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Tuning Fluorescence and Singlet Oxygen Quantum Yields of Subporphyrazines by Axial Functionalization

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In Memoriam Prof. Michael Hanack

The axial functionalization of Subporphyrazines (SubPzs) with unreported alkoxy groups, carboxy and carboperoxy rests, as well as sulfanyl, aryl and amino groups, forming B–O, B–S, B–C, and B–N bonds, respectively, has been investigated. The studied oxygen nucleophiles include aromatic and sterically demanding aliphatic alcohols, along with carboxylic acids and peracids. In general, direct substitution of the chloro-SubPz by oxygen nucleophiles of diverse nature proceeds smoothly, with yields of the isolated alkoxy and carboxy-substituted SubPzs ranging from 49 to 100%. Conversely, direct substitution with sulphur, carbon and nitrogen nucleophiles do not afford the corresponding substituted SubPzs. In these cases, a stepwise procedure involving an axial triflate-SubPz intermediate was employed, affording only the phenyl-SubPz in 8% yield. The major compound under these conditions was the unreported SubPz μ-oxo dimer, presumably arising from substitution of the triflate-SubPz by the *in situ* generated hydroxy-SubPz. This result indicates a quite low reactivity of the TfO-SubPz intermediate with carbon, sulphur and nitrogen nucleophiles. All SubPzs prepared in this work exhibited fluorescence at 510–515 nm with quantum yields ranging from 0.1 to 0.24. Additionally, all SubPzs generated singlet oxygen, with Φ_Δ values ranging from 0.15 to 0.57, which show no apparent correlation with the axial substituents.

Introduction

Subporphyrazines (SubPzs, Figure 1)[1] constitute an appealing class of tripyrrolic macrocycles that belong to the subporphyrinoid family.[2] As for all the other subporphyrinoids, SubPzs are cone-shaped, 14 π-electron aromatic compounds that exclusively coordinate boron (III). The tetracoordinated boron atom gives rise to a 3D cavity formed by the three pyrrole rings and an axial ligand. So far, the BCl_3 assisted cyclotrimerization reaction of maleonitrile derivatives constitutes the only procedure to assemble the SubPz structure, which, by default, bears a chlorine atom at the axial position, arising from the boron template.[1,2,3]

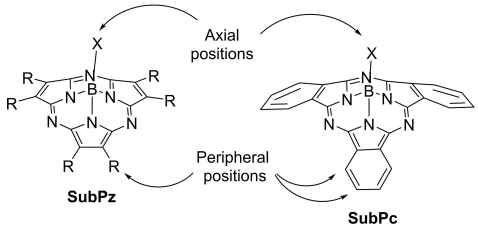

Figure 1. Structures of Subporphyrazine (SubPz) and Subphthalocyanine (SubPc).

The bare SubPz structure exhibits its main absorptions at 294 nm (B-band) and 500 nm (Q-band),[1,4] and a fluorescence band in the green region that mirror images to the absorption.[5] Distinctively, SubPzs display unique electronic tunability by peripheral functionalization.[6] This arises from an unusually strong influence of peripheral substituents on the SubPz π-system, which is especially favoured by the confluence of three structural peculiarities in these systems, namely: (i) the direct attachment of peripheral substituents to the β-positions of the SubPz pyrrole rings; (ii) the *meso*-aza bridges and (iii) the central electron-deficient boron atom. Thus, peripheral substitution constitutes a powerful tool to tune absorption, luminescent and redox profiles of SubPzs using heteroatoms,[1a,7] aryl,[3,6] or

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vinyl groups,[6a] allowing to design chromophores with tailored properties, like red absorbers[6a] and non-fullerene electron-acceptors.[6b] As a direct application of this nascent SubPz chemistry, SubPz-based supramolecular devices for singlet fission,[8] and green-to-NIR photochromic switches,[9] have been recently reported.

