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Chemical Transformations and Photophysical Properties of *meso*-Tetrathienyl-Substituted Porphyrin Derivatives

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The chemistry of *meso*-tetrathienyl-substituted porphyrin derivatives was explored, including synthesis and subsequent metalation, nitration and 1,3-dipolar cycloaddition reactions. *Mono*- and *tetra*-nitro-*meso*-tetrathienylporphyrins were prepared selectively under mild nitration conditions with $NaNO_2$ and trifluoroacetic acid, and the corresponding chlorins and bacteriochlorins were also obtained by reaction with 1,3-dipoles. The products were characterized in detail and their preliminary photophysical properties were evaluated.

Introduction

Thienyl-appended porphyrin derivatives are a relatively unexplored class of aryl-substituted porphyrins that have received growing interest.[1] Some *meso* and β-substituted derivatives have been synthesized and studied since 1968, when *meso*-tetra(thien-2-yl)porphyrin (**1**) was prepared for the first time (Figure 1).[2]

In contrast to *meso*-tetraphenylporphyrin (**2**), the thienyl derivatives present some peculiarities in terms of photophysical, photochemical as well as chemical properties.[3] Recent publications have presented a number of applications in electron-transfer studies,[4] eletrocatalysis,[5] biosensors,[6] self-assembling,[7] photovoltaic cells,[8] and for photoionization and photoconductive processes.[1]

Structurally, the *meso*-tetra(thien-2-yl)porphyrins differ from *meso*-tetraphenyl-porphyrins not only by the molecular formula, but by the way in which the aryl rings are conjugated with the porphyrin core structure. It was determined by X-ray analysis that **1** presents the four thienyl rings almost co-planar with the core structure. On the other hand, in **2** the phenyl rings are almost perpendicular (Figure 1).[9] This structural difference is relevant for the electronic properties, and makes porphyrin derivatives such as **1** an interesting scaffold for many studies and applications. In 2006, Brückner and co-workers[10] demonstrated, after experimental and theoretical studies on *meso*-tetra(thien-2-yl)porphyrins, a quasi-alignment and an efficient π-conjugation between the thienyl rings and the porphyrin core structure. Pryce and co-workers[11] described an interesting effect promoted by this extended resonance in *meso*-thienyl-porphyrins, that is the increase of the HOMO energy, but also the unexpected decrease of the LUMO energy, resulting in a lower HOMO–LUMO energy-gap compared with *meso*-tetraphenyl-porphyrinoids (difference of ca. 0.5 eV). In addition to the electrochemical properties, thienyl-porphyrinoids present a singular reactivity allowing chemo- and regio-selective reactions. Bhavana and co-workers[12] have studied electrophilic substitutions in thienyl-porphyrinoids. These authors also explored halogenations and nitrations, thus evaluating a number of electrochemical and structural properties. It is important to mention that the introduction of electron-withdrawing groups has improved the ability of some porphyrinoids to produce singlet oxygen as well as to avoid photobleaching;[13] such properties are essential for their use as photosensitizers.

We have now evaluated improvements in the synthesis of **1** by different methods, followed by selective nitration and metallation, and studied the reactivity of these thienyl and nitro-thienylporphyrinoids in 1,3-dipolar cycloaddition reactions, thus obtaining new chlorin and bacteriochlorin derivatives. In addition, we have performed a preliminary study of their photophysical properties and explored the potential use of these chemically modified thienyl-porphyrinoids in photodynamic therapy (PDT) studies.

Results and Discussion

Synthesis of Porphyrin 1

Porphyrins are generally synthesized by condensation methods, starting from pyrroles and aryl-aldehydes under

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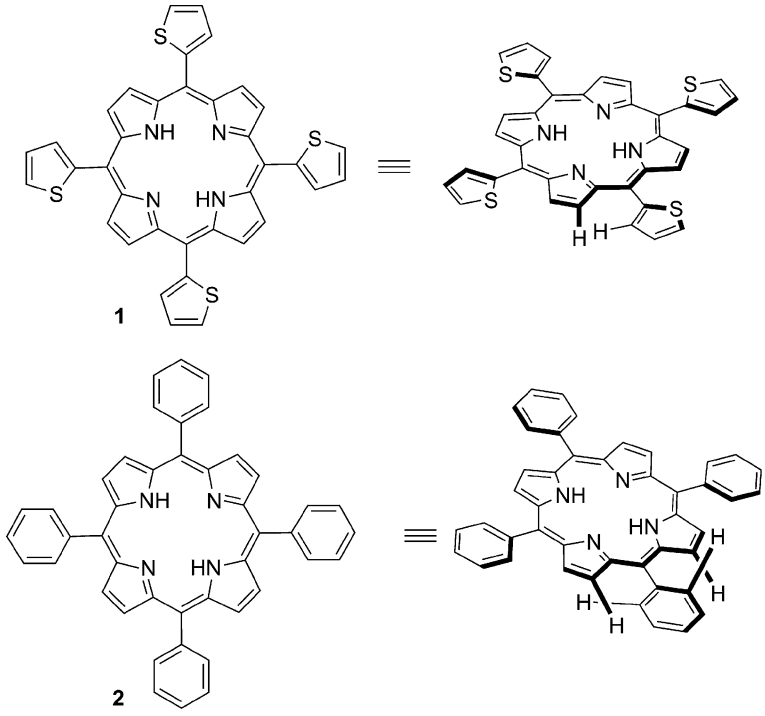
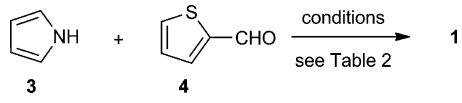


Figure 1. Structures and conformations of aryl groups in tetraaryl-porphyrins.

acid catalysis. This is a consolidated methodology, but frequently produces porphyrins in very low yield, and containing a number of byproducts. In particular, published reports on the synthesis of porphyrin **1** are not consistent, with reports of low (10–20%) up to high (72%) yields (Table 1); moreover, in several cases the purity is not described. For example, some authors describe compound **1** as a purple crystalline solid and others as a brown solid.

