyl-3-butyne-2-ol in THF (5 mL) and the mixture was allowed to stir at room temperature for 10 minute. DBU was added to the reaction mixture and the reaction was allowed to stir vigorously at room temperature open to the atmosphere. After 24 h the reaction mixture was neutralized by HCl and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using hexanes/ethyl acetate as eluent to obtain pure compound. The structure of the compound was confirmed by different spectroscopic data. The ¹H NMR spectrum of the compound shows a singlet at 1.51 ppm for the
twelve methyl protons and another broad singlet at 2.07 ppm assigned for two hydroxy protons. $^{13}$C NMR spectrum of the compound showed four peak at 31.0, 65.54, 66.27 and 83.93 ppm were assigned for methyl carbon and three quaternary carbon respectively.

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\begin{align*}
\text{Scheme 4.14: Synthesis of 2,7-dimethyl-oct-3,5-diyne-2,7-diol}
\end{align*}
\]

![Scheme 4.14: Synthesis of 2,7-dimethyl-oct-3,5-diyne-2,7-diol](image)

**Figure 4.13** $^1$H NMR spectrum of 2,7-diphenyl-oct-3,5-diyn-2,7-diol

![Figure 4.13](image)

**Figure 4.14:** $^{13}$C NMR spectrum of 2,7-dimethyl-oct-3,5-diyn-2,7-diol

![Figure 4.14](image)
4.14. Synthesis of 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene

Synthesis of the titled compound comprised of two steps, first step comprises of the synthesis of NaXH. In a two neck round bottom flask equipped with nitrogen inlet was added sodium borohydride in distilled water. After 10 minutes sulfur powder was added to the solution with open stirring. The color of the reaction mixture become yellow after 20 min, the solution of 2,7-dimethyl-octa-3,5-diyne-2,7-diol in methanol was added to the reaction mixture followed by the addition of silver acetate and the resulting mixture was allowed to stirred for 24 hours under nitrogen. After completion of the reaction the compound was extracted with ethyl acetate. The residue was purified by column chromatography over silica gel using hexanes/ethyl acetate as eluent to obtain pure compound as 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene. The structure of the compound was confirmed by using different spectroscopic techniques. The $^1$H NMR spectrum of the compound in CDCl$_3$ gave three peaks at $\delta$ 1.62 ppm, 2.08 ppm and 6.75 ppm for methyl protons, OH-protons and $\beta$-thiophenic protons respectively. In $^{13}$C NMR spectrum of the compound shows four peaks appeared at $\delta$ 31.01 ppm, 65.52 ppm, 121.46 ppm and 152.70 ppm for methyl carbon, quaternary carbon, $\beta$-thiophenic carbon and $\alpha$-thiophenic carbon respectively.
Figure 4.15: $^1$H NMR spectrum of 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene

Figure 4.16: $^{13}$C NMR spectrum of 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene
4.15. Synthesis of 5,5,10,10,15,15,20,20-octamethyl-22,24-dithiadiazuli porphyrinogen

Compound 5,5,10,10,15,15,20,20-octamethyl-22,24-dithiadiazuli porphyrinogen was synthesized by the reaction of 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene and azulene in dry dichloromethane. The reaction mixture was stirred for 15 minutes under nitrogen atmosphere. After 15 minutes BF$_3$OEt$_2$ was added and the reaction mixture protected from light and stirred for the next 1.5 hours in nitrogen atmosphere at room temperature. After completion of the reaction, the reaction mixture was extracted with chloroform (3×100 ml) and organic phase was combined washed with water (3×100 ml) and dried over anhydrous Na$_2$SO$_4$ and after evaporation of solvent the crude product was subjected to column chromatography. The structure of the compound was confirmed by different spectroscopic data. The $^1$H NMR spectrum of the compound showed doublet of doublet at $\delta$ 8.03 ppm for $2^1,3^1,12^1,13^1$ protons of azulene moiety and two triplets at $\delta$ 7.44 and 7.01 ppm for outer protons of azulene. Peak appeared at $\delta$ 6.77 ppm was assigned for $\beta$-thiophenic protons.

Scheme 4.16: Synthesis of 5,5,10,10,15,15,20,20-octamethyl-22,24-dithiadiazuli porphyrinogen
Figure 4.16: $^1$H NMR spectrum of 5,5,10,10,15,15,20,20-octamethyl-22,24-dithiadiazu porphyrinogen

Figure 4.17: UV-Visible spectrum of 5,5,10,10,15,15,20,20-octamethyl-22,24-dithiadiazu porphyrinogen

$X = 283.325928, Y = 0.654302103$
4.15.1. UV-Visible titrations of 5,5,10,10,15,15,20,20-octamethyl-22,24-dithiadiazuli porphyrinogen with mercuric perchlorate

The complexation studies of compound 5,5,10,10,15,15,20,20-octamethyl-22,24-dithiadiazuli porphyrinogen was carried out with UV-Visible spectroscopy in DMSO at room temperature.
Titrations were performed by adding aliquots of 20 µl of stock solutions (5.0 X 10^{-5} M) of cationic guests (mercuric perchlorate) to the investigated host (5.0 X 10^{-5} M). The UV-Visible spectrum of compound showed an absorption maximum at 283.32 nm. With the addition of mercuric perchlorate to the guest solution the absorption peak gradually increases in intensity giving rise to new peak at 260.88 nm.

4.16. Synthesis of 5,10,15,20-tetrakis(4-pyridyl)porphyrin

The equimolar quantity of pyridine-4-aldehyde and pyrrole in was added in refluxing propionic acid and the mixture was allowed to reflux for 3h, after completion of reaction, reaction mixture was cooled to room temperature and water was added into the reaction mixture and precipitate was filtered, the crude product was purified by column chromatography (Chloroform: methanol, 9:1) to afforded 5,10,15,20-tetrakis(4-pyridyl) porphyrin as purple solid^{62,63}. The appearance of Soret at 416 nm and the four Q-bands at 516, 553, 595 and 649 nm respectively had been observed in the UV-Visible spectrum of 5,10,15,20-tetrakis(4-pyridyl)porphyrin. The most upfield singlet at -3.01 ppm for internal pyrrolic NH protons, two doublets at 8.14 and 8.95 ppm (for eight protons) with coupling constant 4.40 Hz for aryl protons, a singlet at 8.80 for eight β-pyrrolic protons respectively have been observed in proton NMR spectrum of 5, 10, 15,20-tetrakis-(4-pyridyl)porphyrin.

![Scheme 4.17: Synthesis of 5,10,15,20-tetrakis(4-pyridyl)porphyrin](image-url)
4.17. Synthesis of 5,10,15,20-tetrakis(6-azulenyl)porphyrin

Tetra(4-pyridyl)porphyrin and 1-chloro-2,4-dinitrobenzene were dissolved in CHCl₃/MeOH (4/1) and the mixture was refluxed for 3 days. Diethylamine was added to the reaction mixture at room temperature and it was stirred further for 2 days. After 2 days the solvent was evaporated and the residue was dissolved in toluene. Sodium cyclopentadienide (2M THF solution) was added and then the mixture was refluxed for next 3 days. After the completion of the reaction, solvent was evaporated under reduced pressure and the product was separated by column chromatography on silica gel (CH₂Cl₂ as eluent). The product was recrystallized from methanol and dichloromethane. The appearance of Soret at 441.60 nm and the four Q-bands at 520, 547, 590 and 646 nm respectively had been observed in the UV-Visible spectrum of 5,10,15,20-tetrakis(6-azulenyl)porphyrin. The ¹H NMR spectrum of the compound showed most upfielded peak at δ -2.45 ppm for internal NH protons of porphyrin, three doublets appeared at 7.77, 8.22 and 8.65 ppm for azulene protons and a singlet appeared at 8.89 ppm for the eight β-pyrrolic protons.
Scheme 4.18: Synthesis of tetrakis-(6-azulenyl) porphyrin

1. O$_2$N$_2$Cl$_4$NO$_2$CH$_3$OH/CHCl$_3$ (1:4), refluxed, 3 days
2. Et$_2$NH, rt, 2 days
3. toluene, refluxed, 3 days

Figure 4.21: UV-Visible spectrum of tetrakis-(6-azulenyl) porphyrin
4.18. Synthesis of 5,10,15,20-tetra-(2-naphthyl)porphyrin

The equimolar quantity of 2-naphthaldehyde and pyrrole was added in refluxing propionic acid and reaction mixture was allowed to reflux for 3h, after completion of reaction, reaction mixture was cooled to room temperature and water was added into the reaction mixture and precipitate was filtered, the crude product was purified by column chromatography to afforded 5,10,15,20-tetrakis(2-naphthyl) porphyrin as purple solid. The appearance of soreset at 424 nm and the four Q-bands at 517, 554, 594 and 649 nm respectively had been observed in the UV-Visible spectrum of 5,10,15,20-tetrakis(2-naphthyl) porphyrin. The most upfield singlet at -2.58 ppm for internal pyrrolic NH protons, three multiplet at 7.68, 8.01 and 8.16 ppm (for eight protons, four protons and eight of naphthyl ring ) two singlets appeared at 8.67 and 8.44 for four naphthyl and eight β-pyrrolic protons respectively had been observed in proton NMR spectrum of 5,10,15,20-tetrakis(2-naphthyl) porphyrin.
Scheme 4.19: Synthesis of 5,10,15,20-tetrakis-(2-naphthyl)porphyrin

Figure 4.23: UV-Visible spectrum of 5,10,15,20-tetrakis-(2-naphthyl)porphyrin.
4.18.1. Comparative spectroscopic and emission properties of 5,10,15,20-tetrakis (6-azulenyl)porphyrin, 5,10,15,20-tetra-anthrylporphyrin and 5,10,15,20-tetra-2-naphthylporphyrin

The absorption spectra of 5,10,15,20-tetrakis(6-azulenyl)porphyrin, 5,10,15,20-tetra-anthrylporphyrin and 5,10,15,20-tetra-2-naphthylporphyrin synthesized were recorded in CH$_3$Cl and their comparative $\lambda_{\text{max}}$ and log $\varepsilon$ values are given in table 4.1. The soret band for the azulenylporphyrin found to be 20-25 nm red shifted in comparison to those of 5,10,15,20-tetra-2-naphthylporphyrin and 5,10,15,20-tetra-anthrylporphyrin. The Q-bands are also red-shifted by the 5-8 nm.