Contrasting with peripheral substitution, SubPz axial functionalization has been scarcely explored.[2] Axial functionalization of their SubPc relatives (Figure 1) by direct treatment with nucleophiles usually requires high temperatures. This may eventually produce SubPc decomposition by nucleophilic attack to the macrocycle, leading to ring opening processes. For this reason, axial reaction sometimes requires the use of some additives, such as 1,8-diazabicycloundec-7-ene (DBU), triethylamine, pyridine or DIPEA, which neutralize the generated HCl.[2] Besides, alternative synthetic strategies for SubPc axial functionalization have been developed, involving the intermediacy of activated electrophilic boron SubPc species, such as triflates,[10,11] or aluminum complexes.[12,13] Tin(IV) chloride has also been used as activating agent.[14]

Chlorinated subporphyrazines (ClSubPz) early showed a higher tendency to hydrolyze in the presence of water than the corresponding SubPc relatives, suggesting a greater axial reactivity of SubPzs.[1a] However, axial functionalization of the pyrrolic series has been limited so far to the substitution of the original chlorine atom by hydroxy,[1] aryloxy[8,15] or fluorine groups.[15a] Axial functionalization usually does not alter the absorption profile of SubPzs. On the contrary, it produces variable impact – from little to strong – on the SubPz redox properties.[2a] An example of the latter is the axial substitution with rutheroarenes,[2a] which makes macrocycles 200 mV easier to reduce and 145–292 mV more difficult to oxidize.[15b,16] The effect of the axial substitution in SubPz luminescence has not been investigated, although substitution with electron-rich systems has shown to quench SubPz fluorescence, revealing electronic coupling of the axial moieties with the electron-accepting SubPzs.[15b]

In this work, we sought to explore the scope of the direct axial substitution of SubPzs with ligands of different nature, and systematically study the influence of axial substitution on the fluorescence properties, as well as on the singlet oxygen generation ability of the chromophores. Notably, axial functionalization has proven to be a powerful tool to tune singlet oxygen sensitization in other porphyrinoids.[17] The development of red absorbing singlet oxygen generators with luminescent properties could position SubPzs as potential materials for their application in photopharmacology. The axial substitution allows to preserve the SubPz absorption profile. In addition, it constitutes a simpler approach to functionalize SubPzs with two moieties of different nature, related to the preparation of peripheral unsymmetrically substituted macrocycles. The preparation of biocompatible SubPzs with amphiphilic character, i.e., endowed with both a lipophilic and a hydrophilic part, enabling their penetration into different types of cells by passive diffusion, was one of the objectives. To this end, a ClSubPz hexasubstituted with propyl chains at the periphery was selected as the model precursor, and a variety of nucleophiles were tested to be directly incorporated at the axial position. For some of the cases, the introduction of the axial ligands through newly generated synthetic triflate intermediates was also explored.

Results and Discussion

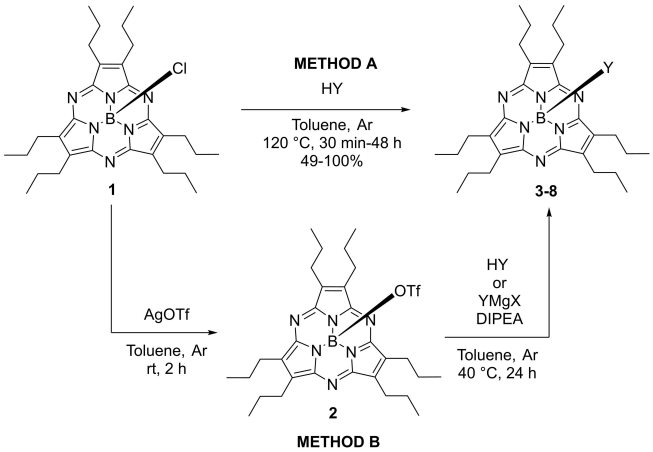
Synthesis

Peripheral hexapropyl substitution was chosen for these studies, because it leads to stable chromophores[18] and provides good solubility in most organic solvents. Propyl chains are also relatively inert, which is a great asset to avoid secondary reactions in the presence of nucleophiles during axial functionalization.

