

RESEARCH ARTICLE

Design and Properties of Azaacene-Fused Porphyrins: Extending π -Systems for NIR-II Absorption

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Abstract: A series of porphyrins featuring various azaacene moieties were designed with the aim to explore the structure–property relationships in extended azaacene systems. The introduction of azaacene groups significantly enhanced the solubility of these chromophores while directly influencing their electronic absorption and emission properties, enabling absorption at longer wavelengths. Protonation of the azaacene-fused porphyrins further extended their absorption into the NIR-II region. The π system extension provided by the new appended diamino aromatic groups were therefore investigated through electrochemical, photophysical, XRD structural studies and complemented by theoretical calculations.

Introduction

The porphyrin family of dyes has often been used for several applications, such as catalytic reduction of CO₂,^[1] photovoltaic cells^[2] and bio-imaging.^[3] In order to tune the desired properties, the post-functionalization of porphyrin has been extensively studied, ranging from simple metalation, to polymer^[4,5] or even 3D covalent cages.^[6,7] On the other hand, the family of acene dyes gathered attention in the last decades for their optical properties as well as their electronic properties for the preparation of organic photovoltaic cells (OPVs),^[8] organic light emitting diodes (OLEDs) or organic field-effect transistors (OFETs).^[9–11]

Heteroacenes, in which a certain number of carbon atoms have been substituted by heteroatoms such as boron,^[12] nitrogen,^[13] or sulfur,^[14,15] have displayed enhanced electronic properties. Azaacenes have thus arisen as interesting candidates for electronic applications, due to their overall increased stability and electronic properties compared to their regular carbon containing analogues.^[16,17] While derivatives of azaacene-fused porphyrins have been synthesized in the past, their electronic and redox properties have often been overlooked. Moreover, their synthesis often revolved around condensation reaction of a diamino moiety onto a diketochlorin or a tetraketobacteriochlorin. The preparation of this precursor usually requires several synthetic steps, consisting of porphyrin reduction into (bacterio)chlorin, followed by silica-mediated hydroxylation and oxidation,^[18] or nitration of the porphyrin followed by reduction to the amine, which is subsequently oxidized and hydrolyzed to a diketone.^[19–21] A second strategy is to exploit Buchwald-Hartwig

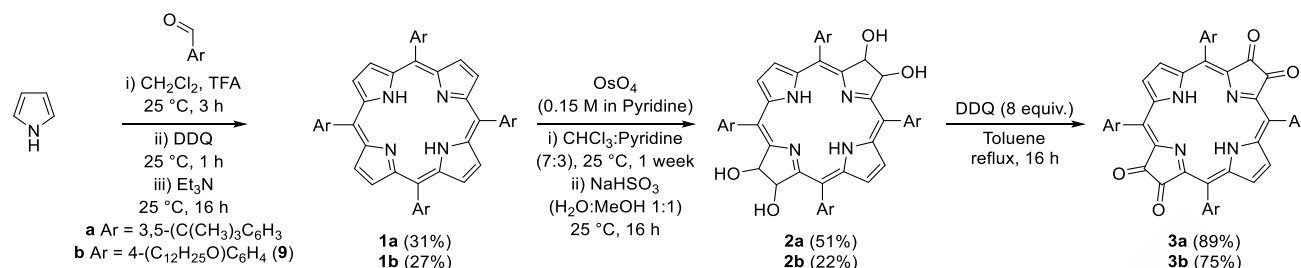
coupling conditions between di- or tetrabromoporphyrins and diamino compounds, the intermediate secondary amine being oxidized with an excess of MnO₂ to afford the desired compound in moderate yields.^[22]

Herein, we wish to report a two-step synthesis to afford tetraone **3**, on which were condensed several diamino moieties with the use of simple conditions to afford new porphyrin incorporating azaacenes **4–8**, with overall satisfying yield. These novel azaacene derivatives were characterized by ¹H and ¹³C NMR, FTIR and high-resolution mass spectroscopy (HR-MS). X-ray diffraction (XRD) analysis were performed on suitable crystals to confirm the structural features and to study the molecular packing of the selected molecules. Additionally, electronic absorption and emission, as well as the redox properties, of these new compounds were investigated and discussed.

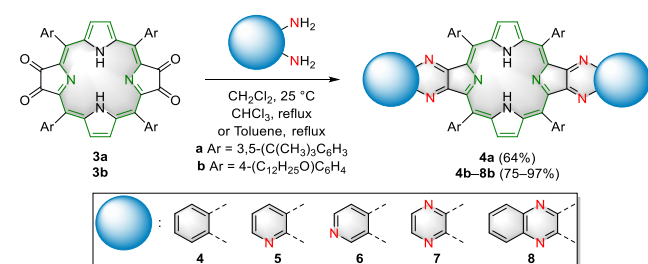
Results and Discussion

Synthesis of Azaacenes-Fused Porphyrins

The tetrakis(3,5-di-*tert*-butylphenyl)porphyrin **1a** and tetrakis(4-dodecyloxyphenyl)porphyrin **1b** were prepared via a Rothmund reaction, employing equimolar amounts of the corresponding substituted benzaldehyde and undistilled pyrrole in CH₂Cl₂ (Scheme 1).^[23] Attempts to hydroxylate **1a** and **1b** through osmium-mediated hydroxylation were explored under less hazardous condition than those commonly reported, using crystalline OsO₄.^[24,25] For instance, using catalytic or stoichiometric amount of microencapsulated OsO₄ resulted in little to no conversion, probably due to the reduced reactivity of encapsulated OsO₄. Similarly, 2.1 equivalents of aqueous osmic acid (4% w/w) only led to low yield of the diol derivative. Thus, optimal conditions employed 2.1–2.5 molar equivalents of OsO₄ in 0.15 M pyridine, followed by *in situ* reduction with NaHSO₃, affording tetraols **2a** and **2b** with a yield of 51% and 22%, respectively. In our hands, only the *syn* isomers **2a** and **2b** were obtained (*vide infra*), and hydroxylation specifically targeted positions 7,8,17 and 18 of the porphyrin macrocycle.^[26]



Scheme 1. Three-step synthesis of tetraketoporphyrin **3a–b**.



Scheme 2. Preparation of porphyrin incorporating azaacenes **4–8**.

However, excess OsO_4 or prolonged reaction times resulted in hexaol^[27] or marginal yield increase. Furthermore, no reaction was observed after heating the reaction to 50 °C for one week, allowing recovery of starting material **1** by simple filtration with CH_2Cl_2 through a ca. 2 cm silica plug. Subsequent oxidation using Swern conditions showed various byproducts, necessitating tedious purification and resulting in low yields.^[28] In contrast, DDQ-mediated oxidation allowed the isolation of the desired tetraones **3a** and **3b** with good yields (89% and 75% respectively), as evidenced by carbonyl signals at 185.99 and 187.01 ppm observed in their respective ¹³C NMR spectra. To date, this is the first report of oxidation of tetrahydroxybacteriochlorins to tetraketobacteriochlorins, whereas diol oxidation with DDQ was previously reported in 2003 by Brückner and collaborators.^[29] Furthermore, DDQ is a safer alternative to reagents like IBX or DMP, while other oxidants, such as silver(I) acetate and CTAP often cause pyrrole ring cleavage.^[30]

To the best of our knowledge, only derivatives of *o*-phenylenediamine were condensed onto di- or tetraones,^[31–34] as well as 1,2,4,5-tetraaminobenzene.^[35–37] In this study, *o*-phenylenediamine, 2,3-diaminopyridine, 3,4-diaminopyridine, 2,3-diaminopyrazine and 2,3-diaminoquinoxaline were reacted with tetraones **3a–b** to yield several new derivatives of porphyrin-like structures incorporating azaacene motifs (Scheme 2). The reaction with the most reactive diamino derivative, *o*-phenylenediamine, was completed within approximately 10 minutes at room temperature in CH_2Cl_2 , as monitored by TLC using pure CH_2Cl_2 as the eluent. In contrast, longer reaction time were required for complete conversion with 2,3-diaminopyridine (30 minutes) and 3,4-diaminopyridine (5 hours), affording **4a**, **5a** and **6a** in yields of 97%, 92% and 89%, respectively.