The Q-band intensity of 5,10,15,20-tetra-anthrylporphyrin was found to be very weak in comparison of 5,10,15,20-tetrakis(6-azulenyl)porphyrin and 5,10,15,20-tetra-2-naphthylporphyrin. The weakness of the Q-bands of the 5,10,15,20-tetra-anthrylporphyrin can be attributed to the bulkiness of the anthryl groups which does not effectively uplift the degeneracy of the HOMO orbital of the porphyrin ring.$^{65}$
Table 4.1: UV-Visible data of 5,10,15,20-tetrakis(6-azulenyl)porphyrin, 5,10,15,20-tetra-anthrylporphyrin and 5,10,15,20-tetra-(2-naphthyl) porphyrin

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\lambda_{\text{max}}$ (log $\varepsilon$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soret</td>
</tr>
<tr>
<td>5,10,15,20-tetrakis-(6-azulenyl) porphyrin</td>
<td>441 (5.35)</td>
</tr>
<tr>
<td>5,10,15,20-tetra-anthrylporphyrin</td>
<td>427 (5.40)</td>
</tr>
<tr>
<td>5,10,15,20-tetrakis-(2-naphthyl) porphyrin</td>
<td>424 (5.90)</td>
</tr>
</tbody>
</table>

The absorption and emission spectra of 5,10,15,20-tetrakis(6-azulenyl) porphyrin are quite different from that of 5,10,15,20-tetrakis-(2-naphthyl) porphyrin. The absorption bands of 5,10,15,20-tetrakis(6-azulenyl) porphyrin are significantly red-shifted with reduction in absorption coefficients compared to those of 5,10,15,20-tetrakis-(2-naphthyl) porphyrin. Thus, the absorption and fluorescence studies indicate that with the replacement of naphthyl group with azulenyl groups at the meso-positions, the electronic properties of the porphyrin are altered considerably. Fluorescence study of 5,10,15,20-tetrakis(6-azulenyl) porphyrin indicates that the presence of azulenyl groups at the meso-positions alters the energy levels of HOMO and LUMO and reduces the energy gap between them, resulting in significant changes in ground and excited-state properties.\(^{66}\)

Figure 4.25: Fluorescence maxima of (a) 5,10,15,20-tetra-(2-naphthyl) porphyrin (b) 5,10,15,20-tetrakis(6-azulenyl)porphyrin
The $^1$H NMR spectrum of free base porphyrin derivatives of $5,10,15,20$-tetrakis(6-azulenyl) porphyrin, $5,10,15,20$-tetra-anthrylporphyrin and $5,10,15,20$-tetra-2-naphthylporphyrin showed that the $\beta$-pyrrolic protons are more downfielded shifted in case of $5,10,15,20$-tetrakis(6-azulenyl)porphyrin in comparison of the anthryl and naphthyl-porphyrins.

Table 4.2: $^1$H NMR spectral data of $5,10,15,20$-tetrakis(6-azulenyl)porphyrin, $5,10,15,20$-tetra-anthrylporphyrin and $5,10,15,20$-tetra-2-naphthylporphyrin

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\delta$ (ppm)</th>
<th>$\beta$-pyrrolic protons</th>
<th>NH-protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5,10,15,20$-tetrakis(6-azulenyl) porphyrin</td>
<td>8.89</td>
<td>-2.45</td>
<td></td>
</tr>
<tr>
<td>$5,10,15,20$-tetra-anthrylporphyrin</td>
<td>8.19</td>
<td>-1.99</td>
<td></td>
</tr>
<tr>
<td>$5,10,15,20$-tetra-2-naphthyl porphyrin</td>
<td>8.84</td>
<td>-2.58</td>
<td></td>
</tr>
</tbody>
</table>

### 4.19. Conclusion

Core-modified carbaporphyrins were synthesized by the reaction of different alkyl ketones and azulene. The reaction of acetone with equimolar amount of azulene in the presence of acid gave the desired $5,5,10,10,15,15,20,20$-octamethyl calix$[4]$azulene in quantitative yields. Compound 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene was synthesized by the reaction of 2,7-dimethyl-octa-3,5-diyne-2,7-diol and sulfur powder in the presence of sodium borohydride and silver acetate. Further the reaction of 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene with azulene in the presence of acid gave the product $5,5,10,10,15,15,20,20$-octamethyl-22,24-dithiadiazuliporphyrinogen in quantitative yield. The complexation studies of the compound $5,5,10,10,15,15,20,20$-octamethyl-22,24-dithiadiazuliporphyrinogen with mercuric perchlorate was examined. $5,5,10,10,15,15,20,20$-octamethyl-22,24-ditelluro-diazuliporphyrinogen and $5,5,10,10,15,15,20,20$-octamethyl-22,24-diselenodiazuliporphyrinogen compounds were also synthesized using the above mentioned procedures. $5,10,15,20$-tetrakis(6-azulenyl) porphyrin was synthesized and their comparative spectroscopic studies were performed with $5,10,15,20$-tetra-anthrylporphyrin, $5,10,15,20$-tetra-2-naphthyl porphyrin and $5,10,15,20$-tetra-1-naphthyl porphyrin.
4.20. Experimental

All melting points are uncorrected and expressed in degree centigrade and were recorded on Thomas Hoover Unimelt capillary melting point apparatus. The infrared spectra were recorded on Perkin-Elmer FT-2000 spectrometer and $\nu_{\text{max}}$ are expressed in cm$^{-1}$. $^1$H NMR was recorded on Jeol-delta-400 spectrometer using tetramethylsilane (TMS) as an internal standard and chemical shifts (δ) are expressed in ppm. ESI-MS were recorded by LC-TOF (KC-455) mass spectrometer of Waters. The starting materials such as pyrrole, acetone, diethyl ketone, ethylmethyl ketone, cyclopentanone, cyclohexanone and methane sulphonic acid were purchased from Spectrochem Chemicals India. 2-naphthaldehyde and 1-naphthaldehyde were purchased from alfa-asar. The azulene and mercury (II) perchlorate were purchased from Aldrich. The pyrrole was distilled prior to use and the solvents used were of analytical reagent grade. The compounds synthesized were separated by column chromatography using neutral alumina and characterized by melting points, $^1$H NMR, $^{13}$C NMR, IR and ESI-MS techniques.


A solution of azulene (100 mg) and paraformaldehyde (96 mg) in dichloromethane (50 mL) was vigorously stirred with Florisil (10.0 g) for 90 min at room temperature. The mixture was diluted to approximately 200 ml with chloroform and the mixture was suction filtered to remove the Florisil. Solvent was evaporated under reduced pressure to gave the pure calix[4]azulene as a bluish-green solid. The crude product was recrystallized from benzene-hexane solution to give fluffy bluish-green crystals.

Physical state: bluish-green solid

$R_f$: 0.69 (1:1, Hexane: CHCl$_3$, v/v)

Yield: 80 mg (69%)

m.p.: 267 °C (lit$^6$7, 265-268 °C)

UV/Vis. (CHCl$_3$): 238, 246, 293, 502, 538 nm

$^1$H-NMR (400 MHz, CDCl$_3$): δ = 4.71 (s, 8H, CH$_2$), 6.91 (t, $J = 10$ Hz, 8Hₚ), 7.05 (4H, s), 7.44 (t, $J = 9.52$ Hz, 4H), 8.27 (d, $J = 9.52$ Hz, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 24.8, 121.2, 129.1, 133.0, 136.3, 137.6, 139.2.
4.20.2. Synthesis of 5,10,15,20-tetratolyl azuliporphyrinogen (28a)

A three necked 500 mL R.B. flask equipped with a stirring bar and nitrogen inlet was charged with freshly distilled dichloromethane (250 mL). Azulene (80 mg, 0.625 mmol) and p-tolyl-aldehyde (73.6 µL, 0.652 mmol) were added to the solution and nitrogen was bubbled through the stirred reaction mixture for 15 min. 1-methyl-3-(4-sulfobutyl)-imidazolium methyl sulfonate (20µL) was then added to the solution and the reaction was protected from light and stirred for 45 minutes. After completion of the reaction, solvent was removed under reduced pressure. The crude residue was chromatographed on a basic alumina column using dichloromethane as eluent. The porphyrinogens mixture was eluted as a first deep blue fraction, which contained mostly isomers αααα and ααββ. ααββ was insoluble in acetone giving blue powder, when concentrated solution of isomers mixture in dichloromethane was treated with acetone and dichloromethane. Acetone solution contained apart from αααα-isomer small amount of αααβ which was separated by column chromatography using neutral alumina and dichloromethane as eluent. The first, greenish fraction contained αααα-isomer.