We tried to reproduce some of these methodologies for the synthesis of the porphyrin **1** (Scheme 1), then examined experimental modifications to improve the yields and purity (Table 2).



Scheme 1. Synthesis of porphyrin **1**.

We first repeated the methodology developed by Li et al. and observed the formation of excessive amounts of pyrrolic polymers that made the purification of **1** difficult.[18] Four to five recrystallizations were necessary to purify **1**, and we also found that column chromatography on silica was not adequate for isolation of this porphyrin on scales of more than 50 mg, because of low solubility. In our hands, porphyrin **1** was obtained in 22% yield as very pure purple crystals, which was confirmed through ^{1}H NMR spectroscopy. The Li conditions[18] were also tested in both 5 and 20 mmol scales with 22 and 20% yield, respectively (entries 1 and 2, Table 2). These results are less efficient than reported (44% yield, Table 1), but we confirmed the high purity of **1**. We also investigated changing the oxidant from $PhNO_2$ to *p*-chloranil (Table 2, entry 3), but under these conditions porphyrin **1** was obtained in only trace amounts. The best conditions for the synthesis of **1** were achieved when the solvent was changed to chlorobenzene instead of ethyl ether, and also when the reaction time was increased to 24 h and the oxidation temperature decreased to 130 °C. Under these conditions, we observed a reduced amount of byproduct formation and porphyrin **1** was isolated in 36%

Table 1. Reported syntheses of porphyrin **1**.

Authors	Publication year	Conditions	Yield [%]	Physical appearance
Triebs et al.[2]	1968	pyridine, 220 °c	9	not reported
Torréns et al.[14]	1972	propionic acid, open flask, reflux	not reported	not reported
Bhyrappa et al.[3a]	2001	propionic acid, open flask, reflux	not reported	not reported
Ormond et al.[15]	2013	propionic acid, open flask, reflux	11	not reported
Ono et al.[16]	1998	(i) TFA, CH_2Cl_2; (ii) *p*-chloranil, r.t.	not reported	not reported
Rochford et al.[11]	2008	(i) $BF_3{\cdot}OEt_2$, CH_2Cl_2; (ii) *p*-chloranil, r.t.	18	not reported
Bonar-Law [17]	1996	(i) SDS, H_2O, HCl; (ii) *p*-chloranil, r.t.	24	purple crystals
Li et al.[18]	2007	$NH_2OH{\cdot}HCl$, Et_2O, $PhNO_2$, 210 °C	44	purple crystals
Fadda et al.[19]	2013	(i) DMF, 100 °C, 10 min; (ii) PTSA, 150 °C, 1 h	72	brown solid

Table 2. Yields and conditions for the synthesis of porphyrin **1**.

Entry	Pyrrole **3** [mmol]	Aldehyde **4** [mmol]	Conditions	Yield of **1** [%]
1	5	5	(i) $NH_2OH{\cdot}HCl$, Et_2O, r.t., 4 h; (ii) $PhNO_2$, 210 °C, 2 h	22
2	20	20	(i) $NH_2OH{\cdot}HCl$, Et_2O, r.t., 4 h; (ii) $PhNO_2$, 210 °C, 2 h	20
3	5	5	(i) $NH_2OH{\cdot}HCl$, Et_2O, r.t., 4 h; (ii) *p*-chloranil, r.t., 12 h	traces
4	5	5	(i) $NH_2OH{\cdot}HCl$, chlorobenzene, r.t., 24 h; (ii) $PhNO_2$, 130 °C, 2 h	36
5	5	5	(i) $NH_2OH{\cdot}HCl$, 1,4-dioxane, r.t., 5 h; (ii) $PhNO_2$, 100 °C, 2 h	2
6	1	1	(i) sodium dodecil sulfate, H_2O, HCl; (ii) *p*-chloranil, r.t., 12 h.	6
7	1.4	1.4	(i) DMF, 100 °C, 10 min; (ii) PTSA, 150 °C, 1 h	13

yield after three recrystallizations as very pure purple crystals. An attempt to improve the yield was undertaken by using dioxane (5 h) and an oxidation temperature of 100 °C (entry 5), but without success (2% yield). Two other methodologies were tested (entries 6 and 7): the Bonar-Law methodology (entry 6) was very interesting in terms of a sustainable procedure, because it uses very mild conditions compared with the other approaches; however, in our hands porphyrin **1** was obtained in only 6% yield (compared with 24% reported yield). In our last test we used *N*,*N*-dimethylformamide (DMF) as solvent and PTSA catalysis (entry 7), and obtained **1** in 13% yield, compared with 72% yield reported by Fadda et al.[19] By using this last methodology, porphyrin **1** was obtained in a pure form after four recrystallizations as purple crystals, and not as a brown solid as described by the authors. The ^{1}H NMR spectrum of **1** presents a broad singlet between δ = 8.96–9.14 ppm corresponding to eight β-pyrrolic hydrogen atoms, and three doublets of doublets between δ = 7.50–8.00 ppm, corresponding to the hydrogen atoms of the thienyl ring.

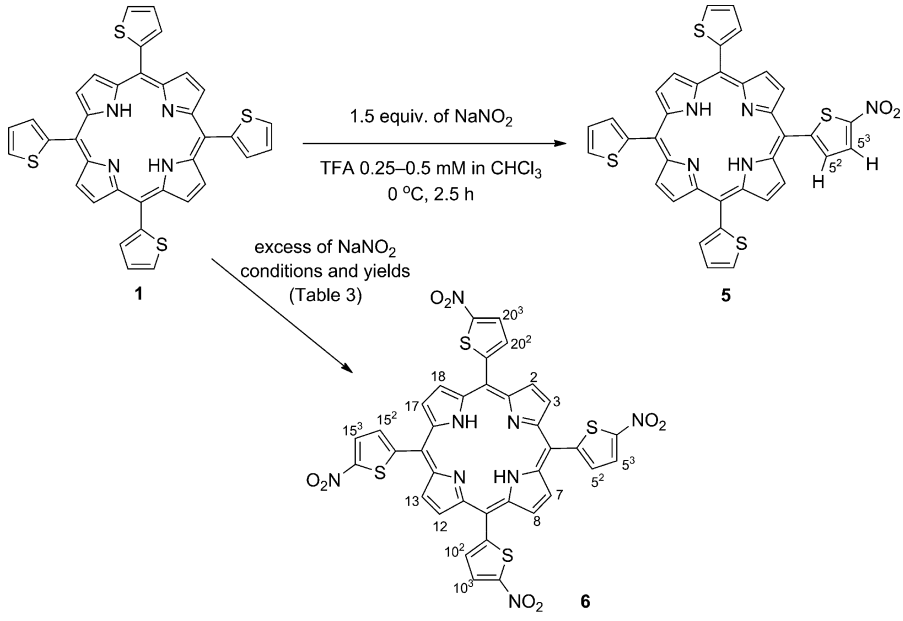
Thus, having explored the synthesis of porphyrin **1**, a good yield (36%) of very pure material was available, and we were able to proceed with a number of transformations and photophysical studies.