The synthesis of the ClSubPz precursor **1** was performed following the reported procedure (Scheme 1).[1a]

Axial substitution of SubPz **1** with phenol had previously been reported by treatment with five equivalents of phenol in toluene at reflux temperature.[15a] Therefore, axial functionalization using the selected HY nucleophiles (Scheme 1) was first attempted using similar, or optimized related reaction conditions, by direct treatment of the isolated SubPz **1** with the corresponding nucleophile in toluene at reflux temperature (Method A). Alternatively, the stepwise, one-pot Method B (Scheme 1) was investigated. Following the reported procedure,[10] ClSubPz **1** was dissolved in toluene in presence of silver triflate (AgOTf) under anhydrous and anaerobic conditions, to generate the more reactive triflate-substituted SubPz **2**. After full conversion, the nucleophile was *in situ* added, along with N,N-diisopropylethylamine (DIPEA). The role of the latter is to trap the triflic acid generated upon triflate substitution with HY.[10]

Nucleophiles of different nature were selected to explore the influence of the heteroatom, forming a bond with the SubPz central boron atom. Thus, the scope of Method A was explored using O, S, N and C nucleophiles. Among the former,



Scheme 1. Methods A and B for axial functionalization of SubPzs.

alcohols, carboxylic acids and carboxylic peracids were essayed (Figure 2).

By using direct Method A, a variety of alcohol derivatives could be introduced with yields ranging from good to quantitative. Among them, previously non-explored aliphatic alkoxy ligands, including alkyl (**3a**) and polyethylene glycol rests (PEG) (**3b**), could be smoothly introduced in 83 and 100% yields, respectively, by treatment with the corresponding primary alcohols. Similar results were obtained upon treatment with the sterically more demanding primary alcohols such as the protected galactose (SubPz **3c**, Figure 2). The reaction of **1** with a secondary alcohol such as mannofuranose provided **3d** in lower yields of 65%. These results strongly contrast with the behaviour observed in the axial substitution of SubPc derivatives, especially, in the case of sterically hindered nucleophiles. The latter tend to be quite unreactive when using the direct approach, requiring long reaction times that give rise to decomposition of SubPc.[10]

For the preparation of **3e**, the corresponding primary, hydrophilic trisubstituted benzyl alcohol **9** (Chart S1) donated with three triethyleneglycol monomethyl ether chains, was prepared through a 3-step pathway.[19] Due to the poor solubility of **9** in toluene, ten equivalents of the alcohol were used, and the reaction time was increased to 48 h, leading to **3e** in 49% yield. Here, the lower yield related to the previous reactions can be explained in terms of the purification process, rather than the efficiency of the substitution reaction, since compound **3e** and its precursor **9** display similar Rf values, hence being difficult to separate by chromatography.

Next, the substitution of the chlorine atom was also attempted with a carboxylic acid *via* the direct Method A. The reaction with benzoic acid was monitored by thin layer chromatography (TLC) and showed to be complete after only 30 minutes. After column chromatography on silica gel, SubPz **4** (Figure 2) was isolated with 91% yield. The much lower reaction times and higher yields achieved evidence the higher reactivity of SubPzs also with carboxylic acids related to their SubPc counterparts.[10]

The chemical characterization of SubPzs **3** and **4** was performed by ^{1}H NMR, ^{13}C NMR, MS and UV/Vis absorption spectroscopies. Both peripheral and axial substituents are strongly influenced by the SubPz diatropic ring current. Upon cyclotrimerization, the peripheral alkyl chains are deshielded by 0.7 ppm with respect to the maleonitrile precursor,[1a] appearing as a multiplet at 3.0–3.2 ppm for protons closer to the aromatic macrocycle (labelled **a**). Signals of protons labelled **b** and **c**, which are located further to the aromatic system, appear downfield shifted by 0.4 and 0.2 ppm, respectively.