**Physical State:** greenish solid

**Yield:** 496 mg, 95%

**1H-NMR (400 MHz, CDCl₃):**

- **αααα-isomer:** δ 8.08 (d; 8H; 2₁,3₁,7₁,8₁,12₁,13₁,17₁,18₁), 7.29 (t; 4H; 2₂,7₂,12₂,17₂;), 6.92 (d; 8H; o-Tol), 6.88 (d; 8H; m-Tol), 6.77 (t; 8H; 2₂,3₂,7₂,8₂,12₂,13₂,17₂,18₂;), 6.71 (s; 4H; 21, 22, 23, 24); 6.52 (s; 4H; 5,10,15,20), 2.23 (s; 12H; CH₃-p-Tol).

- **ααββ-isomer:** δ 8.17 (d; 4H; 2₁,3₁,12₁,13₁), 8.02 (d; 4H; 2₁,3₁,12₁,13₁), 7.46 (t; 2H; 2₂,12₂;), 7.33 (t; 2H; 7₂,17₂;), 6.92 (t; 4H; 2₂,3₂,12₂,13₂;), 6.81 (t; 4H; 2₂,3₂,7₂,18₂;), 6.80 (d; 8H; o-Tol), 6.72 (d; 8H; m-Tol), 6.61 (s; 4H; 21, 23), 6.59 (s; 4H; 22), 6.52 (s; 4H; 5,10,15,20), 2.16 (s; 12H; p-Tol(-CH₃)).

- **αααβ-isomer:** δ 8.41 (d; 2H; 2₁, 3₁), 8.05 (dd; 4H; 7₁,8₁,17₁,18₁), 7.92 (d; 2H; 12₁, 13₁), 7.15 (s; H, 24) 6.72 (s; 2H; 21, 23), 6.51 (s; H; 22), 6.82 (m; 16H, phenyl ring), 2.16 (s; 12H; -CH₃).
4.20.3. Synthesis of 5,10,15,20-tetra-(4-tert-butylphenyl)-azuliporphyrinogen (28b)

**Physical State:** greenish solid

**Yield:** 529 mg, 96%

1H-NMR (400 MHz, CDCl₃): δ _aaaa_-isomer: 8.03 (d; 8H; 2₁,3₁,7₁,8₁,12₁,13₁,17₁,18₁), 7.13 (t; 4H; 2₃,7₃,12₃,17₃), 6.97 (d; 8H; o-phenyl), 6.73 (d; 8H; m-phenyl), 6.65 (t; 8H; 2₂,3₂,7₂,8₂,12₂,13₂,17₂,18₂), 6.42 (s; 4H; 2₁, 2₂, 2₃, 2₄); 6.21 (s; 4H; 5,10,15,20), 2.32 (s; 3₆H; C(CH₃)₃).

1H-NMR (400 MHz, CDCl₃): δ _ααββ_-isomer: 8.23 (d; 4H; 2₁,3₁,12₁,13₁), 8.12 (d; 4H; 7₁,8₁,17₁,18₁), 7.46 (t; 2H; 2₃, 12₃), 7.36 (t; 2H; 7₃,17₃), 6.95 (t; 4H; 2₂,3₂,12₂,13₂), 6.79 (t; 4H; 7₂,8₂,17₂,18₂), 6.75 (d; 8H; o-phenyl), 6.69 (d; 8H; m-phenyl), 6.57 (s; 4H; 2₁, 2₂, 2₃, 2₄), 6.52 (s; 4H; 2₁, 2₂, 2₃, 2₄), 6.46 (s; 4H; 5,10,15,20), 2.33 (s; 1₂H; 3₆H; C(CH₃)₃).

1H-NMR (400 MHz, CDCl₃): δ _ααβα_-isomer: 8.56 (d; 2H; 2₁, 3₁), 8.15 (dd; 4H; 7₁,8₁,17₁,18₁), 7.93 (d, 2H, 12₁, 13₁), 7.23 (s, H, 2₄) 6.76 (s; 2H, 2₁, 2₃), 6.53 (s; H; 2₂), 6.90 (m; 1₆H, phenyl ring), 2.31 (s; 1₂H; -CH₃).

4.20.4. Synthesis of 5,10,15,20-tetraphenyl azuliporphyrinogen (28c)

**Physical State:** greenish solid

**Yield:** 432 mg, 92%

1H-NMR (400 MHz, CDCl₃): δ _aaaa_-isomer: 8.12 (d; 8H; 2₁,3₁,7₁,8₁,12₁,13₁,17₁,18₁), 7.25 (t; 4H; 2₃,7₃,12₃,17₃), 6.86 (m, 1₆H, phenyl), 6.59 (t; 8H; 2₂,3₂,7₂,8₂,12₂,13₂,17₂,18₂), 6.32 (s; 4H; 2₁, 2₂, 2₃, 2₄), 6.03 (s; 4H; 5,10,15,20).

1H-NMR (400 MHz, CDCl₃): δ _ααββ_-isomer: 8.19 (d; 4H; 2₁,3₁,12₁,13₁), 8.07 (d; 4H; 7₁,8₁,17₁,18₁), 7.41 (t; 2H; 2₃, 12₃), 7.29 (t; 2H; 7₁,17₃), 6.83 (t; 4H; 2₂,3₂,12₂,1₃₂), 6.66 (t; 4H; 7₂,8₂,17₂,1₈₂), 6.59 (m, 1₆H, phenyl), 6.53 (s; 4H; 2₁, 2₂, 2₃, 2₄), 6.46 (s; 4H; 2₁, 2₂, 2₃, 2₄), 6.33 (s; 4H; 5,10,15,20).

1H-NMR (400 MHz, CDCl₃): δ _ααβα_-isomer: 8.52 (d; 2H; 2₁, 3₁), 8.12 (dd; 4H; 7₁,8₁,17₁,18₁), 7.83 (d; 2H, 12₁, 13₁), 7.19 (s, H, 2₄), 6.90 (m; 1₆H, phenyl ring), 6.73 (s; 2H, 2₁, 2₂, 2₃, 2₄), 6.56 (s; H; 2₂).
4.20.5. Synthesis of 5,10,15,20-tetra(4-chlorophenyl) azuliporphyrinogen (28d)

Physical State: greenish solid

Yield: 459 mg, 91%

\[ ^1H-NMR \ (400 \ MHz, CDCl_3): \delta \ \text{aaaa-isomer:}\ 8.26 \ (d; \ 8H; 2^1,3^1,7^1,8^1,12^1,13^1,17^1,18^1), \]
7.56 (d; 8H; o-phenyl), 7.31 (t; 4H; 2^3,7^3,12^3,17^3), 7.21 (d; 8H; m-phenyl), 6.67 (t; 8H;
2^2,3^2,7^2,8^2,12^2,13^2,17^2,18^2), 6.42(s; 4H; 21, 22, 23, 24); 6.17 (s; 4H; 5,10,15,20).

\[ ^1H-NMR \ (400 \ MHz, CDCl_3): \delta \ \text{aaββ-isomer:}\ 8.30 \ (d; \ 4H; 2^1,3^1,12^1,13^1), \ 8.11 \ (d;
4H; 7^1,8^1,17^1,18^1), \ 7.76 \ (t; \ 2H; 2^3,12^3), \ 7.52 \ (d; \ 8H; o-phenyl), \ 7.36 \ (t; \ 2H; 7^3,17^3),
6.96 (t; 4H; 2^2,3^2,12^2,13^2), \ 6.90 \ (d; \ 8H; m-phenyl), \ 6.77 \ (t; \ 4H; 7^2,8^2,17^2,18^2), \ 6.51 \ (s;
4H; 21, 22, 23), \ 6.39 \ (s; \ 4H; 22, 24), \ 6.33 \ (s; \ 4H; 5,10,15,20)
\]

\[ ^1H-NMR \ (400 \ MHz, CDCl_3): \delta \ \text{ααββ-isomer:}\ 8.51(d; \ 2H; 2^1,3^1,12^1,13^1), \ 8.12 \ (dd; \ 4 \ H;
7^1,8^1,17^1,18^1), \ 7.96 \ (d, \ 2H, 12^1,13^1), \ 7.32 \ (s, \ H, 24), \ 6.93 \ (m; \ 16H, \ phenyl), \ 6.75 \ (s;
2H, 21, 23), \ 6.47 \ (s; \ H; 22).
\]

4.20.6. Synthesis of 5,5,10,10,15,15,20,20-octamethyl azuliporphyrinogen (30a)

Azulene (104mg, 0.81 mmol) and acetone (60 µl, .81 mmol) was added in freshly
distilled dry dichloromethane and the solution was stirred for 15 min in nitrogen
atmosphere. BF$_3$OEt$_2$ (40µL) was then added to the solution and the reaction was
protected from light and stirred for another 1 hour. After completion of the reaction
the solvent was removed under reduced pressure. The crude reaction mixture was
chromatographed on basic alumina, eluting with chloroform: hexane (2:8, v/v) gave
pure compound as a green solid.

Physical state: green solid

R$_f$: 0.57 (1:1, Hexane: CHCl$_3$, v/v)

Yield: 96 mg (91%)

m.p.: 267°C

\[ ^1H-NMR \ (400 \ MHz, CDCl_3): \delta \ = \ 1.29 \ (s, \ 24H, \ CH_3), \ 5.86 \ (8H, \ s), \ 6.95 \ (t, \ J = 9.52
Hz, 8H), \ 7.39 \ (t, \ J = 9.52 \ Hz, \ 4H), \ 8.45 \ (d, \ J = 9.56 \ Hz, \ 8H)
\]

\[ ^13C\ NMR \ (100 \ MHz, CDCl_3) \delta \ = \ 29.6, \ 53.96, \ 126.09, \ 131.51, \ 133.0, \ 138.32, \ 139.55,
141.21.
\]
4.20.7. Synthesis of 5,5,10,10,15,15,20,20-octaethyl azuliporphyrinogen (30b)

**Physical state:** green solid

R_f: 0.55 (1:1, Hexane: CHCl_3, v/v)

**Yield:** 89 mg (79%)

m.p.: ≤250° C

^1_H-NMR (400 MHz, CDCl_3): δ = 0.85 (t, 24H, -CH_3), 1.75 (q, 16H, -CH_2), 6.10 (s, 8H), 6.79 (t, J = 9.67 Hz, 8H), 7.37 (t, J = 9.67 Hz, 4H), 8.39 (d, J = 9.56 Hz, 8H)

^13_C NMR (100 MHz, CDCl_3) δ = 23.46, 35.23, 57.01, 122.33, 128.91, 134.70, 135.63, 137.6, 138.99.