Chemical Transformations of Porphyrin 1

We first evaluated the reactivity of **1** in nitration (Scheme 2). Regioselective nitrations at the phenyl groups were described for tetraphenylporphyrin **2** by using trifluoroacetic acid (TFA) and $NaNO_2$.[20] Thus, we tested this methodology using porphyrin **1**, but observed only complete degradation of **1**. Nevertheless, when milder conditions were tested using 1.5 equiv. $NaNO_2$ in a solution of TFA (0.25–0.5 mM) in $CHCl_3$ at 0 °C, mono-nitro compound **5** was obtained in 66% yield after purification by silica gel column chromatography (Scheme 2). After characterization using ^{1}H NMR and ^{13}C NMR (1D and 2D) spectroscopic analysis, we were able to confirm this regioselective mono-nitration at the 5-position of the thienyl ring. The ^{1}H NMR spectrum of **5** presents two doublet of doublets and one broad singlet between δ = 8.96–9.14 ppm, corresponding to eight β-pyrrolic hydrogen atoms and indicating the loss of symmetry due to the mono-nitration. We also found a doublet at δ = 8.31 ppm corresponding to H-5^3 (Scheme 2) and a doublet at δ = 7.84 ppm corresponding to H-5^2. The other thienyl hydrogen atoms appear as a multiplet at δ = 7.50–7.95 ppm. We have confirmed the structure of **5** by ^{13}C and 2D-NMR analysis as well as by HRMS-ESI-TOF analysis, which revealed an isotopically correct ion with *m*/*z* 684.0660, calculated for $[M + H]^+$ 684.0656, $C_{36}H_{21}N_5O_2S_4$ (Δ = 0.6 ppm) (see the Supporting Information).

After the successful regioselective mono-nitration of **1**, we investigated the tetra-nitration of this porphyrin (Scheme 2). To this end, we selected the reaction conditions described in Table 3. We started by using a large excess of $NaNO_2$ but controlling the concentration of TFA. The first conditions tried (entry 1) involved the use of 8 equiv. $NaNO_2$ in TFA (0.1–0.9 mM) in $CHCl_3$ at 0 °C. In this case, small aliquots of TFA were added in 1 h intervals to avoid very acid conditions at the start of the reaction. After 9 h, the tetra-nitrated compound **6** was obtained in 24% yield after purification on silica gel. The structure of compound **6** was completely assigned by ^{1}H and ^{13}C NMR (1D and 2D) spectroscopic analysis, as the tetra-nitrated derivative at the 5-positions of the thienyl rings of **1**. The ^{1}H NMR spectrum presents a singlet at δ = 9.32 ppm, corresponding to eight β-pyrrolic hydrogen atoms, a doublet at δ = 8.63 ppm, corresponding to H-5^3, H-10^3, H-15^3, and H-20^3, and a doublet at δ = 8.21 ppm, corresponding to H-5^2, H-10^2, H-15^2, and H-20^2. The structure of **6** was further confirmed by ^{13}C NMR and 2D-NMR analysis, as well as by HRMS-ESI-TOF analysis, which revealed an isotopically correct ion with *m*/*z* 819.0216, calculated for $[M + H]^+$ 819.0203, $C_{36}H_{18}N_8O_8S_4$ (Δ = 1.6 ppm) (see the Supporting Information).

We also performed this reaction using 20 equiv. $NaNO_2$ (entry 2) but at –6 °C using a TFA solution under the same conditions to those described above (entry 1; 0.1–0.7 mM). Compound **6** was isolated in 26% yield after 20 h. When the reaction temperature was reduced to –11 °C and the concentration of TFA was increased from 0.4 to 1.1 mM with addition of TFA in 1 h intervals, we observed the total consumption of **1** after 5 h, and **6** was isolated in 59% yield after purification on silica gel. We also tried the use of more concentrated solutions of TFA (7.8–19.4 mM; entry 4) as well as performing the reaction at –30 °C (entry 5), but the yields were reduced under these conditions. During screening of reaction conditions, we observed the probable di- and tri-nitratated derivatives, but only in trace amounts, since the reactions were designed to produce mono- or tetra-ni-



Scheme 2. Nitration of porphyrin **1**.

Table 3. Conditions for tetra-nitration at the 5-thienyl positions of **1**.

Entry	Temp. [°C]	[TFA] in $CHCl_3$ [mM]	$NaNO_2$ [equiv.]	Time [h]	Yield of **4** [%]
1	0	0.1–0.7	8	9	24
2	–6	0.1–0.7	20	20	26
3	**–11**	**0.4–1.1**	**20**	**5**	**59**
4	–11	7.8–19.4	20	11	35
5	–30	0.4–3.2	20	120	8

trated compounds. Thus, the isolation of these minor compounds was not performed.