For the less soluble diamino derivatives, such as 2,3-diaminopyrazine and 2,3-diaminoquinoxaline, only small amounts of the bis-adduct products (**7b** and **8b**, respectively) were observed after several days at room temperature in CH_2Cl_2 . However, refluxing a mixture of **3b** and 2,3-diaminopyrazine (2,3-diaminoquinoxaline) in CHCl_3 (toluene) overnight allowed the reaction to proceed, thus affording **7b** (**8b**) in 75% (89%) yield. Interestingly, attempts to perform condensation between **3b** and excess 2,3-diaminopyrazine in refluxing toluene resulted in

degradation of the desired product, hinting at a potential instability of **7b** at temperature exceeding the boiling point of CHCl_3 .

While the unsubstituted porphyrins **1a–b** are insoluble in *n*-hexane, their substituted counterparts, tetraols **2a–b**, tetraones **3a–b** and azaacenes **4–8** exhibited good solubility in *n*-hexane. This property enabled the simple removal of most, if not all, excess diamino reagents by filtration using *n*-hexane as the solvent. On the other hand, these compounds remained insoluble in polar solvents, allowing an alternative method to remove unreacted diamino reagents through washing with MeCN, MeOH or acetone. Subsequent purification by silica gel chromatography, employing either a CH_2Cl_2 :MeOH eluent system of pure CH_2Cl_2 , afforded pure azaacenes **4–8** in moderate to excellent yields (64–97%).

As expected, the synthesis of **5b** and **6b** resulted in mixtures of *syn*- and *anti*- isomers (52:48 for **5b** and 48:52 for **6b**). These isomers could not be separated by standard silica gel flash chromatography. The ¹H NMR analysis of the isolated mixture unambiguously confirmed the presence of racemic isomers, due to their different symmetry axes (Figure 1). The clearest evidence is the appearance of two sets of *meso*-aryl signals, as well as the non-trivial multiplicity of the pyrrolic proton signals in the 9.03–8.87 ppm range (refer the insert on Figure S19). In the *syn*- isomer **5b**, the two hydrogen atoms in each pair of pyrrolic protons are equivalent due to the molecule's C₂ symmetry, resulting in singlets. Conversely, in the *anti*- isomer **5b**, these protons are magnetically non-equivalent, leading to signal splitting. The very same reasoning applies to 3,4-diaminopyridine incorporating **6b**, which also featured two distinct sets of signals in its ¹H NMR spectrum (refer to the insert on Figure S21).

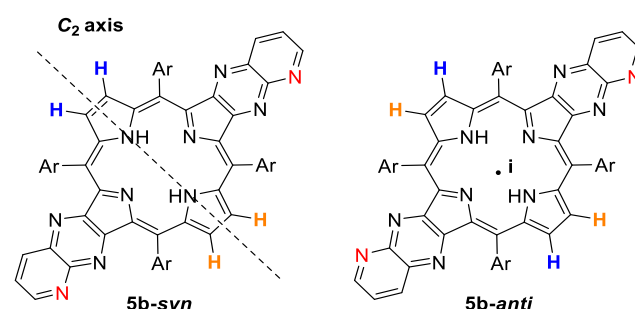


Figure 1. The difference in symmetry between the *syn*- and *anti*- isomers within the mixture of **5b** (Ar = 4-dodecyloxyphenyl). The hydrogens with matching colors share a similar chemical and magnetic environment.

Fortunately, theoretical calculations (*vide infra*) predicted nearly identical frontier molecular orbitals for both isomers of **5b** and **6b**, enabling us to discuss the optical and redox properties of these racemic mixtures. As expected, the symmetrical azaacene-fused porphyrins **4a–b** (*o*-phenylenediamine), **7b** (2,3-diaminopyrazine) and **8b** (2,3-diaminoquinoxaline) showed

perfect symmetry, as evidenced by their NMR spectra and corroborated by XRD data for azaacenes **4a** and **4b**. While compound **4a** was first reported in 1991 by Crossley and co-workers,^[31] we herein report XRD data of the free base **4a** (*vide infra*).

Structural Analysis of Porphyrin Derivatives

Crystals of sufficient quality were obtained for compounds **1a**, **1b**, **2a**, **3a**, **4a** and **4b**, either through slow evaporation of an adapted solvent or by slow diffusion between two solvents (refer to ESI for detailed crystallization conditions and crystallographic data, see Figure S59–60 and Tables S3–8). Compound **1b** shows a typical porphyrin structure, with a flat macrocycle and orthogonally oriented aromatic substituents.

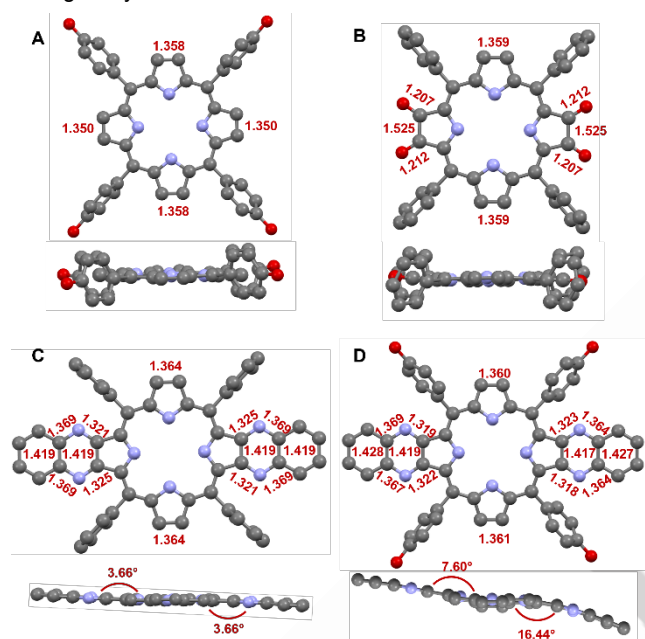


Figure 2. XRD structures (front and side views) of compounds **1b** (A), **3a** (B), **4a** (C) and **4b** (D). Hydrogen atoms and phenyl substituents were omitted for the sake of clarity. The discussed bond lengths (Å) and angles are indicated in red on the corresponding structure.

The structure reveals distinct bond length for the localized double bond (1.358(4) Å) and the localized one (1.350(4) Å), as shown in the Figure 2A. Similar values were observed in the case of di-*tert*-butylphenyl derivative **1a** (1.357(2) Å and 1.350(2) Å, respectively, see Figure S55 in the ESI).