4.20.8. Synthesis of 5,5,10,10,15,15,20,20-tetrakis spirocyclohexyl azuliporphyrinogen (30c)

**Physical state:** green solid

R_f: 0.61 (1:1, Hexane: CHCl_3, v/v)

**Yield:** 99 mg (93%)

^1_H-NMR (400 MHz, CDCl_3): δ = 1.40-1.47 (24H, m), 1.89-1.92 (16H, m), 5.91 (8H, s), 7.03 (t, J = 9.52 Hz, 8H), 7.51 (t, J = 9.52 Hz, 4H), 8.41 (d, J = 9.56 Hz, 8H)

^13_C NMR (100 MHz, CDCl_3) δ = 22.69, 25.96, 37.13, 39.55 (hexyl C), 53.96, 121.2, 129.1, 133.0, 136.3, 137.6, 139.2.

4.20.9. Synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)azuliporphyrin (33a)

Azulene (50 mg, 0.39 mmol), 4-chlorobenzaldehyde (220 mg, 1.56 mmol) and pyrrole (81 mg, 1.17 mmol) were dissolved in chloroform (480 mL) and the resulting solution purged with nitrogen for 10 min. A 10% solution of boron trifluorodiethyl ether in chloroform (0.3 mL) was then added and the reaction stirred for 16 h under nitrogen atmosphere in the dark. DDQ (200 mg) was added and the solution stirred for an additional 1 h. The mixture was washed with water and saturated NaHCO_3 solution, back extracting with chloroform at each stage, and the combined organic solutions dried over sodium sulfate, filtered and the solvents evaporated under reduced pressure. The residue was purified by column chromatography over basic alumina,
eluting with 20:80 hexanes/CH₂Cl₂. Tetrakis(4-chlorophenyl)porphyrin eluted initially followed by trace amounts of carbaporphyrins, and then a deep reddish-brown fraction corresponding to the azuliporphyrin product was collected. Further purification by flash chromatography over neutral alumina and eluting with a gradient of CH₂Cl₂/CHCl₃ gave lustrous green powder.

4.20.10. Synthesis of 5,10,15,20-tetra (4-chlorophenyl)-porphyrin (32a)

**UV/Visible (CHCl₃, nm):** 421, 515, 549, 589, 647

**¹H-NMR (400 MHz, CDCl₃):** δ -2.9 (brs, 2H, NH), 7.66 (d, 8H, Ar₉H), 8.04 (d, 8H, Ar₈meta-H), 8.76 (s, 8H, β-pyrrolic).

4.20.11. Synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)azuliporphyrin (33a)

**Yield:** 36 mg, (15%)

**m.p.** 281 °C. (lit-282-285 °C)

**UV/Visible (CHCl₃, nm):** 425 (4.56), 486 (4.61), 555 (4.77), 664 (4.21), 731 (3.79), 825 (3.99).

**UV/Visible (1% TFA/CHCl₃, nm):** 331 (4.38), 410 (4.73), 467 (4.83), 523 (5.02), 618 (4.01), 683 (3.94).

**¹H-NMR (400 MHz, CDCl₃):** δ = 3.02 (s, 1 H), 4.58 (s, 1 H), 6.87 (t, J = 9.92 Hz, 2H), 7.09 (d, J = 4.8 Hz, 2H), 7.16 (dd, 4H), 7.28 (s, 4H), 7.31 (t, J = 9.6 Hz, 2H), 7.61 (s, 4H), 8.08 (d, J = 9.8 Hz, 2 H).

**¹³C NMR (100 MHz, CDCl₃):** δ = 114.5, 123.2, 126.6, 127.9, 128.1, 129.3, 130.4, 134.5, 134.9, 135.1, 135.9, 138.9, 139.1, 139.8, 140.1, 141.0, 144.0, 155.6, 165.5.


Compound 32b and 33b was prepared by the same procedure applied for the synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)azuliporphyrin 33a.

5,10,15,20-Tetraphenyl porphyrin (32b)

**Physical state:** purple solid

**Yield:** 106 mg (15%)

185
$R_f$: 0.66 (1:2, v/v, Petroleum ether: CHCl$_3$)

$\text{mp}$: $>300$ °C, (lit$^{68}$ mp 300 °C)

UV-Visible $[\lambda_{\text{max}} \text{CDCl}_3, (\varepsilon \times 10^{-4}, \text{cm}^{-1}, \text{M}^{-1})]$: 416 (2.50), 514 (1.8), 548 (0.77), 590 (0.54), 644 (0.46).

$^1\text{H} \text{ NMR} \quad \delta \ (400\text{MHz}, \text{CDCl}_3)\quad \delta = -2.59\text{ (bss, 2H, NH)}, \quad 7.74\text{ (d, } J = 7.36 \text{ Hz, 2H, aryl H)}, \quad 8.21-8.23\text{ (m, 3H, aryl H)}, \quad 8.84\text{ (s, 2H, } \beta\text{-pyrrolic-H)}.$

4.20.13. Synthesis of 5,10,15,20-tetraphenylazuliporphyrin (33b)

Physical state: lustrous green powder

Yield: (29 mg, 10%)

$R_f$: 0.32 (1:2, v/v, Petroleum ether: CHCl$_3$)

$\text{mp}$: $>300$ °C

UV-Visible $[\lambda_{\text{max}} \text{CDCl}_3, (\varepsilon \times 10^{-4}, \text{cm}^{-1}, \text{M}^{-1})]$: 439 (5.05), 545 (4.19), 594 (4.00), 744 nm (3.795).

$^1\text{H} \text{NMR} \ (400 \text{MHz}, \text{CDCl}_3): \ 3.35\text{ (s, 1H)}, \ 5.10\text{ (br s, 1H)}, \ 6.92\text{ (t, } J = 10 \text{ Hz, 2H)}, \ 7.25\text{ (t, } J = 9.72 \text{ Hz, 1H)}, \ 7.32\text{ (d, } J = 4.6 \text{ Hz, 2H)}, \ 7.52-7.60\text{ (m, 6H)}, \ 7.62\text{ (s, 2H)}, \ 7.63-7.68\text{ (m, 8H)}, \ 7.81-7.84\text{ (m, 4H)}, \ 7.95-7.97\text{ (m, 6H)}.$


Compound 32c and 33c was prepared by the same procedure applied for the synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)azuliporphyrin 33a.

Synthesis of 5,10,15,20-Tetra-tolyl porphyrin (32c)

Physical state: purple solid

$R_f$: 0.45 (CHCl$_3$)

Yield: 97mg (10%)

m.p.: $>300$ °C

UV-Visible ({$\lambda_{\text{max}} \text{CHCl}_3$}) : 418.56, 516.33, 556.67, 596.62, 649.75 nm.

$^1\text{H} \text{ NMR} \ (400\text{MHz}, \text{CDCl}_3, 25^\circ\text{C})\quad \delta = -2.77\text{ (brs, 2H, NH)}, \quad 3.65\text{ (s, 12H, } -\text{CH}_3), \quad 7.23\text{ (d, } J = 8.04 \text{ 2H, Ar-H)}, \quad 8.07\text{ (d, } J = 8.04 \text{ 2H, Ar-H)}, \quad 8.83\text{ (s, 2H, } \beta\text{-pyrrole CH).}$
$^{13}$C NMR (100 MHz, CDCl$_3$): 29.11, 115.55, 123.51, 127.03, 127.39, 127.56, 127.64, 128.32, 129.26, 130.28, 130.63, 133.80, 134.95, 135.17, 135.67, 138.99, 139.22, 139.63, 141.54, 142.81, 144.13, 155.66, 165.72.

4.20.15. Synthesis of 5,10,15,20-tetra-tolyl azuliporphyrin (33c)

Physical state: lustrous green powder

Yield: (19 mg, 8%)

$R_f$: 0.35 (CHCl$_3$)

mp: $>300$ °C


$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.55 (s, 6H, CH$_3$), 2.60 (s, 6H, CH$_3$), 3.40 (s, 1H, CH), 5.16 (s, 1H, NH), 6.94 (t, $J = 9.8$ Hz, 2H), 7.25 (t, $J = 9.6$ Hz, 1H), 7.31 (d, $J = 4.8$ Hz, 2H), 7.37 (d, $J = 7.6$ Hz, 4H), 7.45 (d, $J = 8$ Hz, 4H), 7.60 (s, 2H), 7.65-7.71 (m, 4H), 7.83 (d, $J = 7.6$ Hz, 4H), 7.94 (d, $J = 4.4$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$, TMS): $\delta = 21.59, 21.75, 115.32, 123.50, 127.17, 128.25, 128.43, 129.11, 130.10, 130.35, 133.69, 134.91, 135.76, 136.92, 138.30, 138.69, 138.99, 139.38, 139.95, 144.14, 155.65, 165.76 ppm.