The opposite effect is observed for axial ligands, as they fall in the aromatic shielding cone, hence, resonances corresponding to these substituents appear upfield shifted. Figure 3 shows the ^{1}H NMR spectrum of **3c** illustrating the typical spectrum for an axially substituted SubPz. Hydrogens on the carbon atom directly attached to the axial oxygen link typically show an upfield shift of 2.5 ppm, while protons attached to the β-position of the oxygen link, display a lower shielding effect of 1.3 ppm. For protons at γ-position and further, shielding is observed in the order of 0.5 ppm.

The introduction of a peracid, namely, *meta*-chloroperoxybenzoic acid (*m*-CPBA), was also tested *via* Method A. The ^{1}H NMR spectrum of the sample after purification by chromatography on silica gel using a mixture of hexane and EtOAc (16:1) revealed four signals in the aromatic region – one doublet of doublet of doublets at 7.15 ppm (J=7.9, 1.6 and 1.1 Hz), accompanied by a triplet at 7.09 ppm (J=1.6 Hz), a doublet of triplets at 7.05 ppm (J=7.9 and 1.6 Hz) and a triplet at 6.94 ppm (J=7.9 Hz), respectively – that are compatible with the presence of **5**. However, the MS spectrum (Figure S33) was dominated by a cluster at m/z=651–655, which isotopic pattern clearly matched that of an ion corresponding to $[M-O]^+$ expected for **5**, accompanied by the corresponding borenium cation at m/z=496–498 and the hydroxylated ion at m/z=513–516, generated under the MS conditions. The cluster assignable to $[M]^+$ appeared as a very weak ion at m/z=667–671 (Figure S33). MS/MS confirmed that all the observed ions

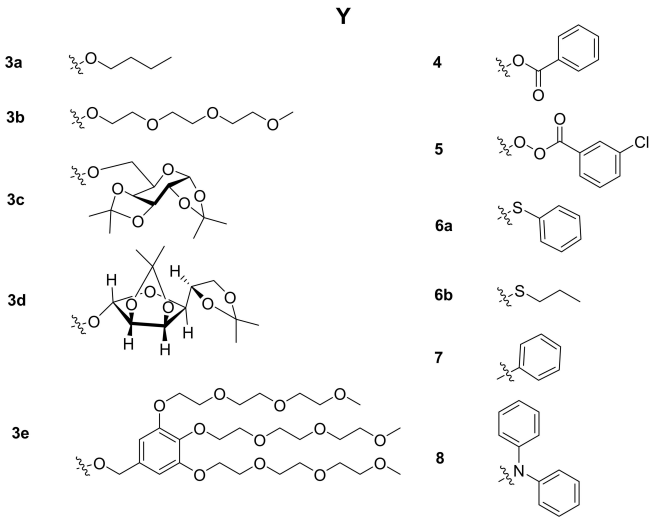


Figure 2. Nucleophiles studied in this work.

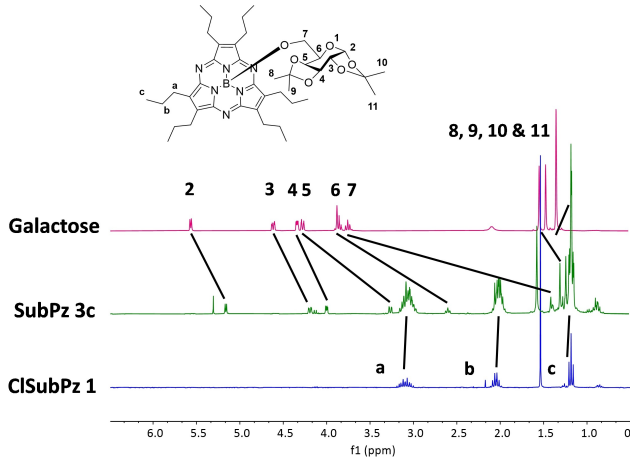


Figure 3. Comparative ^{1}H NMR spectra of ClSubPz **1**, SubPz **3c** and -D-galactose precursor in $CDCl_3$.

can arise from the fragmentation of the molecular ion $[M]^+$ corresponding to **5** (Figure S34).