Crystals of compound **2a** revealed a bowl-like structure (Figure 3). This crystallographic data, combined with the unambiguous characterization of only one isomer by NMR spectroscopy, suggests that only the *syn* isomer **2a** was isolated from the osmium-mediated hydroxylation reaction. Surprisingly, no *trans* isomer was detected in the reaction mixture, as indicated by the ¹H NMR spectrum (Figure 3), which showed signals for a mixture of dihydroxychlorin (pyrrole signal at 6.33 ppm) and **2a** (signal at 6.18 ppm). This indicates that the hydroxylation reaction exclusively yielded the *syn* isomer under these conditions.

Subsequent oxidation to afford tetraone **3a** led to a flat porphyrin-like structure, as evidenced by its crystallographic data (Figure 2B). The measured carbon–oxygen bond lengths (1.207(4)–1.212(4) Å) suggest minimal electronic delocalization into the ketone groups, with the electron density being mostly delocalized over the bacteriochlorin ring. This conclusion is further confirmed by the length of the carbon–carbon bond between the two ketone functions, measured at 1.525(5) Å.

Azaacene **4a** adopts a slight Z-shape conformation, with one azaacene moiety positioned above the porphyrin plane and the other below, each tilted by 3.66° relative to the porphyrin plane (Figure 2C). The advert reader may be interested in the corresponding nickel(II) complex, reported by Song and co-workers in 2021,^[22] which exhibits a similar Z-shape geometry. Regarding **4a**, the data indicates a symmetric structure centered on an inversion point within the porphyrin macrocycle. The carbon–nitrogen bond lengths in the azaacene moiety show an inner bond length slightly shorter than the outer one, with measured lengths of 1.321(3)–1.325(3) Å and 1.369(3) Å, respectively. This indicates partial electron delocalization between the porphyrin core and the azaacene moiety, considering that standard simple and double carbon–nitrogen bond lengths are approximately 1.47 and 1.30 Å respectively.^[38,39] Furthermore, the pyrrolic carbon–carbon bond length of 1.419(3) Å highlights the occurrence of electronic delocalization. In contrast, in the regular porphyrin **1b**, the same bond is approximately 1.350 Å, reflecting a localized double-bond character.^[40]

Interestingly, the dodecyloxy analogue **4b** exhibits reduced symmetry compared to **4a**, along with a more pronounced Z-shape distortion. The angles between the azaacene planes and the porphyrin plane were measured at 7.60° and 16.44°, respectively (Figure 2D).

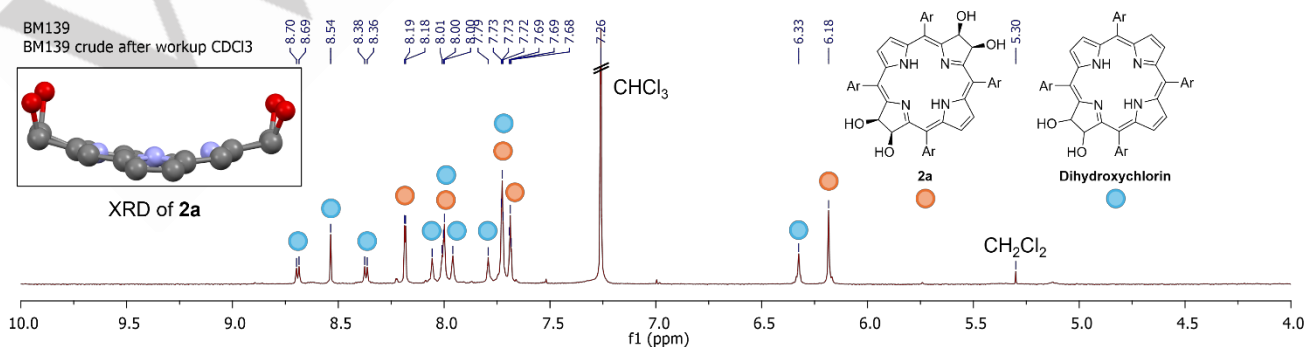


Figure 3. ¹H NMR spectrum (400 MHz) in CDCl₃ (zoomed on the 4 to 10 ppm range) of the crude residue obtained after work-up of the osmium mediated hydroxylation performed on **1a**. Ar = 3,5-di-*tert*-butylphenyl. The insert is a side-view of the XRD structure of **2a**, with hydrogen atoms and phenyl substituents omitted for clarity.

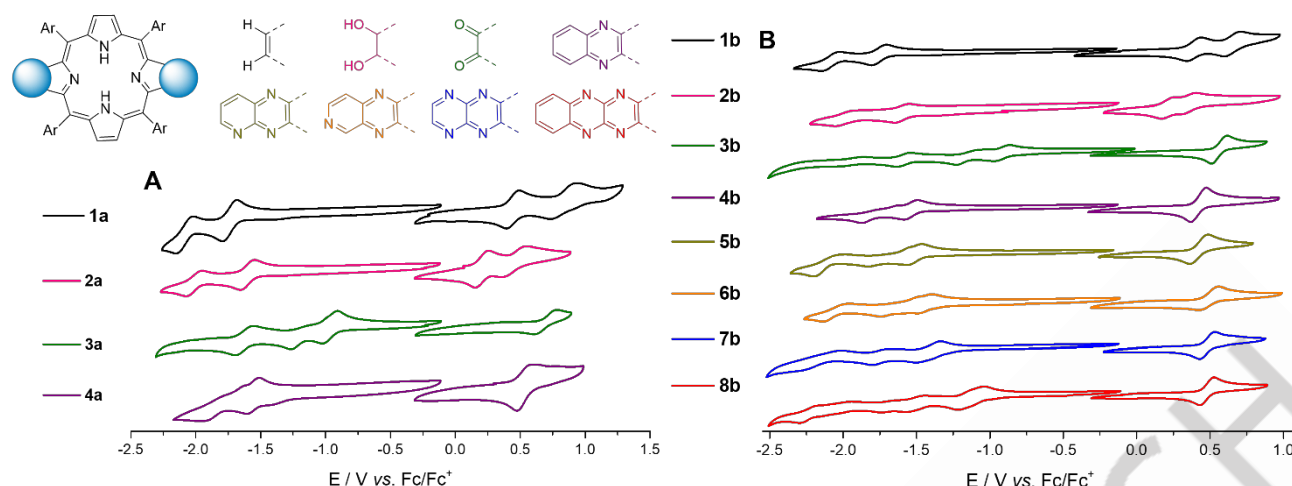


Figure 4. Cyclic voltammograms (V vs. Fc/Fc⁺, IUPAC conventions) of compounds 1a–4a (A, Ar = 3,5-di-*tert*-butylphenyl) and of 1b–8b (B, Ar = 4-dodecyloxyphenyl) in CH₂Cl₂ containing 0.1 M of [(nBu₄N)PF₆], with a scan rate of 100 mV.s⁻¹.

Similar to **4a**, the carbon–nitrogen bonds appear to be localized, with the double bond associated with the porphyrin moiety (1.318(2)–1.323(2) Å) and the single bond with the azaacene moiety (1.364(2)–1.369(2) Å).