4.20.16. Synthesis of 5,10,15,20-tetrakis(4-tert-butylphenyl)azuliporphyrin:

Synthesis of 5,10,15,20-Tetrakis(4-tert-butylphenyl)porphyrin (32d)

Physical state: purple solid

$R_f$: 0.51 (CHCl$_3$)

Yield: 97mg (10%)

m.p.: $>300$ °C

UV-Visible ($\lambda_{max}$ CHCl$_3$): 418.56, 516.33, 556.67, 596.62, 649.75 nm

$^1$H NMR (400MHz, CDCl$_3$, 25°C) $\delta =$ -2.77 (brs, 2H, NH), 2.79 (s, 36H, -CH$_3$), 7.20 (d, $J = 8.04$ 2H, Ar-H), 8.01 (s, 2H, $\beta$-pyrrole CH), 8.13 (d, $J = 8.04$ 2H, Ar-H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 115.55, 123.51, 127.03, 127.39, 127.56, 127.64, 128.32, 129.26, 130.28, 130.63, 133.80, 134.95, 135.17, 135.67, 138.99, 139.22, 139.63, 141.54, 142.81, 144.13, 155.66, 165.72.
4.20.17. Synthesis of 5,10,15,20-tetrakis(4-tert-butylphenyl)azuliporphyrin (33d)

Physical state: lustrous green powder

Yield: (23 mg, 10%)

R<sub>f</sub>: 0.35 (CHCl<sub>3</sub>)

mp: >300 °C

UV/Visible (1% TFA/CHCl<sub>3</sub>, nm): 332 (4.22), 366 (4.30), 419 (4.61), 465 (4.25), 527 (4.19).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.79 (s, 6H), 2.65 (s, 6 H), 3.51 (s, 1 H), 5.52 (s, 1 H), 6.97 (t, J = 9.8 Hz, 2H), 7.23 (t, J = 9.6 Hz, 1H), 7.36 (d, J = 4.8 Hz, 2 H), 7.42 (d, J = 7.6 Hz, 4 H), 7.54 (d, J = 8 Hz, 4 H), 7.67 (s, 2 H), 7.95-8.11 (m, 4 H), 8.26 (d, J = 7.6 Hz, 4 H), 8.37 (d, J = 4.4 Hz, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ = 21.59, 21.75, 22.01, 115.32, 123.50, 127.17, 128.25, 128.43, 129.11, 130.10, 130.35, 133.69, 134.91, 135.76, 136.92, 138.30, 138.69, 138.99, 139.38, 139.95, 144.14, 155.65, 165.76 ppm.

4.20.18. Synthesis of 5,10,15,20-tetra-(4-tert-butyl-phenyl)-22,24-dithiadiazuliporphyrinogen

Synthesis of 2,5-bis[1-(4-tert-butylphenyl)-1-hydroxymethyl]thiophene (36a)

Thiophene (1.5 g, 16.1 mmol) was added to a solution of n-BuLi (22 mL of 1.6 M in hexanes, 36 mmol) and TMEDA (5.6 mL, 37 mmol) in 50 mL of hexanes under an Ar atmosphere. The reaction mixture was heated at reflux for 1 h, cooled to ambient temperature, and transferred via a cannula to a pressure-equalizing dropping funnel. This dilithiothiophene suspension was then added dropwise to a solution of 4-tert-butylbenzaldehyde (5.1 g, 32 mmol) in of anhydrous THF 50 mL cooled to 0 °C, which had been degassed with Ar for 15 min. After the addition was complete, the mixture was warmed to ambient temperature, NH<sub>4</sub>Cl 8 mL (aqueous 1 M solution) was added, and the organic phase was separated. The aqueous phase was extracted with dichloromethane (4×50 mL). The combined organic extracts were washed with water (3 × 50 mL) and brine (300 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give yellow oil. The
crude product was precipitated by the slow addition of hexanes to crude solution of 2,5-
bis[1-(4-tert-butyl-phenyl)-1-hydroxymethyl]thiophene to give 3.92 g (59%) of 2,5-
bis[1-(4-tert-butyl-phenyl)-1-hydroxymethyl]thiophene as white amorphous powder.

**Physical state:** white amorphous powder.

**Rf:** 0.47 (9:1, CHCl₃: MeOH, v/v)

**Yield:** 3.92 (59%)

**mp:** 144 °C (lit. mp 69)

**IR (KBr pellet, cm⁻¹):** 3377 (br, OH), 2963, 2867, 1395, 1265, 1204, 1107, 1009, 815, 779;

**¹H NMR (400MHz, CDCl₃, 25°C) δ =** 2.32 (s, 18H, -C(CH₃)₃) 2.13 (s 2H, -OH) 5.93 (s, CH) 6.69 (s, 2H, β-thiophene CH ) 7.33-738 (m, 8H, aryl CH)

**¹³C NMR (100MHz, CDCl₃, 25°C) δ =** 31.31(CH₃) 34.55 (C(CH₃)₃) 72.44 (CH) 124.31 (β-thiophene CH) 125.44-125.99 (aryl CH) 139.88 (Cq) 148.05 (C- C(CH₃)₃) 151.00 (α-thiophene CH).

### 4.20.19. Synthesis of 2,5-bis[1-(4-methylphenyl)-1-hydroxymethyl]thiophene (36b)

2,5-Bis[1-(4-methylphenyl)-1-hydroxymethyl]thiophene was prepared as described for
the preparation of (50) using thiophene (1.3 g, 16 mmol), n-BuLi (22 mL of 2.5 M in
hexanes, 55 mmol), TMEDA (8.7 mL, 55 mmol), and 4-tolualdehyde (3.7 g, 30 mmol)
Product yield was (1.4 g 30%) as white amorphous powder.

**Physical state:** white amorphous powder.

**Rf:** 0.52 (9:1, CHCl₃: MeOH, v/v)

**Yield:** 1.4 g (30%)

**IR (KBr pellet, cm⁻¹):** 3363 (br, OH), 2953, 2868, 1037;

**¹H NMR (400MHz, CDCl₃, 25°C) δ =** 2.18 (s, 6H, CH₃) 2.51 (s, 2H, -OH) 5.73 (s, 2H, CH) 6.61 (s, 2H, β-thiophene CH) 7.01 (d, J = 8.08 Hz, 4H, aryl -CH), 7.27 (d, J = 8.04 Hz, 4H, Ar-H)

**¹³C NMR (100MHz, CDCl₃, 25°C) δ =** 21.34 (CH₃) 82.32 (CH) 125.34 (β-thiophene CH) 127.21-127.82 (aryl CH) 129.01 (Cq) 139.81 (Cq) 148.57 (α-thiophene CH).
4.20.20. Synthesis of 2,5-bis[1-(4-methoxyphenyl)-1-hydroxymethyl]thiophene(36c)

2,5-Bis[1-(4-methoxyphenyl)-1-hydroxymethyl]thiophene was prepared as described for the preparation of (50) using thiophene (1.3 g, 16 mmol), n- BuLi (22 mL of 2.5 M in hexanes, 55 mmol), TMEDA (8.7 mL, 55 mmol), and 4-tolualdehyde (5.6 g, 30 mmol) Product yield was 3 g (50%) as white amorphous powder.

Physical state: white solid

Rf: 0.37 (8:2, CHCl₃: MeOH, v/v)

Yield: 3.0 g (50%)

IR (KBr pellet, cm⁻¹): 3343 (br, OH), 2948, 2844, 1053;

¹H NMR (400MHz, DMSO, 25°C) δ = 3.68 (s, 6H, -OCH₃) 5.71 (s 2H, -OH) 5.95 (s, CH) 6.56 (s, 2H, β-thiophene CH) 6.81 (d, J = 8.04, 4H, aryl CH) 7.22 (d, J = 8.40, 4H, aryl CH)

¹³C NMR (100MHz, CDCl₃, 25°C) δ =  55.08 (CH) 70.38 (-OCH₃) 113.47 (aryl C) 122.75 (β-thiophene C) 127.32 (aryl C) 137.09 (Cq aryl) 149.50 (α-thiophene C) 158.37 (Cq aryl).

4.20.21. Synthesis of 2,5-bis[1-(4-tert-butyl-phenyl)-1-hydroxymethyl]furan (36d)

Furan (2 mL, 29.3 mmol) was added to the solution of TMEDA (8.78 mL, 58.6 mmol) in 50 mL of hexanes under an Ar atmosphere. The reaction mixture was heated at reflux for 1 h, cooled to ambient temperature, and transferred via a cannula to a pressure-equalizing dropping funnel. This dilithiothiophene suspension was then added dropwise to a solution of 4-tert-butylbenzaldehyde (9.8 mL, 58 mmol) in 50 mL of anhydrous THF cooled to 0 °C, which had been degassed with Ar for 15 min. After the addition was complete, the mixture was warmed to ambient temperature, 8 mL of NH₄Cl (aqueous 1 M solution) was added, and the organic phase was separated. The aqueous phase was extracted with dichloromethane (4×50 mL). The combined organic extracts were washed with water (3 × 50 mL) and brine (300 mL), dried over Na₂SO₄, and concentrated to give yellow oil. The crude product was precipitated by the slow addition of hexanes to crude solution of 2,5-bis[1-(4-tert-butyl-phenyl)-1-hydroxymethyl]furan to give 1.5 g (30%) of 2,5-bis[1-(4-tert-butyl-phenyl)-1-hydroxymethyl]furan as white amorphous powder.
Physical state: white amorphous powder.