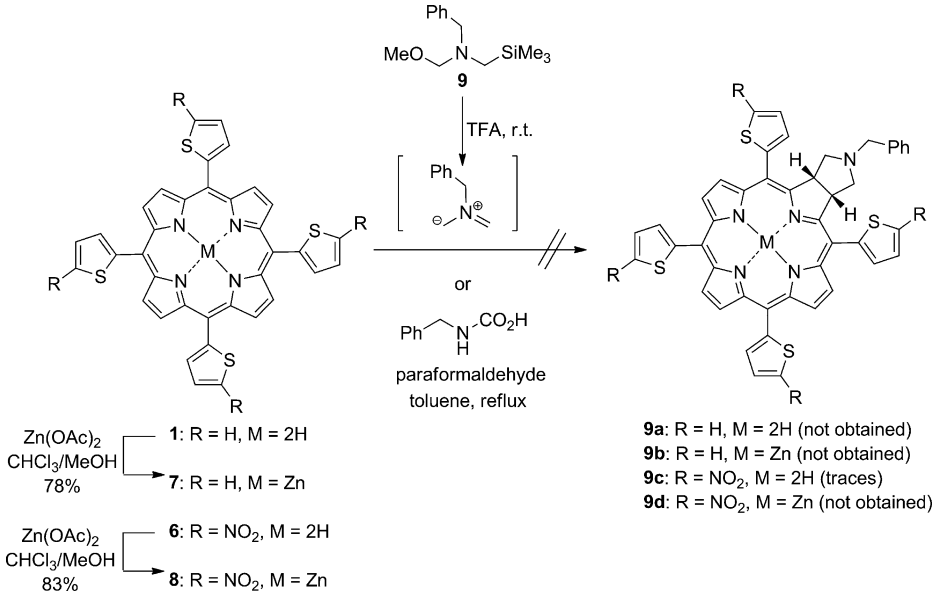
At this point, we have achieved a selective and efficient methodology to perform mono- or tetra-nitrations of **1**, thus opening the possibility of future strategic functionalizations and photophysical studies.

1,3-Dipolar Cycloaddition Reactions of Porphyrins 1 and 6, and Their Metalated Derivatives 7 and 8

Chlorin and bacteriochlorin derivatives are porphyrinoids reduced at the β-positions, with a number of applications in photobiological processes.[21] Therefore, we investigated β-functionalizations of **1**. Cavaleiro's group has demonstrated a number of successful transformations using 1,3-dipolar cycloaddition reactions in porphyrins.[22] We have also recently demonstrated the usefulness of this reaction in porphyrins by using bulky ylides, thus providing chlorins that are prevented from aggregating because if their steric bulk.[23]

Based upon our previous success, we investigated the reactivity of porphyrins **1** and **6** as well as their metalated derivatives **7** and **8**. First, compounds **1** and **6** were metalated with $Zn(OAc)_2/CH_2Cl_2/MeOH$, giving porphyrins **7** and **8** in 78 and 83% yield, respectively, after purification by crystallizations (Scheme 3). We then tried to perform the 1,3-dipolar cycloaddition reaction between the porphyrinoid derivatives **1**, **6**, **7**, and **8** with the benzylic azomethine ylide generated by two different methods (Scheme 3). The first of these methods starts with a silyl derivative and proceeds under mild conditions and acid catalysis to generate the azomethine ylide. The second method starts from *N*-benzylglycine and paraformaldehyde under heating to generate the same azomethine ylide. However, only chlorin **9c** was obtained in trace amounts by using the second method, and none of the other reactions gave any isolable products. Compound **9c** was characterized by ^1H NMR, HRMS-MALDI-TOF (Supporting Information) and UV/Vis (Figure 2) analysis. We observed two signals at δ = 2.73–2.76 and 3.10–3.20 ppm in the ^1H NMR spectrum, corresponding to the methylene groups of the pyrrolidine ring, as well as a singlet at δ = 3.41 ppm, corresponding to the methylene hydrogen atoms of the benzyl group. A broad signal corresponding to the hydrogen atoms of the ring junction was observed at δ = 5.49 ppm, and signals from all twenty aromatic hydrogen atoms are present between δ = 6.94 and 8.93 ppm. The HRMS-ESI-TOF analysis revealed a typical and isotopically correct ion with *m/z* 952.109123, calculated for $[M + H]^+$ 952.109447, $C_{45}H_{29}N_9O_8S_4$ (Δ = 0.3 ppm) (see the Supporting Information).

We also explored nitrile oxide dipole chemistry with these porphyrinoid derivatives because it is well known that this dipole reacts with a number of substrates through normal, neutral or inverse electron demand. The first test was performed by using porphyrin **1** as dipolarophile and the nitrile oxide precursor **10**, under argon atmosphere and with heating (80 °C) (Scheme 4). In this case, chlorin **11a** was obtained in 17% yield after purification. This reaction was investigated using three different amounts of the dipole generator **10** (Table 4), however, there were no significant



Scheme 3. 1,3-Dipolar cycloaddition reaction studies using an azomethine ylide.

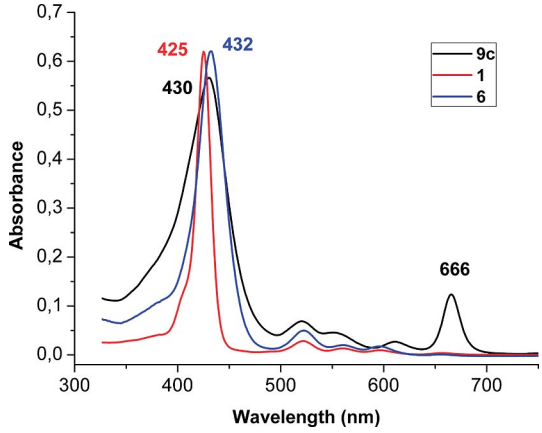


Figure 2. UV/Vis spectra of compounds **1**, **6** and **9c**.

differences between the reaction yields obtained for chlorin **11a** (13–17%; entries 1–3). In all cases, the reactions were monitored until complete consumption of starting material **1**. Some degradation products were also observed, probably as a result of polymerization.

After the relative success of the 1,3-dipolar cycloaddition reaction between **1** and the nitrile oxide generated in situ from **10** (Scheme 4), we tested the same reaction using Zn-porphyrin **7** under the same conditions. However, only low yields of **11b** were obtained (2–9%), indicating the lower reactivity of porphyrin **7** compared with **1**.