Electrochemical Analysis of Compounds 1–8

The cyclic voltammograms (CVs) of compounds **1a–4a** and **1b–8b** were recorded in CH₂Cl₂ containing 0.1 M of [(nBu₄N)PF₆], with analyte concentrations of approximately 1 mM (Figure 4). The corresponding half-wave and peak potentials for oxidation and reduction are summarized in Table 1, referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. Unsubstituted porphyrin **1** and its tetraol derivative **2** both exhibit two reversible oxidation and reduction waves. Notably, the oxidation of the tetraol derivative is slightly easier, with a cathodic shift of 23 mV for the **a** series and 18 mV for the **b** series.

An anodic shift of approximately 15 mV is observed upon hydroxylation of porphyrins **1a–b**. Oxidation to tetraones **3a** (**3b**) induces a substantial anodic shift of 640 mV (680 mV) in the first reduction wave, likely due to the reduction of one ketone group. Tetraone **3** and the corresponding azaacenes **4a** and **4b–8b** display a single reversible oxidation wave and up to four reduction waves. The first reduction wave is reversible in all cases, while the second one is quasi-reversible, requiring a higher potential to facilitate electron transfer. The third reduction wave, observed for **3a**, **3b**, and **5b–8b**, is reversible for tetraones **3a–b** and the pyridine bearing **5b** and **6b**.

However, this phenomenon appears to be quasi-reversible for pyrazine (**7b**) and quinoxaline (**8b**) derivatives. A comparison of pristine porphyrins **1a–b** with their azaacene-fused counterparts **4a** and **4b–8b** reveals an anodic shift in the first oxidation wave (3–10 mV). The first reduction wave shows a more pronounced anodic shift, ranging from 18 to 33 mV for compounds **4–7**. For the quinoxaline derivative **8b**, a significant anodic shift of 62 mV (29 mV relative to the pyrazine substituted **7b**) indicates LUMO stabilization due to the extended aromaticity. As expected, *meso*-dodecyloxyphenyl-substituted compounds (**b** series) are slightly easier to oxidize than their *meso*-3,5-di-*tert*-butylphenyl counterparts (**a** series), owing to the electron-donating effects of the phenyloxy groups, which destabilize the HOMO.

However, the *meso* substituents have a minimal impact on the LUMO energy, confirming that these groups are not involved in the LUMO. Functionalization of porphyrin **1** reduces the electrochemical HOMO–LUMO gap (ΔE). For instance, the gap decreases from 2.14 and 2.18 eV for unsubstituted porphyrins **1a** and **1b**, respectively, to 1.81 eV for tetrahydroxylated derivatives **2a** and **2b**. Oxidation to tetraones **3** further lowers the gap to 1.66 eV for **3a** and 1.48 eV for **3b**. Condensation with diamino groups results in a slight reduction in the first oxidation potential (ranging from 0.88 to 0.99 V vs. Fc/Fc⁺) and a significant increase in the first reduction potential (from –1.56 to –1.13 V vs. Fc/Fc⁺). Consequently, the HOMO–LUMO gap for azaacenes **4–8** is significantly higher than those of substituted bacteriochlorin **2–3** but remains lower than the starting porphyrins **1**.

Photophysical Properties of Compounds 1–8

Azaacene-fused porphyrins **4–8** show good solubility in various of nonpolar solvents but are mostly insoluble in polar solvents such as MeOH, MeCN, DMF or DMSO. Consequently, the electronic absorption spectra of these derivatives were only recorded at room temperature in low-polarity solvents, including *n*-hexane ($E_T(30) = 31.0$ kcal/mol), CH₂Cl₂ ($E_T(30) = 40.7$ kcal/mol), THF ($E_T(30) = 37.4$ kcal/mol) and toluene ($E_T(30) = 33.9$ kcal/mol).^[41] Figure 5 presents the electronic absorption spectra of compounds **1–8** in the dodecyloxyphenyl series (**b**), measured in neutral (left, Figure 5a and 5b) and acidified CH₂Cl₂ (right, Figure 5c and 5d), at ca. 5×10^{-6} M. Absorption maxima, molar absorption coefficients, emission maxima and fluorescence quantum yields are summarized in Table 2 for compounds **1b–8b**. Photophysical data for compounds **1a–4a**, which are slightly blueshifted compared to the dodecyloxy series **b**, are shown in the Figures S52, 54 and 55, as well as in Table S1 in the ESI.

Additionally, solvatochromism data for compounds **4–8** are available in the Figure S53. Porphyrin **1b** displays a typical porphyrin spectrum,^[42] characterized by an intense Soret band ($S_0 \rightarrow S_2$ transition) at 422 nm ($\epsilon^{422} = 45.03 \times 10^4$ M⁻¹.cm⁻¹) and four weaker Q-bands between 519–651 nm ($S_0 \rightarrow S_1$ transition). Tetraol **2b** shows a blueshifted, less intense Soret band centered at 381 nm ($\epsilon^{381} = 20.55 \times 10^4$ M⁻¹.cm⁻¹) and four Q-bands at 553, 593, 649 and 707 nm, with the first and the last bands being

Table 1. Half-wave potentials (V versus Fc/Fc⁺) of compounds 1a–4a and 1b–8b measured in CH₂Cl₂ containing 0.1 M of [(nBu₄N)PF₆] (scan rate of 100 mV.s⁻¹).

Compound	Reduction (V vs. Fc/Fc ⁺)				Oxidation (V vs. Fc/Fc ⁺)		ΔE (eV) ^[a]
	Fourth	Third	Second	First	First	Second	
1a			-2.08	-1.74	0.44		2.18
1b			-2.09	-1.75	0.39	0.65	2.14
2a			-2.01	-1.60	0.21	0.46	1.81
2b			-1.99	-1.60	0.21	0.36	1.81
3a		-1.63	-1.19	-0.96	0.70		1.66
3b		-1.59	-1.16	-0.92	0.56		1.48
4a			-1.78	-1.56	0.53		2.09
4b			-1.75	-1.54	0.42		1.96
5b		-2.11	-1.69	-1.52	0.43		1.95
6b		-2.05	-1.61	-1.44	0.49		1.93
7b		-2.14	-1.75	-1.42	0.48		1.90
8b	-2.24	-1.70	-1.51	-1.13	0.48		1.61

[a] HOMO–LUMO electrochemical gap calculated by $\Delta E = E_{1/2}(\text{ox}_1) - E_{1/2}(\text{red}_1)$.

relatively intense ($\epsilon^{553} = 4.53 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ and $\epsilon^{707} = 9.05 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$). The overall spectrum of **2b** is consistent with that of a bacteriochlorin structure.^[43]

For tetraone **3b**, broad, low-intensity absorption features span the visible spectrum, with a prominent Soret at 388 nm ($\epsilon^{388} = 14.21 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$), resulting in panchromatic absorption. Subsequent condensation with diamino derivatives produces absorption profiles reminiscing of porphyrin **1b**, with an intense Soret band to 454 nm (1670 cm⁻¹ shift, $\epsilon^{454} = 18.22 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$), while the Q-bands shift to lower energies (539–670 nm, with shifts ranging from 436 to 715 cm⁻¹) with intensities similar to those of

1b. Increasing the number of nitrogen atoms in the azaacene moieties –six for **5b** and **6b**, and eight for **7b** and **8b**– induces a hypsochromic shift in the Soret band. The Soret band shifts from 454 nm for **4b** to 451 nm (**5b**), 458 nm (**6b**), 429 nm (**7b**) and 439 nm (**8b**). This translates to a shift ranging from 147 cm⁻¹, in the case of 2,3-diaminopyridine adduct **5b**, to 1284 cm⁻¹ for the pyrazine one **7b**.