**R**$_f$: 0.57 (9:1, CHCl$_3$; MeOH, v/v)

**Yield:** 1.5 g (30%)

**IR (KBr pellet, cm$^{-1}$):** 3354 (br, OH), 2942, 2856, 1034

$^1$H NMR (400 MHz, CDCl$_3$, 25$^\circ$C) $\delta$ = 1.30 (s, 18H, (C(CH$_3$)$_3$)), 2.31 (s 2H, -OH) 5.74 (s, CH) 5.97 (s, 2H, $\beta$-furanic CH ) 7.33 (m, 8H, aryl CH)

$^{13}$C NMR (100 MHz, CDCl$_3$, 25$^\circ$C) $\delta$ = 31.40 (CH$_3$), 34.51 (Cq) 69.58 (CH) 107.92 ($\beta$-furan-CH) 125.08, 126.82 (aryl CH) 137.63 (Cq) 150.86 (Cq) 155.97 ($\alpha$-furanic CH).

4.20.22. Synthesis of 2,5-bis[1-(4-tolyl-phenyl)-1-hydroxymethyl]furan (36e)

$^1$H-NMR (400 MHz, CDCl$_3$): 7.23 (d, 2H, Ar$_{ortho}$-H), 7.06 (d, 2H, Ar$_{meta}$-H), 5.46 (s, 2H, $\beta$-Furan), 5.13 (s, 2H, CH(OH)), 3.84 (brs, 2H, OH), 1.5 (s, 6H, CH$_3$).

4.20.23. Synthesis of 5,10,15,20-tetra-(4-tert-butyl)-22,24-dithiadiazuliporphyrinogen (37a)

2,5-Bis[(4-tert-buty1)hydroxymethyl]thiophene (0.6 mmol, 170.7 mg) and azulene (0.6 mmol, 78 mg) were added to dry CH$_2$Cl$_2$ (250 mL) under nitrogen atmosphere. After 15 minutes of stirring Et$_2$O·BF$_3$ (20 µL) was added and the reaction mixture protected from light and stirred for the next 40 minutes. The mixture was evaporated under reduced pressure and then subjected to chromatography over basic alumina eluting with dichloromethane. The porphyrinogen was eluted as a deep blue fraction. After chromatography, the product was precipitated from dichloromethane as blue powder/crystals. Further the isomers were separated through preparative chromatography using chloroform:hexane (1:1, v/v) as a eluting solvent.

4.20.23.1. $\alpha\alpha\alpha\alpha$ 5,10,15,20-tetra-(4-tert-butyl)-22,24-dithiadiazuliporphyrinogen

$^1$H NMR (400 MHz, CDCl$_3$, 25$^\circ$C) $\delta$ = 8.22 (d, $J$ = 9.52 Hz, 2$^1$, 3$^1$, 12$^1$, 13$^1$ 4H); 7.69 (s, 2H, 21,23-H); 7.31 (t, 2$^3$, 12$^3$-H, $J$ = 10.1 Hz, 2H); 6.99 (m, Ar-H), 6.78 (t, 2$^2$, 3$^2$, 12$^2$, 13$^2$, $J$ = 9.9 Hz, 4H); 6.41 (s, 4H, 7,8-H, 17,18-H); 6.14 (s, 4H, 5,10,15,20-H); 2. 23 (s, 36H, t-butyl).
4.20.23.2. ααββ 5,10,15,20-tetra-(4-tert-butyl)-22,24-dithiadiazuliporphyrinogen

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 8.23 (d, $2^1\;\text{J}=9.5$ Hz, 4H); 8.16 (d, $7^1,8^1,17^1,18^1\;\text{J}=9.5$ Hz, 4H); 7.83 (d, $J=2.29$ Hz, 2H, 21,23-H); 7.42 (t, $2^3\;\text{J}=10.1$ Hz, 2H,); 7.18 (brs, 16H, m-Tol, o-Tol), 6.98 (t, $2^2\;\text{J}=9.7$ Hz, 4H); 6.18 (s, 4H, 5,10,15,20-H); 2.31 (s, 18H, tert-butyl-CH$_3$); 2.29 (s, 18H, tert-butyl-CH$_3$).

4.20.23.3. αααβ 5,10,15,20-tetra-(4-tert-butyl)-22,24-dithiadiazuliporphyrinogen

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 8.42 (d, $2^1\;\text{J}=9.6$ Hz, 2H); 8.16 (dd, $7^1,8^1,17^1,18^1\;\text{J}=9.2$ Hz, 4H); 7.99 (d, $12^1\;\text{J}=9.6$ Hz, 2H); 7.61 (s, 2H, 21,23-H); 7.42 (t, $2^3\;\text{J}=10.1$ Hz, 2H); 7.18 (brs, 16H, m-Tol, o-Tol), 6.98 (t, $2^2\;\text{J}=9.7$ Hz, 4H); 6.49 (s, 4H, 7,8-H, 12,13-H); 6.07 (s, 4H, 5,10,15,20-H); 2.29 (s, 18H, tert-butyl-CH$_3$); 2.20 (s, 18H, tert-butyl-CH$_3$).

4.20.24. Synthesis of 5,10,15,20-tetra-4-tolyl-22,24-dithiadiazuliporphyrinogen (37b)

4.20.24.1. αaaaα 5,10,15,20-tetra-4-tolyl-22,24-dithiadiazuliporphyrinogen

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 8.18 (d, $2^1\;\text{J}=9.6$ Hz, 2H, 21,23-H); 7.46 (t, $2^3\;\text{J}=10.2$ Hz, 2H,); 7.19 (d, $8^1\;\text{J}=9.6$ Hz, 2H, o-Ar), 6.98 (d, $8^1\;\text{J}=9.6$ Hz, 2H, m-Ar), 6.76 (t, $2^2\;\text{J}=9.7$ Hz, 4H,); 6.45 (s, 4H, 7,8-H, 17,18-H); 6.14 (s, 4H, 5,10,15,20-H); 1.37 (s, 12H, CH$_3$).

4.20.24.2. ααββ 5,10,15,20-tetra-4-tolyl-22,24-dithiadiazuliporphyrinogen

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 8.16 (d, $2^1\;\text{J}=9.2$ Hz, 4H); 8.02 (d, $7^1,8^1,17^1,18^1\;\text{J}=9.6$ Hz, 4H); 7.91 (s, 2H, 21,23-H); 7.36 (t, $2^3\;\text{J}=9.9$ Hz, 2H); 7.19 (brs, 16H, m-Tol, o-Tol), 7.01 (t, $2^2\;\text{J}=9.6$ Hz, 4H); 6.79 (t, $2^2\;\text{J}=9.6$ Hz, 4H); 6.10 (s, 4H, 5,10,15,20-H); 1.51 (s, 6H, CH$_3$); 1.31 (s, 6H, CH$_3$).
4.20.24.3. \textit{aaa\beta-5,10,15,20-tetra-4-tolyl-22,24-dithiadiazuliporphyrinogen}

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 8.56 (d, 2, 3, $^1$J = 9.8 Hz, 2H); 8.21 (dd, 7,8,17,18, $^3$J = 9.35 Hz, 4H); 8.13 (d, 12, 13, $^3$J = 9.6 Hz, 2H); 7.93 (s, 2H, 21,23-H); 7.57 (t, 2, 3, $^3$J = 9.86 Hz, 2H); 7.15 (m, 16H, m-Tol, o-Tol), 6.99 (t, 2, 3, 12, 13, $^3$J = 9.6 Hz, 4H); 6.79 (t, 2, 3, 12, 13, $^3$J = 9.66 Hz, 4H); 6.51 (s, 4H, 7,8-H, 12,13-H); 6.11 (s, 4H, 5,10,15,20-H); 1.56 (s, 6H, CH$_3$); 1.27 (s, 6H, CH$_3$).

4.20.25. \textit{Synthesis of 5,10,15,20-tetra-(4-methoxyphenyl)-22,24-dithiadiazuliporphyrinogen (37c)}

4.20.25.1. \textit{aaa\alpha-5,10,15,20-tetra-(4-methoxyphenyl)-22,24-dithiadiazuliporphyrinogen}

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 8.29 (d, 4H, 2, 3, 12, 13, $^3$J = 10.3 Hz, 2H); 7.39 (t, 2, 3, $^3$J = 10.1 Hz, 2H); 7.03 (d, $^3$J = 6.2 Hz, o-Ar, 8H), 6.79 (d, $^3$J = 6.2 Hz, m-Ar, 8H), 6.66 (t, 2, 3, 12, 13, $^3$J = 9.75 Hz, 4H); 6.37 (s, 4H, 7,8-H, 17,18-H); 6.12 (s, 4H, 5,10,15,20-H); 2.25 (s, 12H, -OCH$_3$).

4.20.25.2. \textit{aa\beta\beta-5,10,15,20-tetra-(4-methoxyphenyl)-22,24-dithiadiazuliporphyrinogen}

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 8.26 (d, 2, 3, 12, 13, $^3$J = 9.2 Hz, 4H); 8.16 (d, 7,8,17,18, $^3$J = 9.2 Hz, 4H); 7.83 (s, 2H, 21,23-H); 7.42 (t, 2, 3, $^3$J = 10.1 Hz, 2H); 7.18 (brs, 16H, m-Tol, o-Tol), 6.98 (t, 2, 3, 12, 13, $^3$J = 9.7 Hz, 4H); 6.85 (t, 2, 3, 12, 13, $^3$J = 9.7 Hz, 4H); 6.49 (s, 4H, 7,8-H, 12,13-H); 6.18 (s, 4H, 5,10,15,20-H); 2.31 (s, 6H, -OCH$_3$); 2.29 (s, 6H, -OCH$_3$).