The reaction between the tetra-nitrated porphyrin **6** and the nitrile oxide dipole (Scheme 4) gave a number of products, including three major compounds that were identified as chlorin **11c**, and the isomeric bacteriochlorins **12c** and **13c** in different proportions, depending on the reaction conditions (Table 5).

Using 5 equiv. of the 1,3-dipolar precursor **10**, products **11c**, **12c** and **13c** were obtained in 7, 3 and 7% yield, respectively. Starting from 20 equiv. **10**, the yields were improved to 15, 13 and 14%, respectively. When 50 equiv. was used the reaction also produced some highly polar byproducts, justifying the lower yields. In addition, we also verified a lower reactivity of the Zn-derivative **8** compared with the corresponding metal-free **6**.

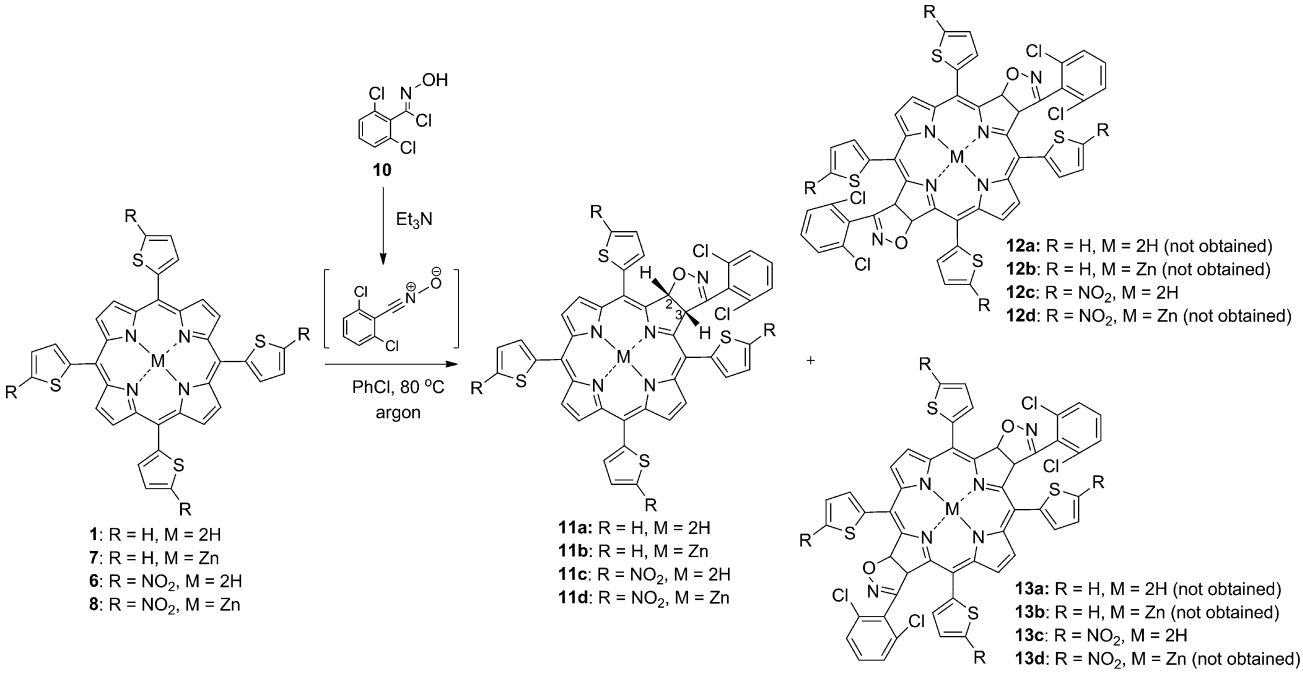
The reaction between **8** and **10** (20 equiv.) yielded only chlorin **11d** (22%), and bacteriochlorins **12d** and **13d** were not detected. Further equivalents of **10** were tested with no improvements in the yield of **11d** and no formation of **12d** or **13d**.

Regarding the characterization of these last cycloadducts, we can highlight for chlorin **11a** the signals in the ^{1}H NMR spectrum at δ = 7.36 and 7.98 ppm corresponding to the hydrogen atoms of the ring junction (H-2 and H-3). The N–H hydrogen signals appear as two singlets at δ = –1.71 and –1.77 ppm due to the loss of symmetry. All the other hydrogen signals and the ^{13}C NMR spectra were assigned on the basis of 2D NMR spectroscopic analysis (see the Supporting Information).

The structure of **11a** was also confirmed by HRMS-MALDI-TOF analysis, which presented a typical and isotopically correct ion with *m*/*z* 826.0414, calculated for $[M + H]^+$ 826.0397, $C_{43}H_{25}Cl_2N_5OS_4$ (Δ = 1.8 ppm) (see the Supporting Information). The UV/Vis spectrum confirmed the occurrence of cycloaddition, giving a typical band at 656 nm (Figure 3).

Compound **11b** presented very similar ^{1}H NMR signals to those of **11a**, except for the NH signals with a negative chemical shift, and the structure of **11b** was confirmed by HRMS-MALDI-TOF as well as by UV/Vis spectroscopic analysis (Figure 3 and the Supporting Information). Compound **11b** presented an isotopically correct ion with *m*/*z* 886.9454 (Δ = 1.0 ppm) and a band at 622 nm in the UV/Vis spectrum (Figure 3).

Highlighting the ^{1}H NMR spectrum of compound **11c**, two doublets at δ = 7.38 and 8.04 ppm were observed, cor-



Scheme 4. 1,3-Dipolar cycloaddition reactions using the nitrile oxide.

Table 4. Conditions for chlorin **11a** synthesis.

Entry	Temp. [°C]	Dipole precursor **10** [equiv.]	Et_3N [equiv.]	Time [h]	Yield of **11a** [%]
1	80	5	7	48	17
2	80	20	25	26	13
3	80	50	53	10	14

Table 5. Conditions for chlorin **11c** synthesis.