A redshift is observed for the Q-bands, with absorption maxima reaching up to 714 nm (**8b**), corresponding to a shift of 920 cm⁻¹.

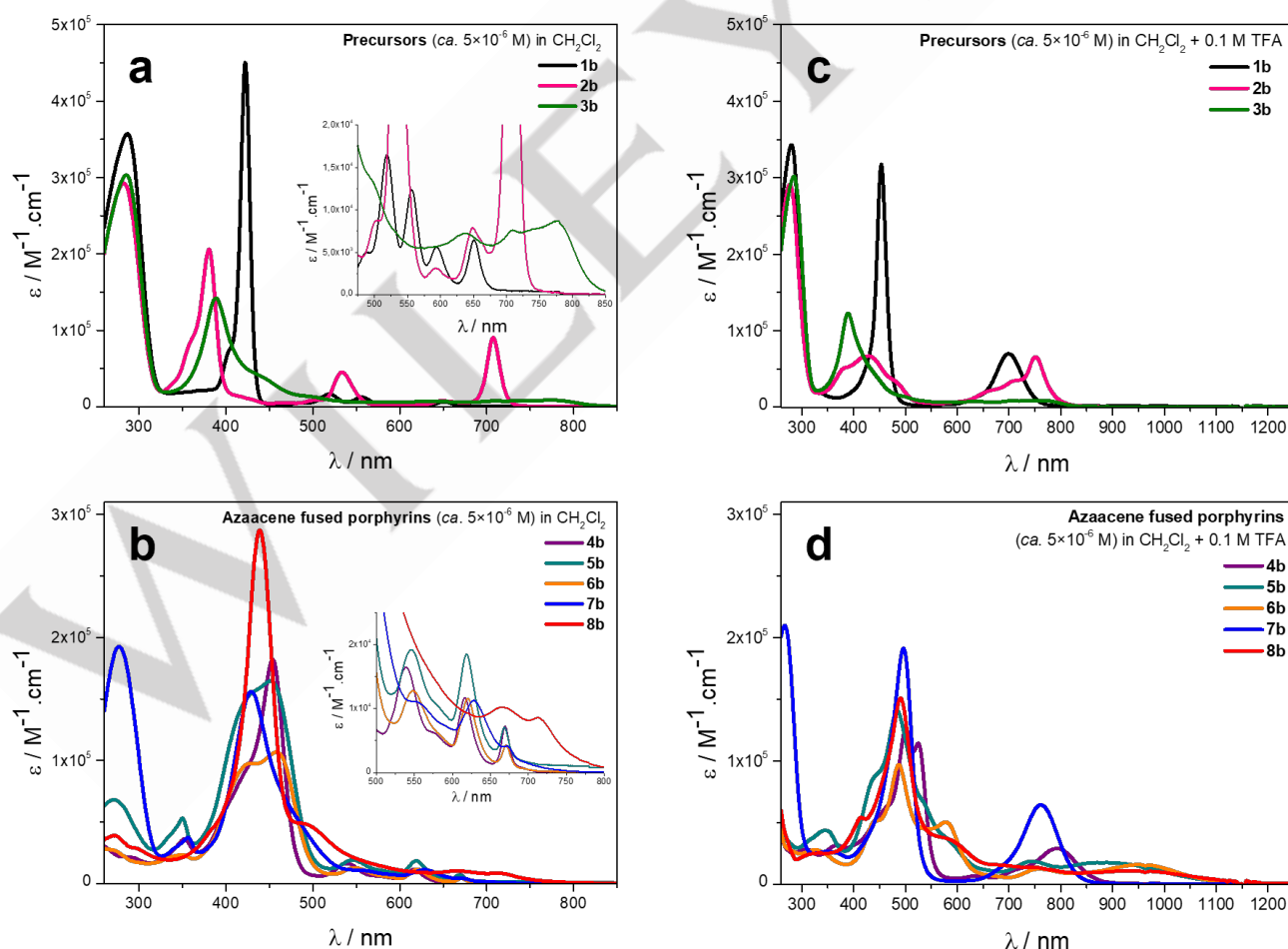
**Figure 5.** Electronic absorption spectra of (a) precursors 1b, 2b and 3b, (b) products 4b, 5b, 6b, 7b and 8b, (c) protonated precursors 1b, 2b and 3b and (d) protonated products 4b, 5b, 6b, 7b and 8b. The inserts in spectra (a) and (b) is a zoom on the Q-bands area of the spectra.

Table 2. Electronic absorption and emission of porphyrin 1–8 in the dodecyloxyphenyl series (b) in CH₂Cl₂.

Compound	Solvent	Soret band λ_{max} (nm) (ϵ (10^4 M ⁻¹ .cm ⁻¹))	Q bands λ_{max} (nm) (ϵ (10^4 M ⁻¹ .cm ⁻¹))	λ_{em} (nm)	$\Phi_f^{[a]}$ (%)
1b	CH ₂ Cl ₂	422 (45.03)	519 (1.65), 556 (1.24), 594 (0.56), 651 (0.65)	658, 722	9.2
	CH ₂ Cl ₂ /TFA ^[c]	454 (31.74)	669 (7.00)	743	21.4
2b	CH ₂ Cl ₂	381 (20.55)	553 (4.53), 593 (0.32), 649 (0.78), 707 (9.05)	706	10.1
	CH ₂ Cl ₂ /TFA ^[c]	430 (6.69)	656 (2.02), 707 (3.39), 751 (6.60)	[b]	[b]
3b	CH ₂ Cl ₂	388 (14.21)	495 (1.36), 636 (0.72), 708 (0.76), 777 (0.87)	[b]	[b]
	CH ₂ Cl ₂ /TFA ^[c]	389 (12.27)	495 (1.42), 636 (0.76), 708 (0.83), 777 (0.83)	[b]	[b]
4b	CH ₂ Cl ₂	454 (18.22)	539 (1.64), 577 (0.62), 617 (1.17), 670 (0.72)	672, 749	3.2
	CH ₂ Cl ₂ /TFA ^[c]	525 (11.43), 501 (12.64)	636 (0.67), 717 (1.22), 793 (2.90)	[b]	[b]
5b	CH ₂ Cl ₂	451 (16.46), 429 (15.46)	546 (1.91), 580 (1.05), 619 (1.85), 669 (0.70)	671, 712, 750	3.2
	CH ₂ Cl ₂ /TFA ^[c]	484 (14.05)	741 (1.85), 889 (1.75)	[b]	[b]
6b	CH ₂ Cl ₂	458 (10.68), 425 (9.73)	548 (1.28), 621 (1.16), 671 (0.43)	673, 712, 751	3.2
	CH ₂ Cl ₂ /TFA ^[c]	487 (9.68)	761 (1.23), 950 (1.58)	[b]	[b]
7b	CH ₂ Cl ₂	429 (15.61)	555 (1.10), 629 (1.13), 672 (0.42)	[b]	[b]
	CH ₂ Cl ₂ /TFA ^[c]	497 (19.14)	762 (6.43)	[b]	[b]
8b	CH ₂ Cl ₂	439 (28.73)	667 (1.02), 714 (0.85)	[b]	[b]
	CH ₂ Cl ₂ /TFA ^[c]	490 (15.01)	943 (1.06)	[b]	[b]

[a] Quantum yields were measured with an integration sphere. [b] No fluorescence was observed. [c] CH₂Cl₂ mixture with TFA (0.1 M).