4.20.25.3. \textit{aa\alpha\beta-5,10,15,20-tetra-(4-methoxyphenyl)-22,24-dithiadiazuliporphyrinogen}

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 8.42 (d, 2, 3, $^3$J = 9.6 Hz, 2H); 8.16 (dd, 7,8,17,18, $^3$J = 9.2 Hz, 4H); 7.99 (d, 12, 13, $^3$J = 9.6 Hz, 2H); 7.96 (s, 2H, 21,23-H); 7.45 (t, 2H, 2, 3, $^3$J = 10.1 Hz); 7.36 (s, 2H, 22,24-H), 7.10 (brs, 16H, m-Tol, o-Tol), 6.91 (t, 4H, 2, 3, 12, 13, $^3$J = 9.7 Hz); 6.87 (t, 4H, 2, 3, 12, 13, $^3$J = 9.7 Hz); 6.32 (s, 4H, 7,8-H, 12,13-H); 6.15 (s, 4H, 5,10,15,20-H); 2.76 (s, 6H, -OCH$_3$); 2.59 (Br, 6H, -OCH$_3$).

2,5-Bis[(4-tert-butylphenyl)hydroxymethyl]furan (0.6 mmol, 153.7 mg) and azulene (0.6 mmol, 78 mg) were added to dry CH$_2$Cl$_2$ (250 mL) under nitrogen atmosphere. After 15 minutes of stirring Et$_2$O·BF$_3$ (20µL) was added and the reaction mixture protected from light and stirred for the next 40 minutes. The mixture was evaporated under reduced pressure and then subjected to chromatography (basic Al$_2$O$_3$, CH$_2$Cl$_2$). The porphyrinogen was eluted as a deep blue fraction. After chromatography, the product was precipitated from CH$_2$Cl$_2$ with the addition of CH$_3$OH as blue powder/crystals (for the mixture of stereoisomers). Further the isomers were separated through preparative chromatography using chloroform:hexane (1:1, v/v) as a eluting solvent.

4.20.26.1. $\alpha\alpha\alpha\alpha$-5,10,15,20-tetra-(p-tert-butyl-phenyl)-22,24-dioxadiaziuliporphyrinogen

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 8.03 (d, 8H, $2^1$, $3^1$, $12^1$, $13^1$, $7^1$, $8^1$, $17^1$, $18^1$), 7.94 (s, 2H,21,23), 7.21 (d, 8H, o-phenyl), 6.95, (t, $2^3$, $12^3$ -H, $3J = 10.1$ Hz, 2H), 6.92 (d, 8H, m-phenyl), 6.49 (t, $2^2$, $3^2$, $12^2$, $13^2$ -J = 9.7 Hz, 4H), 6.22 (s, 4H, 7,8-H, 12,13-H), 5.92 (s, 4H, 5, 10, 15, 20), 2.05 (s, 36H, tert-butyl).

4.20.26.2. $\alpha\alpha\beta\beta$-5,10,15,20-tetra-(p-tert-butyl-phenyl)-22,24-dioxadiaziuliporphyrinogen

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 8.36 (d, $2^1$, $3^1$, $12^1$, $13^1$, $3J = 9.2$ Hz, 4H); 8.19 (d, $7^1$, $8^1$, $17^1$, $18^1$, $J = 9.2$ Hz, 4H); 7.86 (s, 2H, 21,23-H); 7.56 (t, $2^3$, $12^3$ -H, $3J = 10.1$ Hz, 2H); 7.21 (brs, 16H, m-Tol, o-Tol), 6.96 (t, $2^2$, $3^2$, $12^2$, $13^2$, $J = 9.7$ Hz, 4H); 6.79 (t, $2^2$, $3^2$, $12^2$, $13^2$, $J = 9.7$ Hz, 4H); 6.55 (s, 4H, 7,8-H, 12,13-H); 6.21 (s, 4H, 5,10,15,20-H); 2.33 (s, 18H, tert-butyl-CH$_3$); 2.25 (s, 18H, tert-butyl-CH$_3$).

4.20.26.2. $\alpha\alpha\alpha\beta$-5,10,15,20-tetra-(p-tert-butyl-phenyl)-22,24-dioxadiaziuliporphyrinogen

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 8.42 (d, 2H, $2^1$, $3^1$, $J = 9.6$ Hz); 8.16 (dd, $7^1$, $8^1$, $17^1$, $18^1$, $J = 9.2$ Hz, 4H); 7.99 (d, $12^1$, $13^1$, $J = 9.6$ Hz, 2H); 7.83 (s, 21,23-H, 2H); 7.42 (t, $2^3$, $12^3$ -H,
\( J = 10.1 \ \text{Hz}, \ 2H \); \( 7.18 \) (brs, 16H, m-Tol, o-Tol), \( 6.98 \) (t, 2, 2, 3, 12, 13, \( 3 \ J = 9.7 \ \text{Hz}, \ 4H \); \( 6.85 \) (t, 2, 2, 3, 12, 13, \( 3 \ J = 9.7 \ \text{Hz}, \ 4H \); \( 6.49 \) (s, 4H, 7,8-H, 12,13-H); \( 6.18 \) (s, 4H, 5,10,15,20-H); \( 2.31 \) (s, 18H, tert-butyl-CH\(_3\)); \( 2.29 \) (s, 18H, tert-butyl-CH\(_3\)).

### 4.20.27. Synthesis of 2,7-dimethyl-octa-3,5-diyne-2,7-diol

To a solution of 2-methyl-3-butyne-2-ol (500mg, 4.9 mmol) in THF (25 mL), CuCl\(_2\) (65 mg, 0.49 mmol) was added and the mixture was allowed to stir at room temperature for 10 min. DBU (895 mg, 5.88 mmol) was added to the reaction mixture which was allowed to stir vigorously at room temperature open to the atmosphere. After 24 h the reaction mixture was neutralized by HCl and concentrated under reduced pressure and the residue obtained was purified by column chromatography over silica gel using hexanes/ethyl acetate (70:30, v/v) as eluent to obtain pure.

**Physical state:** white shiny crystals

**Rf:** 0.37 (1:2, ethylacetate:hexane, v/v)

**Yield:** 463 mg (95%)

\(^1\)H NMR (400MHz, CDCl\(_3\), 25°C) \( \delta = 1.51 \) (s, 12H, CH\(_3\)), 2.07 (brs, 2H, OH)

\(^{13}\)C NMR (100MHz, CDCl\(_3\), 25°C) \( \delta = 31.02 \) (CH\(_3\)) 65.54 (C-(CH\(_3\))\(_2\)/(OH)), 66.29 (qC), 83.96 (Cq).

### 4.20.28. Synthesis of 2,7-diphenyl-octa-3,5-diyne-2,7-diol

To a solution of 1-Phenyl-prop-2-yn-1-ol (200 mg, 1.96 mmol) in THF (5 mL), CuCl\(_2\) (30 mg, 0.196 mmol) was added and the mixture was allowed to stir at room temperature for 10 min. DBU (234 mg, 2.352 mmol) was added to the reaction mixture which was allowed to stir vigorously at room temperature open to the atmosphere. After 24 h the reaction mixture was neutralized by HCl and concentrated under reduced pressure and the residue obtained was purified by column chromatography over silica gel using hexanes/ethyl acetate (70:30, v/v) as eluent to obtain pure.

**Physical state:** white solid

**Rf:** 0.35 (1:2, ethylacetate:hexane, v/v)

**Yield:** 109 mg (35%)
1H NMR (400MHz, CDCl₃, 25°C) δ = 2.65 (brs, 2H, OH), 5.77 (s, 2H, CH(OH)), 7.31 (m, 10 H, phenyl)

13C NMR (100MHz, CDCl₃, 25°C) δ = 50.80 (C-(OH)), 66.29 (qC), 83.96 (qC).

4.20.29. Synthesis of 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene

In a two neck round bottom flask equipped with nitrogen inlet was added sodium borohydride (2.4 g, 62.65 mmol) in a portion in distilled water (20 ml). The solution was stirred for 20 min and after then sulfur powder (500 mg, 15.66 mmol) was added slowly to the solution with continuous stirring. After 10 mins the color of the solution become yellowish and then the solution of 2,7-dimethyl-octa-3,5-diyne-2,7-diol (2 g, 12.04 mmol) and silveracetate (100 mg) in methanol was added under nitrogen atmosphere. The reaction was allowed to stir for 24 hours. After completion of the reaction the product was extracted by ethyl acetate and was further chromatographed in silica 60-120 mesh by ethylacetate:hexane (1:1, v/v) to gave the pure compound as white solid.

Physical state: white solid

Rf: 0.32 (1:1, ethylacetate:hexane, v/v)

Yield: 1.2 g (43%)

1H NMR (400MHz, CDCl₃, 25°C) δ = 1.63 (s, 12H, CH₃), 2.08 (brs, 2H, OH), 6.75 (s, 2H, β-thiophenic)

13C NMR (100MHz, CDCl₃, 25°C) δ = 31.01 (CH₃) 65.52 (C-(CH₃)₂(OH)), 121.46 (β-thiophenic), 152.70 (α-thiophenic).