Entry	Temp. [°C]	Dipole precursor **10** [equiv.]	Et_3N [equiv.]	Time [h]	Yield [%]		
					11c	**12c**	**13c**
1	80	5	7	48	7	3	7
2	80	20	25	24	15	13	14
3	80	50	53	10	11	8	12

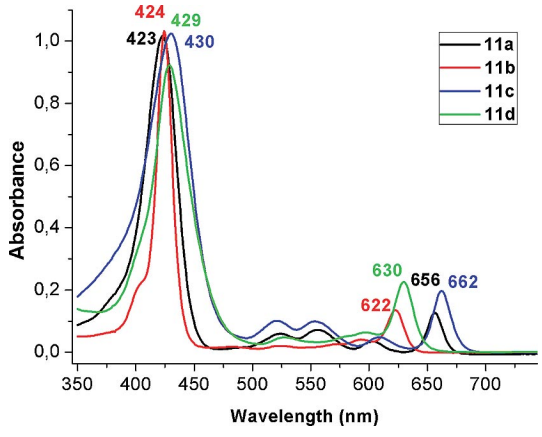


Figure 3. UV/Vis spectra of compounds **11a**–**d** in CH_2Cl_2.

responding to the hydrogen atoms of the ring junction (H-2 and H-3), and also two singlets at δ = –1.80 and –1.86 ppm, assigned to the two nonequivalent N–H hydrogen atoms.

The structure of **11c** was additionally confirmed by HRMS-MALDI-TOF analysis, which revealed an isotopically correct ion with *m*/*z* 1005.9793 (Δ = 0.2 ppm). The ^{1}H NMR spectrum of compound **11d** was very similar to that of compound **11c**, but without the NH signals at a negative chemical shift. The structure of compound **11d** was confirmed by HRMS-ESI-TOF analysis, which presented an ion *m*/*z* 1067.89393 (Δ = 0.89 ppm), and also a typical Q-band at 630 nm in UV/Vis spectrum (Figure 3 and the Supporting Information).

The bacteriochlorins **12c** and **13c** were characterized with the support of reported data for similar compounds.[24b] This publication uses symmetry elements to assign the isomers **12c** and **13c**. The ^{1}H NMR spectrum of compound **12c** presented only one broad singlet at δ = –1.82 ppm corresponding to the N–H hydrogen atoms, and one doublet at δ = 8.31 ppm and one doublet of doublets at δ = 8.63 for the four β-pyrrolic hydrogen atoms. The occurrence of only one N–H signal indicates higher symmetry of the molecule and corroborates the structure of compound **12c**.[24] It is important to mention that compound **12c** was obtained as the *cis* and *trans* stereoisomers in a ratio of 88:12, which is consistent with similar reported results.[24] The separation of these stereoisomers was not possible by conventional chromatographic methods.

The ^{1}H NMR spectrum of **13c** presented two broad singlets at δ = –1.82 and –1.76 ppm corresponding to the two N–H hydrogen atoms, and two doublets at δ = 8.31 and 8.63 ppm assigned to the β-pyrrolic hydrogen atoms. The occurrence of two N–H signals confirms the structure of the less symmetric bacteriochlorin **13c**, in agreement with previous reports for similar compounds.[24] Compounds **12c** and **13c** presented a typical and isotopically correct ion with *m*/*z* 1192.9419 (Δ = 2.7 ppm) and *m*/*z* 1192.9416 (Δ =

2.4 ppm), respectively, and both present bands at 728 nm in their UV/Vis spectra (Figure 4 and the Supporting Information).

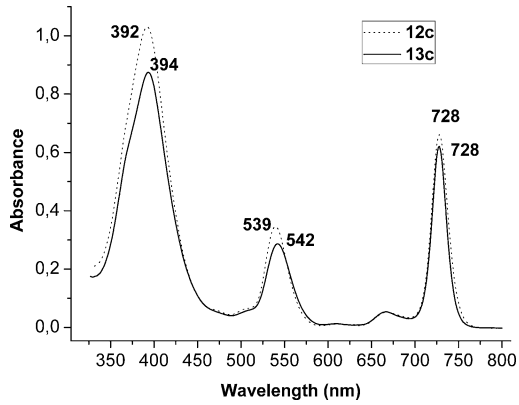


Figure 4. UV/Vis spectra of compounds **12c** and **13c** in CH_2Cl_2.

Photophysical Studies

Singlet Oxygen ($^1O_2$) Generation Quantum Yield (Φ_Δ) and Fluorescence Quantum Yield (Φ_{fl})

Photophysical studies of the compounds synthesized here were performed to evaluate and compare the potential of these molecules as photosensitizers. All the chlorins and porphyrins exhibited very low fluorescence quantum yields (Table 6). Indeed, the values measured were below 0.1, which indicates that the radiative decay process from the first excited singlet state of these photosensitizers is not as significant as competitive processes that can occur [fluorescence, intersystem crossing (ISC) and internal conversion]. Fluorescence quantum yields of porphyrins and chlorins are usually below 0.1.[25–28] The observed tendency of low fluorescence quantum yield is an expected property because ISC and fluorescence are competitive events, and it is known that porphyrins and chlorins are good triplet-state forming compounds, that are able to exhibit high singlet oxygen production quantum yields.[25–28] Porphyrins **1**, **6** and **7** showed singlet oxygen production quantum yields around 0.5, and **8** around 0.8 (Table 6). The insertion of NO_2 groups in the periphery of the thienyl rings (compound **6**) had no influence on the singlet oxygen generation when compared with compound **1**. The insertion of zinc (compound **7**) also led to no significant difference. Nevertheless, zinc insertion in the $-NO_2$ modified porphyrin (compound **8**) resulted in a very significant increase in singlet oxygen generation (0.84). Usually electron-withdrawing groups increase singlet oxygen production of porphyrins as well as zinc insertion.[28] However, in the chlorin series the effects are distinct from these observed in porphyrins. The -NO_2 groups at the periphery of the aromatic rings reduce by 40% the singlet oxygen production quantum yield (0.65 for **11a** and 0.40 for **11c**). Zinc inclusion caused reduction to the same extent (0.65 for **11a** and 0.40 for **11b**). Indeed, when both substitutions were performed, the singlet oxygen production quantum yield became even smaller (0.18 for **11d**). Bacteriochlorins **12c** and **13c** exhibited very similar singlet oxygen quantum yields (0.32–0.42) and can be compared to those of chlorins **11b**–**c** (0.40).