This shift is particularly pronounced in the case of quinoxaline bearing **8b**, while for compounds **5b**, **6b** and **7b**, the shifts are much smaller, in the range of 22–44 cm⁻¹. One can then safely assume that the introduction of two additional aromatic rings using quinoxaline is responsible for the significant bathochromic shift of the Q-bands. Additionally, broad Soret bands are observed for the pyridine derivative **5b** and **6b**, likely due to the mixture of *syn*- and *anti*- isomers (Figure 1), with each isomer exhibiting a different S₀→S₂ transition due to the different substitution patterns. However, the corresponding Q-bands remain consistent with those observed for the symmetric **4b**.

The behavior of compounds **1b** to **8b** was also investigated under acidic conditions with the use of 0.1 M of trifluoroacetic acid (TFA) solutions (Figure 5c and Figure 5d). Tetraone **3b** shows no significant spectral shift upon protonation, with the overall spectrum remaining unchanged.

This suggests that **3b** does not undergo protonation under these conditions, and any small shifts observed can likely attributed to experimental error, such as slight variations in solution preparation or the minor polarity shift due to TFA. An overall redshift of the electronic absorption is observed for compounds **1b**, **2b** and azaacenes **4b–8b** under acidic conditions. The Soret band of protonated porphyrin **1b** is shifted to 454 nm (1670 cm⁻¹), with a broad Q-band at 669 nm (413 cm⁻¹), indicating a recovery of symmetry due to the presence of four protons at the

inner center. The Soret band of protonated tetraol **2b** shifts to 430 nm (*i.e.* a shift of 2990 cm⁻¹), while its lowest-energy Q-band shifts to 751 nm (829 cm⁻¹).

For protonated azacenes-fused porphyrin **4b–8b**, the Soret band absorption maxima shift from 429–458 nm to 484–525 nm (1300–3190 cm⁻¹), accompanied by an overall hypochromic effect, except for pyrazine bearing **7b**, which shows a slight increase in intensity (from $\epsilon^{429} = 15.61 \times 10^4$ M⁻¹.cm⁻¹ to $\epsilon^{497} = 19.14 \times 10^4$ M⁻¹.cm⁻¹). The low-energy absorption bands also undergo substantial shifts following protonation, resulting in broadening of the absorption in the NIR region of the spectrum. Protonated **4b** and **7b** show broad absorption bands centered at 793 and 714 nm, respectively, with λ_{onset} extending to 870 nm and 825 nm.

Moreover, protonated **5b**, **6b** and **8b** exhibit low-intensity absorptions centered at 889 nm ($\epsilon^{889} = 1.75 \times 10^4$ M⁻¹.cm⁻¹), 950 nm ($\epsilon^{950} = 1.58 \times 10^4$ M⁻¹.cm⁻¹) and 943 nm ($\epsilon^{943} = 1.06 \times 10^4$ M⁻¹.cm⁻¹), with λ_{onset} in the NIR-II region at 1118 nm, 1106 nm and 1169 nm, respectively. These shifts after protonation are reminiscent of hyperporphyrin behavior,^[44,45] which can be attributed to the electron-donating effect of the dodecyloxyphenyl groups at the *meso* positions.

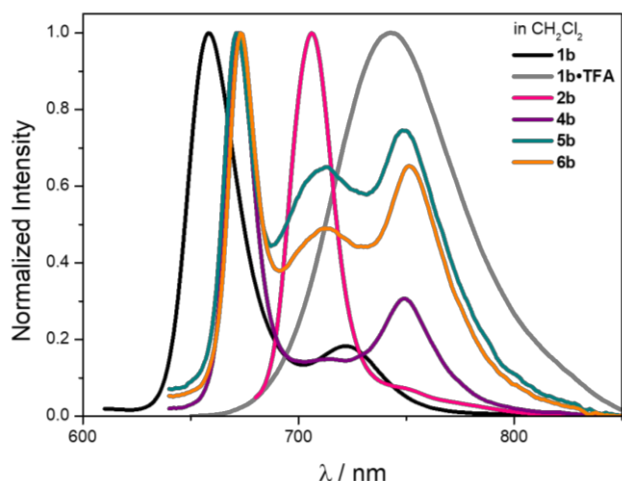


Figure 6. Normalized emission spectra of compounds **1b** (—), protonated **1b** (—), **2b** (—), **4b** (—), **5b** (—) and **6b** (—), in CH_2Cl_2 at room temperature.

The emissive properties of compounds **1–8** were studied in both neutral and acidic CH_2Cl_2 , with fluorescence quantum yields (Φ_f 's) measured using an integrating sphere across five consecutive experiments. As expected, the fluorescence quantum yields were not significantly affected by shifting the excitation wavelength from the Soret band to the Q-bands. In neutral CH_2Cl_2 , porphyrin **1b** exhibits typical tetrakis-*meso*-aryl-substituted porphyrin behavior, with dual emission bands centered at 6580 nm and 722 nm, and an overall Φ_f of approximately 9%. The tetraol derivative **2b** shows emission at 706 nm, with a similar quantum yield ($\Phi_f \approx 10\%$). Azaacene-fused porphyrins **4b**, **5b** and **6b** display slightly different emission maxima, with 672 nm (749 nm), 671 nm (712, 750 nm), and 673 nm (712, 751 nm), for their first (second, third) emission bands, respectively.

However, the fluorescence quantum yield remains about 3% in all cases. Multiple excitation spectra were recorded for **5b** and **6b** to ensure that all three emission bands originated from the studied compound (refer to Figure S56). On the other hand, tetraone **3b**, pyrazine-substituted **7b**, and quinoxaline derivative **8b** do not exhibit any emissive properties. This lack of emission is consistent with the Energy Gap Law,^[46] where low electronic gap chromophores typically favor radiationless de-excitation

pathways. Additionally, protonation with TFA results in the loss of emission for all emissive compounds, which can be attributed to the further reduction in the HOMO–LUMO gap, thereby promoting non-radiative de-excitation.

Theoretical Calculations

DFT and Time-dependent DFT (TD-DFT) calculations were performed to investigate the structural, electronic and optical properties of azaacenes-fused porphyrins **4–8**. For the sake of computational cost, the four 4-dodecyloxyphenyl substituents were simplified to 4-methoxyphenyl groups, which are expected to have minimal to no impact on the results for this study. The initial structures were fully optimized based on the coordinates obtained from the XRD analysis of **4b**.

Given that both cam-B3LYP and B3LYP are widely used methods for theoretical calculations on porphyrin structures, these two methods were employed,^[47,48] and their results were compared to the experimental data. For this purpose, cam-B3LYP was paired with a 6-311G+(d,p) basis set, and B3LYP with a 6-31G(d,p) basis set. Although the XRD structure of **4b** shows no symmetry (C1 symmetry, refer to the Figure 2D), the optimized geometries for **4b**, **7b** and **8b** exhibit perfect symmetry (C_s symmetry). This suggests that the Z-shape observed in the XRD structure of diaminobenzene bearing **4a** and **4b** may be induced by solvent or packing effects.