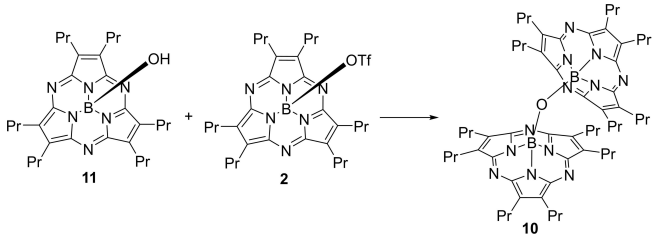
Other reaction conditions related to previously reported procedures for peroxy-substituted subporphyrins were tested.[20] ClSubPz **1** and *m*-CPBA were dissolved in CH_2Cl_2 and stirred for 15 minutes at room temperature, leading to decomposition of the SubPz.

The substitution reaction of **1** with other types of nucleophiles containing different (hetero)atoms, namely, with thiols, Grignard reagents and secondary amines, was first essayed using Method A, to explore the formation of **6a**, **b**, **7** and **8** (Figure 2). Under Method A, the sulfanyl substituted SubPz **6a** was not detected by ^{1}H NMR nor MS. The latter showed a cluster at *m/z* = 1009–1012 that was assigned to the unreported SubPz μ-oxodimer **10**.[2,20] The other SubPz derivatives **6b**, **7** and **8** were not detected either using Method A. Hence, the preparation of **6a** through the stepwise Method B (Scheme 1) using thiophenol as the nucleophile, was attempted. Under these conditions, a major compound that was identified as the μ-oxodimer **10** (Scheme 2) was isolated after column chromatography on silica gel, using a mixture (8:1) of hexane and EtOAc.

SubPz μ-oxodimer **10** showed in ^{1}H NMR the signals corresponding to the SubPz α-located methylene as a multiplet at 2.8–3.0 ppm, slightly shielded due to the presence of the second SubPz ring. ^{13}C NMR showed a strong desymmetrization of the SubPz halves as an effect of one another. The MS spectrum was dominated by a cluster at *m/z* = 1008–1013 that was assigned to the molecular ion $[M]^+$. The formation of **10** can be rationalized considering an axial substitution reaction between the triflate derivative **2** and the hydroxy-SubPz derivative **11** (Scheme 2). This looks in principle possible if the reaction conditions are not strictly anhydrous and the triflate derivative partially hydrolyses to form the hydroxy-substituted SubPz derivative. Unlike the corresponding Subporphyrin μ-oxodimer, dimer **10** resulted to be quite stable under chromatographic conditions and could be readily isolated.[20]

The formation of **6a** could only be observed as a trace in the MS spectrum of one of the chromatographic fractions, as a very weak cluster at *m/z* = 606–608, assignable to $[M+H]^+$, when Method B was applied under strictly anhydrous conditions. However, the major products of this reaction still were the dimer **10** and the hydroxy SubPz **11** (Scheme 2). Assuming that ClSubPz **1** could readily be converted into the triflate-substituted SubPz, this result could only be rationalized in terms of a low reactivity of the thiol with triflate **2** that would lead to partial hydrolysis of the triflate and dimerization under work-up conditions. This hypothesis was reinforced when we studied the reaction with phenylmagnesium bromide as the nucleophile. In this case, SubPz **7** was obtained in 8% yield after purification by column chromatography on silica gel using a 8:1 mixture of hexane and EtOAc as eluent, followed by separation from dimer **10**, which resulted to be the major compound, by gel permeation chromatography on Biobeads SX-1 using toluene as the eluent.

The overall results obtained with the various nucleophiles by both Methods A and B are summarized in Table 1.



Scheme 2. Structure of SubPz μ-oxo dimer **10** and the proposed pathway for its formation.