Table 6. Spectroscopic data. Singlet oxygen generation quantum yield (Φ_Δ) and singlet oxygen lifetimes obtained by bi-exponential fitting of the decay curves (τ_1 and τ_2) in chloroform, and fluorescence quantum yield (Φ_{fl}) in chloroform.

PS	Φ_Δ	τ_1 [μs]	τ_2 [μσ]	Φ_{fl}
1	0.46 ± 0.16[a]	40 ± 3	164 ± 5	0.01 ± 0.006[c]
7	0.46 ± 0.03[a]	34 ± 12	87 ± 26	0.02 ± 0.01[c]
6	0.44 ± 0.04[a]	45 ± 3	210 ± 1	0.02 ± 0.01[c]
8	0.84 ± 0.13[a]	48 ± 1	183 ± 21	0.04 ± 0.02[c]
11a	0.65 ± 0.07[b]	44 ± 3	167 ± 6	0.06 ± 0.02[c]
11b	0.40 ± 0.05[b]	28 ± 13	60 ± 5	0.11 ± 0.06[c]
11c	0.40 ± 0.06[a]	47 ± 2	196 ± 5	0.08 ± 0.03[c]
11d	0.18 ± 0.06[b]	42 ± 1	189 ± 1	0.05 ± 0.02[c]
12c	0.36 ± 0.07[a]	47 ± 5	209 ± 1	0.08 ± 0.03[c]
13c	0.42 ± 0.08[a]	41 ± 1	210 ± 1	0.08 ± 0.03[c]
2	0.50[d],[a]	43 ± 2	150 ± 9	0.10 ± 0.01[c]

[a] Excitation wavelength 532 nm. [b] Excitation wavelength 635 nm. [c] Excitation wavelength 515 nm. [d] 5,10,15,20-Tetraphenylporphyrin (**2**) solution in chloroform value obtained from the literature.[29]

Porphyrin **7** and chlorin **11b** exhibited significantly lower singlet oxygen lifetimes when compared with the other porphyrinoids (Table 6). Quantum calculations and further photophysical experiments will be carried out to explain better these differences.

Aggregation Studies by UV/Vis Spectroscopy

We have shown in recent publications that porphyrinoids with bulky moieties in a perpendicular orientation to the core structure are prevented from π-stacking interactions, and thus prevented from aggregation in solution.[21c,21d,23]

To evaluate the aggregation behavior of compounds **11a**–**d**, **12c** and **13c** in solution, we studied aggregation phenomena by UV/Vis analysis in CH_2Cl_2. We observed that there was no shift at the maximum absorbance wavelengths and there was a linear increase in the absorption vs. concentration at 1–10 μM, indicating no aggregation for any of the studied compounds (see an example for compound **11a** in Figure 5, and the Supporting Information for others).

Photobleaching Studies

Efficient photosensitizers must be stable when exposed to light for long periods of time. Thus, photobleaching studies are an important parameter for the study of photodegradation of photosensitizers after irradiation with light, whereby singlet oxygen reacts with the photosensitizer promoting its own degradation.[30] Compounds **11a**–**d**, **12c** and **13c** presented very good resistance to light exposure after 10 irradiation periods of 1 min each with a red laser at 661 nm and 50 mW, having its maximum absorbance with time as a linear constant (see an example for compound **11a** in the Figure 6, and the Supporting Information for others).

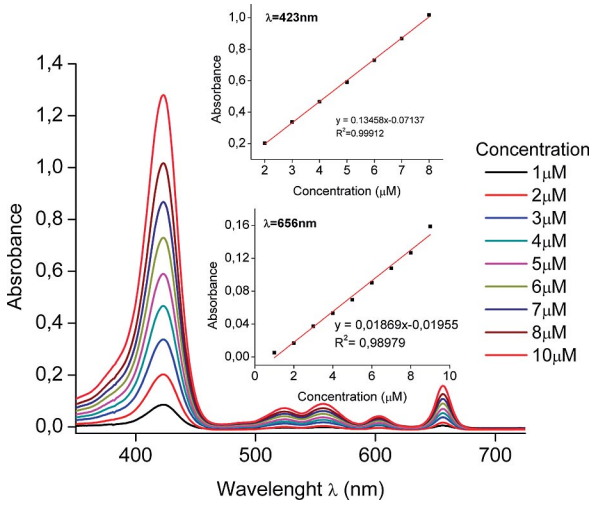


Figure 5. Aggregation study for compound **11a** in CH_2Cl_2.

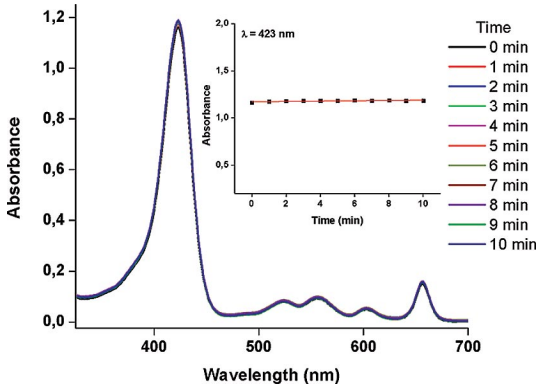


Figure 6. Photobleaching study for compound **11a** in CH_2Cl_2 using a red laser (50 mW) at 661 nm.

Conclusions

In this study, we have explored the chemistry of tetrathienylporphyrins, including nitration reactions and 1,3-dipolar cycloadditions. We have demonstrated that the mono- or tetra-nitro derivatives can be obtained chemoselectively in both cases. No β-substituted porphyrinoids were observed. We have also found that the tetranitroporphyrinoids are more reactive than the nonsubstituted porphyrinoids, under 1,3-dipolar cycloaddition reaction conditions. The nitrile oxide ylide under study yields only bacteriochlorin derivatives and no isobacteriochlorins, as previously observed in tetraphenylporphyrin chemistry. Preliminary investigations on the photophysical properties of the compounds were undertaken and they confirmed that these compounds (porphyrins, chlorins and bacteriochlorins) are good dyes for use in PDT studies.