Interestingly, we found that the results from the B3LYP and the cam-B3LYP methods led to different geometrical configurations. The cam-B3LYP method predicted a fully flat structure (except for **7b** and **8b**, as shown in Figure S58), which was expected for these molecules. In contrast, the B3LYP/6-31G(d,p) calculations suggested a bowl-like structure with asymmetric bending angles of 10.42° and 6.98° for **4b** and **5b**, respectively (see Table S2 for other compounds).

To investigate this further, we performed geometry optimizations on three different structural forms: the flat, bowl-like and Z-shape configurations using both cam-B3LYP and B3LYP methods to assess their relative stabilities (see Figures S57 and S58). The energy difference between the flat and bowl-like structure was minimal ($\Delta E = 0.25 \text{ kcal.mol}^{-1}$), whereas the Z-shape was significantly less stable ($\Delta E = 12.06 \text{ kcal.mol}^{-1}$) according to the B3LYP method.

Table 3. Orbital energy as well as the corresponding theoretical and experimental electronic gap (in eV) for compounds **4b–8b**.

Compound	Method	HOMO-1 (eV)	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)	ΔE_{th} (eV) ^[a]	ΔE_{cv} (eV) ^[b]	ΔE_{uv} (eV) ^[c]
4b	B3LYP	−5.065	−4.966	−2.451	−2.185	2.596	1.96	1.82
	cam-B3LYP	−6.471	−6.289	−2.027	−1.660	4.262		
5b-syn	B3LYP	−5.200	−4.991	−2.557	−2.307	2.434	1.95	1.82
	cam-B3LYP	−6.528	−6.413	−2.116	−1.769	4.297		
5b-anti	B3LYP	−5.201	−4.993	−2.558	−2.306	2.435	1.93	1.82
	cam-B3LYP	−6.528	−6.413	−2.116	−1.768	4.297		
6b-syn	B3LYP	−5.326	−5.147	−2.695	−2.468	2.452	1.93	1.82
	cam-B3LYP	−6.689	−6.556	−2.258	−1.943	4.298		
6b-anti	B3LYP	−5.326	−5.147	−2.697	−2.460	2.450	1.90	1.81
	cam-B3LYP	−6.689	−6.553	−2.263	−1.940	4.290		
7b	B3LYP	−5.333	−5.040	−2.731	−2.461	2.309	1.61	1.65
	cam-B3LYP	−6.576	−6.538	−2.246	−1.906	4.292		
8b	B3LYP	−5.228	−5.024	−2.928	−2.792	2.096	1.61	1.65
	cam-B3LYP	−6.578	−6.454	−2.408	−2.091	4.046		

[a] Calculated as $\Delta E_{th} = \text{HOMO} - \text{LUMO}$. [b] Same value as reported in Table 1. [c] Approximated value from the λ_{onset} of the electronic absorption.

Despite these structural differences, the calculated HOMO–LUMO gap were much larger using cam-B3LYP ($\Delta E_{\text{th}} = 4.046$ – 4.297 eV, see Table 3). In contrast, the B3LYP-calculated gaps were more consistent with experimental data, ranging from 2.096 to 2.596 eV.

Furthermore, the frontier molecular orbitals of compound **4b–8b**, including the two isomers for pyridine bearing **5b** and **6b**, were analyzed using DFT with the B3LYP/6-31G(d,p) basis set (Figure 7). As expected from the cyclic voltammetry, the HOMO is localized on the porphyrin core and the *meso*-substituents, while the LUMO is extended over the azaacene moieties. Increasing the number nitrogen atoms in the structure leads to a reduction in the HOMO–LUMO gap. For example, the introduction of 2,3-diaminopyridine in **5b** results in slight stabilization of the HOMO and LUMO by 0.03 eV and 0.10 eV, respectively. In contrast, the addition of 3,4-diaminopyridine in **6b** leads to a greater stabilization of both the HOMO (0.18 eV) and LUMO (0.24 eV), thereby reducing the electronic gap to 2.309 eV, which agrees with both electrochemical measurements and the observed electronic absorption.

Interestingly, the relative positions of the two additional nitrogen atoms in **5b** and **6b** (*i.e.* *syn*- vs. *anti*- isomers) had little to no impact on the energy levels, as seen in the results for various isomers (**5b-syn**, **5b-anti**, **6b-syn**, **6b-anti**). For pyrazine derivative **7b**, the introduction of four additional nitrogen atoms stabilizes the HOMO (0.07 eV) and of the LUMO (0.28 eV), thereby reducing the electronic gap to 2.309 eV, which agrees with both electrochemical measurements and the observed electronic absorption.

Table 4. Calculated lowest energy vertical transition for compounds **4b–8b** determined with the cam-B3LYP/6-311+G(d,p) level of theory.

Compound	Conformation	λ_{max} (nm) (f) ^[a]
4b	Z-shape	629.0 (0.0179)
	Flat	621.7 (0.0315)
	Bowl-like	629.0 (0.0118)
5b	<i>syn</i>	631 (0.0032)
	<i>anti</i>	631 (0.0035)
6b	<i>syn</i>	631.6 (0.0035)
	<i>anti</i>	631.9 (0.0037)
7b	-	637.3 (0.0001)
8b	-	654.4 (0.0102)

[a] Theoretical vertical absorption maximum determined in gas phase (f: corresponding to oscillator strength, see the ESI for details).

Finally, the incorporation of quinoxaline in **8b** significantly stabilizes the LUMO by 0.197 eV, although this comes at the cost of a slight destabilization of the HOMO by 0.016 eV. While the energy values obtained differ from those measured through electronic absorption and cyclic voltammetry, the observed trends remain consistent with the theoretical calculations. Additionally, time-dependent DFT (TD-DFT) calculations were performed based on the optimized geometries obtained using the B3LYP functional with a 6-31G(d,p) basis set. These calculations aimed to compare the vertical transitions with the experimental data. To further explore the differences between the B3LYP and cam-B3LYP functionals, the first twenty singlet excited states were calculated using the TD-SCF method with either B3LYP/6-31G(d,p) or cam-B3LYP/6-311+G(d,p).