4.20.30. Synthesis of 2,5-bis(1-dimethyl-hydroxymethyl)-tellurophene

Physical state: white solid

Rf: 0.46 (1:1, ethylacetate:hexane, v/v)

Yield: 1.64 g (59%)

1H NMR (400MHz, CDCl₃, 25°C) δ = 1.59 (s, 12H, CH₃), 2.29 (brs, 2H, OH), 7.22 (s, 2H, β-tellurophene)

13C NMR (100MHz, CDCl₃, 25°C) δ = 32.24 (CH₃) 74.94 (C-(CH₃)₂(OH)), 130.24 (β-tellurophene), 161.74 (α-tellurophene).
4.20.31. Synthesis of 2,5-bis(1-dimethyl-hydroxymethyl)-selenophene

Physical state: white solid

Rf: 0.32 (1:1, ethylacetate:hexane, v/v)

Yield: 1.56 g (57%)

$^1$H NMR (400MHz, CDCl$_3$, 25°C) $\delta$ = 1.62 (s, 12H, CH$_3$), 2.09 (brs, 2H, OH), 6.88 (s, 2H, $\beta$-thiophenic)

$^{13}$C NMR (100MHz, CDCl$_3$, 25°C) $\delta$ = 32.27 (CH$_3$) 72.76 (C-(CH$_3$)$_2$(OH)), 123.22 ($\beta$-selenophene-C), 163.55 ($\alpha$-selenophene-C).

4.20.32. Synthesis of 2,5-bis(1-phenyl-hydroxymethyl)-tellurophene

Synthesis was carried out according to the procedure described for compound 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene except 2,7-diphenyl-octa-3,5-diyne-2,7-diol and tellurium powder was taken in the place of 2,7-dimethyl-octa-3,5-diyne-2,7-diol and sulfur powder.

Physical state: white solid

Rf: 0.35 (1:1, ethylacetate:hexane, v/v)

Yield: 83 mg (32%)

$^1$H NMR (400MHz, CDCl$_3$, 25°C) $\delta$ = 2.36 (brs, 2H, OH), 5.97 (s, 2H, -CH(OH)) 6.88 (s, 2H, $\beta$-thiophenic), 7.41 (m, 10H, phenyl)

$^{13}$C NMR (100MHz, CDCl$_3$, 25°C) $\delta$ = 32.27 (CH$_3$) 72.76 (C-(CH$_3$)$_2$(OH)), 123.22 ($\beta$-tellurophene), 163.55 ($\alpha$-tellurophene).

4.20.33. Synthesis of 2,5-bis(1-phenyl-hydroxymethyl)-selenophene

Synthesis was carried out according to the procedure described for compound 2,5-bis(1-dimethyl-hydroxymethyl)-thiophene except 2,7-diphenyl-octa-3,5-diyne-2,7-diol and selenium powder was taken in the place of 2,7-dimethyl-octa-3,5-diyne-2,7-diol and sulfur powder.

Physical state: white solid

Rf: 0.39 (1:1, ethylacetate:hexane, v/v)
Yield: 76 mg (29%)

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 2.22 (brs, 2H, OH), 5.93 (s, 2H, -CH(OH)) 6.91 (s, 2H, β-thiophenic), 7.36 (m, 10H, phenyl)

$^{13}$C NMR (100MHz, CDCl$_3$, 25°C) δ = 32.27 (CH$_3$), 72.76 (C-(CH$_3$)$_2$(OH)), 123.22 (β-selenophene), 163.55 (α-selenophene).

4.20.34. Synthesis of 5,5,10,10,15,15,20,20-octamethyl-22,24-dithiadiazuliporphyrinogen

2,5-bis(1-dimethyl-hydroxymethyl)-thiophene (1 mmol, 200 mg) and azulene (1 mmol, 128 mg) were added to dry dichloromethane (250 mL) under nitrogen atmosphere. After 15 minutes of stirring Et$_2$OBF$_3$ (60µL) was added and the reaction mixture protected from light and stirred for the next 40 minutes. The mixture was evaporated under reduced pressure and then subjected to chromatography over basic alumina eluting with dichloromethane. The porphyrinogen was eluted as a deep green fraction using chloroform:hexane (7:3, v/v) as a eluting solvent. After chromatography, the product was precipitated from dichloromethane with the addition of CH$_3$OH as greenish crystals.

Physical state: green crystal

Rf: 0.39 (1:1, ethylacetate:hexane, v/v)

Yield: 156 mg (65%)

$^1$H NMR (400MHz, CDCl$_3$, 25°C) δ = 1.27 (s, 24H, CH$_3$), 6.56 (s, 2H, 21, 23-H), 6.77 (s, 4H, β-thiophene), 7.01 (t, 4H, 2$_2$, 3$_2$, 12$_2$,13$_2$), 7.45 (t, 2H, 2$_3$,12$_3$), 8.03 (d, 2H, $J$ = 8.8 Hz).

4.20.35. Synthesis of 5,10,15,20-tetrakis-(4-pyridyl)porphyrin

Physical state: purple solid

Yield: 500 mg (17%)

R$_f$: 0.36 (1:2, v/v, Petroleum ether: CHCl$_3$)

mp: >300°C

UV-Visible [λ$_{max}$ CDCl$_3$, (log ε)]: 416 (25), 512 (0.78), 548 (0.65), 589 (0.5), 644 (0.46)

$^1$H NMR δ (400MHz, CDCl$_3$) δ = -2.90 (brs, 2H, NH), 7.80 (m, 6H, meta and para phenyl), 8.18 (m, 8H, Ar$_{ortho}$ and 3,5-pyridyl), 8.86 (m = 8H, β-pyrrolic-H), 9.07 (d, $J$ = 5 Hz, 2,6-pyridyl-H).
4.20.36. Synthesis of 5,10,15,20-tetrakis(6-azulenyl)porphyrin

Tetra(4-pyridyl)porphyrin (500 mg, 0.81 mmol) and 1-chloro-2,4-dinitrobenzene (1.5 g mg, 7.1 mmol) were dissolved in CHCl$_3$/MeOH (4/1, 100 mL) and the mixture was refluxed for 3 days. Diethylamine (7.5 mL, 72.5 mmol) was added to the reaction mixture at room temperature, and it was stirred for next 2 days. The solvent was evaporated and the residue was dissolved in toluene (100 mL). Sodium cyclopentadienide (5.0 mL, 2M THF solution) was added and then the mixture was refluxed for 3 days. The solvent was evaporated and the product was separated by column chromatography over silica gel using dichloromethane as eluent. The product was recrystallized from MeOH and CH$_2$Cl$_2$.

**Yield:** 10 mg (2%)

**UV-Visible (CHCl$_3$):** $\lambda_{max}(\log \varepsilon) =$ 441, 520, 557, 599, 665 nm.

$^1$H NMR $\delta$ (400MHz, CDCl$_3$) $\delta =$ –2.54 (s, 2H, NH), 7.77 (d, $J = 4.1$ Hz, 8H, 1,3-H of azulene), 8.22 (d, $J = 10.1$ Hz, 8H, 5,7-H of azulene), 8.65 (d, $J = 10.1$ Hz, 8H, 4,8-H of azulene), and 8.89 (s, 8H, $\beta$-H of pyrrole).

4.20.36. Synthesis of 5,10,15,20-tetrakis-anthrylporphyrin

The condensation of pyrrole (1.4 ml, 20 mmol) and 9-anthraldehyde (4.1 g, 20 mmol) started upon addition of BF$_3$·OEt$_2$ (120 µl, 60 mmol) at room temperature in dry chloroform (1 L) under nitrogen atmosphere. After 1 min, the yield of porphyrinogen reached a maximum value, and a stoichiometric amount of DDQ dispersed in benzene was added quickly to convert the porphyrinogen to porphyrin. After evaporation of the solution to dryness, the residue was redissolved in a minimum of CHCl$_3$ and chromatographed over two successive columns of silica gel. CHCl$_3$ and CHCl$_3$/hexane were used as eluents for the first and the second column chromatography, respectively. The second column chromatography was employed mainly to remove anthraldehyde. The brown eluate was then evaporated, and the residue reprecipitated from chloroform-hexane to give compound 49a as purple solid.

**UV-Visible (CHCl$_3$):** $\lambda_{max} =$ 427 (5.40), 517 (4.39), 551 (3.60), 579 (3.79), 642 (3.14) nm.

$^1$H NMR $\delta$ (400MHz, CDCl$_3$) $\delta =$ -1.79 (s, 2H, NH), 7.04 (m, 8H, anthryl H$_2$,7), 7.42 (m, 8H, anthryl H$_3$,6), 8.22 (d, 8H, anthryl H$_4$,5), 8.85 (s, 4H, anthryl H10), 8.10 (s, 8H, pyrrole $\beta$H).
4.20.37. Synthesis of 5,10,15,20-tetrakis-2-naphthylporphyrin

Pyrrole (1.35 ml, 20 mmol) was added in the refluxing solution of 2-naphthaldehyde (3.12 g, 20 mmol) in propionic acid in two neck 500ml round bottom flask equipped with an efficient water condenser and magnetic stirrer. After 3h reaction mixtures was cooled to room temperature and allow to stand overnight. Filtration under suction pump on Buchner funnel and water washing afforded a purple product in quantitative yield. The TLC analysis showed formation of porphyrin which was purified by column chromatography on silica gel (60-120 mesh). The elution of column with petroleum ether/ chloroform (4:1, v/v,) gave 5,10,15,20-tetrakis(2-naphthyl)porphyrin.

Physical state: purple solid

Yield: 2.7g, 17%

UV-Visible (CHCl\textsubscript{3}): $\lambda_{\text{max}} = 424$ (5.90), 517 (4.38), 554 (4.06), 594 (3.83), 649 (3.65) nm.

$1^H$ NMR $\delta$ (400MHz, CDCl\textsubscript{3}) $\delta = -2.58$ (s, 2H, NH), 7.68 (m, 8H, naphthyl H-6,7), 8.06-8.17 (m, 12H, naphthyl H-3,4,5), 8.37 (d, $J = 8.04$ Hz, 4H, naphthyl H-8), 8.67 (s, 4H, naphthyl H-1), 8.84 (s, 8H, $\beta$-pyrrole H).
4.21. References


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