UV-Visible, fluorescence spectroscopies and singlet oxygen generation

All SubPzs **1**–**8** showed in $CHCl_3$ an absorption maximum at 499 nm accounting for the Q-band, as well as 2 peaks at 330 and 290 nm that correspond to the B band, (Figure 4a), thus evidencing once more the lack of influence of the axial substitution in the absorption properties of SubPzs.[2,4,15] As for their fluorescence profile, regardless of the axial ligand

Table 1. Axial functionalization of SubPzs explored in this report.

SubPz	Method	HY[a]	t (h)	Yield[b]
3a	A	390[c]	3	83
3b	A	10	22	100
3c	A	25	22	100
3d	A	5	22	65
3e	A	10	48	49
4	A	5	0.5	91
5	A	5	0.5	28
6a	A	15	4	Nd[d]
	B	2	22	T[e]
6b	A	1	24	Nd[d]
7	A	15	24	Nd[d]
	B	2	22	8
8	A	1	22	Nd[d]

[a] Equiv. [b] Isolated compound. [c] Neat. [d] Not detected. [e] Trace.

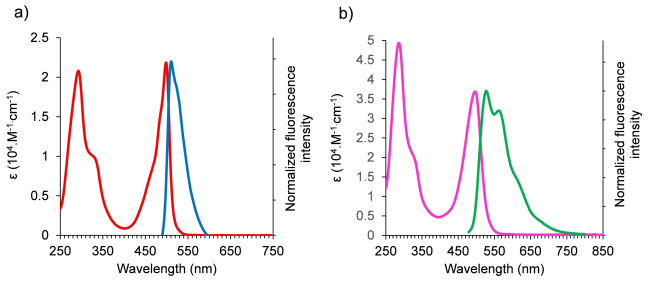


Figure 4. UV-Vis and fluorescence (λ_{ex} = 480 nm) spectra of **1** and **10** in chloroform: a) Red line, absorption spectrum of **1**; blue line, emission spectrum of **1**. b) Pink line, absorption spectrum of **10**; green line, emission spectrum of **10**.

Table 2. Fluorescence and singlet oxygen sensitization quantum yields displayed by SubPzs.

SubPz	1	3a	3b	3c	3d	3e	4	5	7	10
Φ_F[a]	0.12	0.11	0.11	0.10	0.11	0.10	0.12	0.18	0.09	0.24
Φ_Δ[b]	0.51	0.34	0.37	0.45	0.57	0.29	0.36	0.15	0.55	0.26

[a] In $CHCl_3$ at 293 K. [b] In dmso.

introduced, all SubPzs showed fluorescence in the green region with a maximum of emission at 510–515 nm and Stokes shift of 471 cm^{-1} when excited at $\lambda_{ex} = 480$ nm.

The μ-oxo dimer **10** showed in $CHCl_3$ a broader Q-band (54 nm half width *vs* 34 nm for monomeric SubPzs) with a maximum at 496 nm, as well as 2 absorption peaks at 331 and 286 nm, similarly to **1** (Figure 4b). The B:Q relative intensity changes are of 1.05 to 1.34 on going from a monomeric SubPzs to the dimeric **10**, both effects reminding the spectroscopic changes observed in porphyrinoids upon aggregation. Yet, the molar absorptivity coefficient ε of the dimer at the Q-band is almost twice as high as that of **1**. The dimer **10** also shows a broader emission band when excited at $\lambda = 488$ nm, stretching from 490 to 650 nm, with a maximum at 560 nm and larger Stokes shift of 2304 cm^{-1}.

Neither fluorescence or singlet oxygen quantum yields are very much altered by axial functionalization. Room temperature fluorescence quantum yields, were obtained by the comparative method[21] using rubrene in chloroform solution, $\Phi_F = 0.54$, as reference compound.[22]

The Φ_F values for SubPzs **1**–**7** in chloroform at room temperature ranged from 0.09 to 0.18, the lowest being for phenyl-substituted SubPz **7** and the largest for peroxo-SubPz **5**. No relevant changes are observed upon axial substitution with chlorine, alkoxy, carboxy and carbon nucleophiles. μ-oxo dimer **10**, on the other hand, showed the highest fluorescence quantum yield of the series (Table 2).