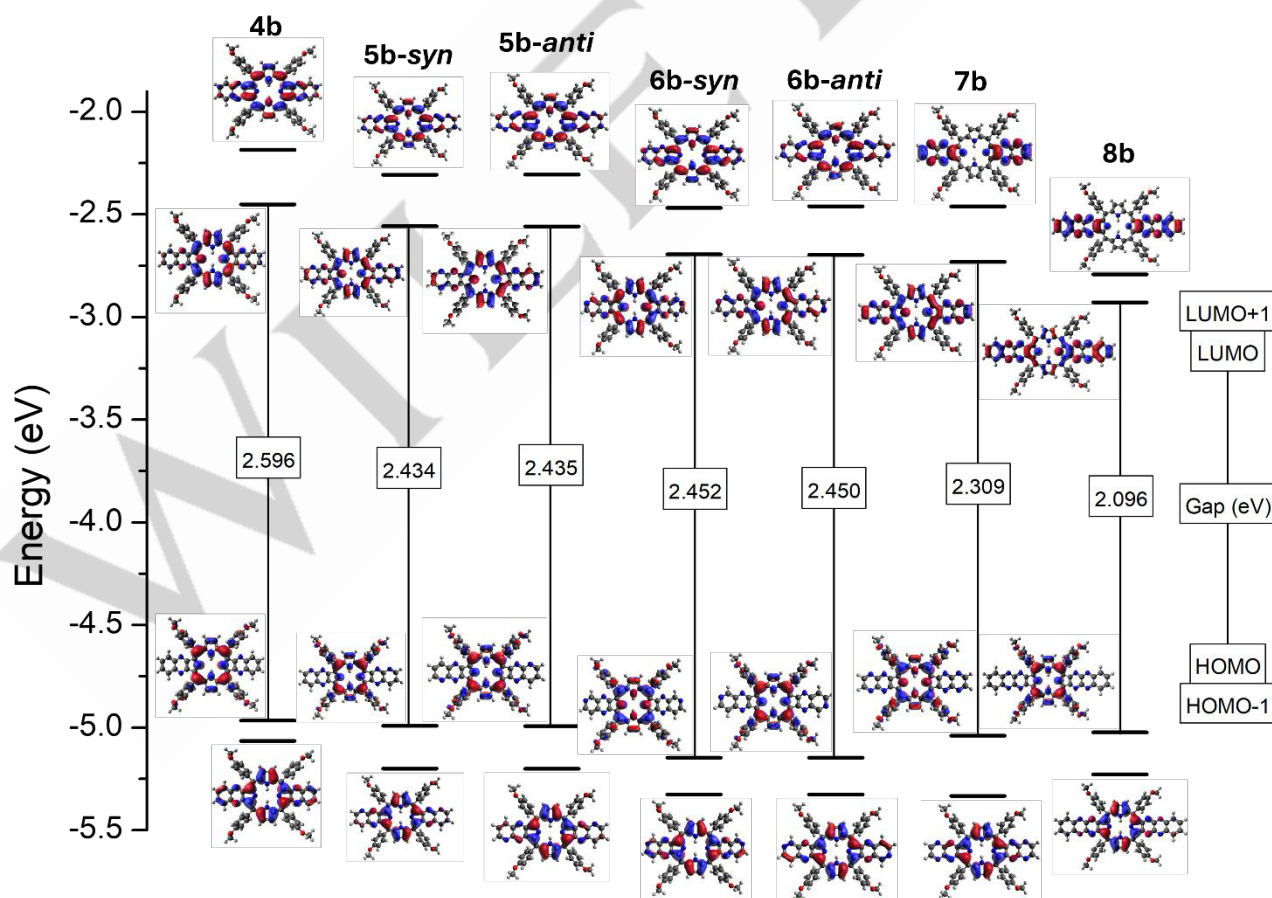


Figure 7. Plots of the calculated frontier orbitals and values of the HOMO–LUMO gaps (in eV) of **4b–8b** with B3LYP/6-31G(d,p) level of theory..

This comparative analysis provides deeper insight into the accuracy and limitations of the two functionals when applied to the optical properties of these systems.

In this instance, the cam-B3LYP functional provided a better match to experimental photophysical data, albeit with the commonly observed hypsochromic shift in the absorption maxima, which ranged from 35–60 nm (820–1290 cm⁻¹) (Table 4). The results highlight that increasing the number of nitrogen atoms in the azaacene moieties induces a progressive redshift in the absorption maxima. For example, in compounds containing four nitrogen atoms within the azaacene units, such as **4b**, the absorption maximum is located at 629.0 nm (621.7 nm) for the Z-shape and bowl-like (flat) configurations.

The incorporation of two additional nitrogen atoms, as seen in the pyridine derivatives **5b** and **6b**, results in a slight redshift of 60–70 cm⁻¹. Meanwhile, introducing eight nitrogen atoms using pyrazine leads to a more significant bathochromic shift of approximately 200 cm⁻¹. Quinoxaline derivative **8b**, also containing eight nitrogen atoms, exhibits an even larger shift of 600 cm⁻¹ relative to **4b** (410 cm⁻¹ relative to **7b**). This pronounced redshift is attributed to the extended aromaticity introduced by the two additional six-membered rings in its structure. Overall, the theoretical data align well with the trends observed in the experimental electronic absorption measurements, reinforcing the relationship between nitrogen incorporation and the redshift of absorption.

Conclusion

This work reported the synthesis and the characterization of novel azaacene-fused porphyrins featuring various diamino aromatic groups, which significantly influence their absorption, emission properties, and redox behavior.

These azaacene-extended porphyrins exhibit a moderate bathochromic shift in the optical properties typically associated with porphyrins, alongside high molar absorptivity and notable absorption in the NIR-II region upon protonation.

Cyclic voltammetry measurements indicate that the observed redshift in photophysical properties is primarily due to the stabilization of the LUMO level upon the introduction of azaacene motifs, while the HOMO level remains largely unaffected. This hypothesis was further corroborated by comprehensive DFT and TD-DFT calculations, providing deeper insight into the electronic structure of these compounds.

In addition to their optical and electronic advantages, these compounds exhibit remarkable stability compared to traditional unsubstituted azaacenes. Furthermore, they are readily soluble in a wide range of apolar solvents, including aliphatic and aromatic hydrocarbons (e.g., *n*-hexane, *n*-octane, *n*-dodecane, benzene, toluene) to heterocyclic solvents (THF, 1,4-dioxane) and chlorinated solvents (dichloromethane, dichloroethane, chlorobenzene). This exceptional solubility facilitates their synthesis, purification, and their use for potential applications in optoelectronic devices.

Supporting Information

The authors have cited additional references within the Support Information.^[49–53] Experimental protocols, NMR spectra, FTIR

spectra, HR-MS spectra, single-crystal X-ray and additional spectroscopic data are available in the Electronic Supporting Information (ESI) PDF file.

Single-Crystal X-Ray

CCDC 2416754 (compound **1a**), CCDC 2416756 (compound **1b**), CCDC 2417184 (compound **2a**), CCDC 2416755 (compound **3a**), CCDC 2416753 (compound **4a**) and CCDC 2415624 (compound **4b**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033.

Author Contributions

BM for synthesis, characterization, optical and redox investigations. BM and YM for (TD-)DFT investigations. YM and NA for XRD analysis and structural resolution. HY for project design, supervision and funding acquisition. All authors critically reviewed the manuscript draft and approved the final version for submission.

Acknowledgements

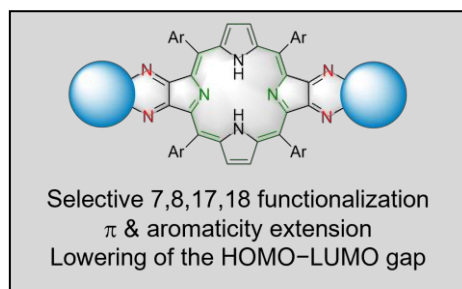
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Keywords: Azaacene • Porphyrin • π -extension • NIR dyes

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Entry for the Table of Contents



Herein, we provide the straightforward synthesis of new azaacene-fused porphyrins, accompanied by an in-depth investigation of their optical and electrochemical properties. These experimental findings were further supported by comprehensive theoretical calculations, providing valuable insights into the structure–property relationship of these compounds.

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