Singlet oxygen sensitization quantum yields (Φ_Δ) were obtained by direct measurement of the characteristic phosphorescence emission of $^1O_2$ at 1276 nm, after laser excitation at 355 nm of aerated dimethylsulfoxide (DMSO) solutions of the SubPzs derivatives.[21] The observed kinetic traces were attributed to the photosensitized phosphorescence emission decay of singlet oxygen since: (i) these were well fitted with a single-exponential decay law with lifetimes of ~6.0 μs in DMSO solution, which are in good agreement with the characteristic lifetime of singlet oxygen in this solvent (5.7 μs), respectively[23] and (ii) the signal was quenched when degassing the solutions with N_2 for at least 20 min. The Φ_Δ values were determined using a comparative method (using phenalenone in toluene, $\Phi_\Delta = 0.93$,[24] as reference photosensitizer) by plotting the initial phosphorescence intensity (at 1276 nm) as a function of the laser dose and comparing the slope with that obtained for the reference compound obtained in identical experimental conditions.

All the studied SubPzs generate singlet oxygen, with Φ_Δ values ranging from 0.15 to 0.57. The different values do not apparently correlate with the chlorine, alkoxy, carboxyloxy and carbon nature of the nucleophiles. Here, the lowest value corresponds to the peroxo-SubPz **5**, while the highest corresponds to the chlorine, mannose (alkoxy) and phenyl-substituted compounds (Table 2).

Conclusions

A general synthetic protocol to functionalize the axial position of the SubPz structure with novel alkoxy groups carrying lipophilic and hydrophilic residues and/or sterically hindered moieties, as well as carboxy and carboperoxy residues, has been established. The approach involves the direct substitution of the axial chlorinated SubPz derivative with the corresponding oxygen nucleophiles, encompassing aliphatic alcohols, carboxylic acids and peracids. Remarkably, this direct reaction proves to be quite straightforward in SubPz derivatives, exhibiting superior efficiency in some cases compared to the corresponding stepwise reaction in SubPcs using activated intermediates. This direct method, however, fails to produce the corresponding axially substituted SubPzs when carbon, sulphur and nitrogen nucleophiles are used. To address these cases, a stepwise procedure mediated by a reactive triflate-substituted SubPz intermediate was investigated. This approach enabled the formation of an axially substituted SubPz with a carbon nucleophile using a Grignard reagent, although the stepwise reaction does not afford the corresponding substituted compounds with thiols and amines. Instead, the unreported SubPz μ-oxodimer emerges as the predominant product, suggesting a lower reactivity of the TfO-SubPz intermediate towards carbon, sulphur and nitrogen nucleophiles.

All tested SubPzs showed fluorescence properties and generate singlet oxygen, with quantum yields high enough to explore the application of these chromophores as fluorescent markers or as singlet oxygen photosensitizers.

Supporting Information

Experimental procedures, spectroscopic data and NMR, UV-Vis, MS and HRMS spectra.

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Subporphyrazines · Axial substitution · Fluorescence · Singlet oxygen · Boron

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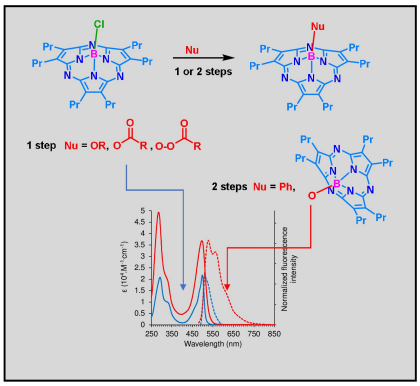
RESEARCH ARTICLE

Efficient direct axial substitution reactions on Chloro-Subporphyrazines with oxygen nucleophiles provide alkoxy, carboxy and carboperoxy-Subporphyrazines, while the introduction of carbon nucleophiles is mediated by a triflate intermediate.



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