Experimental Section

General Methods: All reagents were of analytical grade and were purchased from Aldrich or national suppliers. When necessary, solvents and reagents were purified according to standard procedures.[31] ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrometer at 400.15 and 101 MHz, respectively. $CDCl_3$, CD_2Cl_2, [D_5]pyridine and [D_6]DMSO were used as solvents and TMS as the internal reference. ^1H and ^{13}C signal assignments were carried out by using 2D gCOSY ($^1H/^1H$), gHSQC ($^1H/^{13}C$), gHMBC ($^1H/^{13}C$), and NOESY experiments (mixing time of 800 ms). The chemical shifts are expressed in δ (ppm) and coupling constants (J) are given in Hertz (Hz). HRMS were obtained by using ESI-TOF (Max Impact Bruker). The UV/Vis spectra were recorded with a Perkin–Elmer Lambda 25 spectrophotometer using 1 cm optical length quartz cuvettes at 25 °C and dichloromethane as solvent. Fluorescence emission spectra were recorded with a Cary 50 Fluorescence Spectrophotometer (VARIAN – Victoria, Australia) using chloroform as solvent. Singlet oxygen ($^1O_2$) generation quantum yields (Φ_Δ) and $^1O_2$ lifetimes were determined with a Continuum Surelite III Nd:YAG laser. Column chromatography was carried out using silica-flash 230–400 mesh from Aldrich. Analytical preparative thin-layer chromatography was performed on aluminum sheets (1 mm thick) Merck TLC silica-gel 60 F_{254}.

5,10,15,20-Tetra(thien-2′-yl)porphyrin (1): Pyrrole (**3**; 0.35 mL, 5 mmol), 2-thiophenecarbaldehyde (**4**; 0.47 mL, 5 mmol) and $NH_2OH{\cdot}HCl$ (5 mmol) were dissolved in anhydrous monochlorobenzene (25 mL) at room temperature and reacted for 24 h. Nitrobenzene (20 mL) was added and the mixture was heated at 130 °C for 2 h. The monochlorobenzene and nitrobenzene were distilled off to give a crude product. The crude product was precipitated from DMSO/MeOH. After filtration, product **1** was recrystallized from 1:2 $CHCl_3$/MeOH and this procedure was repeated three to five times to obtain **1** (0.291 g, 0.455 mmol, 36%) as a purple solid. UV/Vis ($CHCl_3$): λ_{max} (logε) = 426 (5.57), 522 (4.23), 561 (3.91), 596 (3.79), 656 (3.39) nm. ^1H NMR (400.15 MHz, $CDCl_3$): δ = –2.65 (s, 2 H, N–H), 7.51 (dd, J = 5.3, 3.4 Hz, 4 H, H-5^3, H-10^3, H-15^3, H-20^3), 7.86 (dd, J = 5.3, 1.1 Hz, 4 H, H-5^4, H-10^4, H-15^4, H-20^4), 7.92 (dd, J = 3.3, 1.1 Hz, 4 H, H-5^2, H-10^2, H-15^2, H-20^2), 9.04 (s, 8 H, H-β) ppm. HRMS (ESI-TOF): m/z calcd for $C_{36}H_{22}N_4S_4$ [M + H]$^+$ 639.0800; found 639.0794.

5,10,15,20-Tetra(thien-2′-yl)porphyrinatozinc(II) (7): Porphyrin **1** (153.9 mg, 0.24 mmol) was solubilized in a mixture of CH_2Cl_2/MeOH (8:2, 60 mL), followed by the addition of $Zn(OAc)_2{\cdot}2H_2O$ (1.58 g, 30 equiv., 7.20 mmol). The reaction mixture was stirred at 40 °C for 40 min, then the solvent was removed under vacuum and the remaining residue was extracted with CH_2Cl_2 and water. The organic layer was washed with water and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum and the product was recrystallized from CH_2Cl_2 and hexane to afford porphyrin **7** (132.9 mg, 0.189 mmol, 78%). UV/Vis (CH_2Cl_2): λ_{max} (logε) = 427 (5.24), 519 (3.45), 555 (4.03), 598 (3.42) nm. ^1H NMR (400.15 MHz, [D_5]pyridine): δ = 7.53 (dd, J = 5.3, 3.4 Hz, 4 H, H-5^3, H-10^3, H-15^3, H-20^3), 7.98 (dd, J = 5.3, 1.1 Hz, 4 H, H-5^4, H-10^4, H-15^4, H-20^4), 8.05 (dd, J = 3.3, 1.1 Hz, 4 H, H-5^2, H-10^2, H-15^2, H-20^2), 9.34 (s, 8 H, H-β) ppm. ^{13}C NMR (101 MHz, [D_5]-pyridine): δ = 113.9 (C-5, C-10, C-15, C-20), 127.1 (C-5^3, C-10^3, C-15^3, C-20^3), 128.8 (C-5^4, C-10^4, C-15^4, C-20^4), 133.0 (C-β), 134.5 (C-5^2, C-10^2, C-15^2, C-20^2), 144.9 (C-5^1 C-10^1, C-15^1, C-20^1), 152.3 (C-1, C-4, C-6, C-9, C-11, C-14, C-16, C-19) ppm. HRMS-ESI-TOF: m/z calcd for $C_{36}H_{20}N_4S_4Zn$ [M]$^+$ 699.9857; found 699.9851.

5-(5′-Nitrothien-2′-yl)-10,15,20-tri(thien-2′-yl)porphyrin (5): Porphyrin **1** (50 mg, 0.078 mmol) was solubilized in $CHCl_3$ (5 mL) followed by the addition of $NaNO_2$ (8.1 mg, 0.117 mmol, 1.5 equiv.) and TFA (0.4 mL). The mixture was stirred at 0 °C for 2.5 h, then the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc (50 mL). The organic layer was washed with

water (2 × 100 mL), dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum. The product was purified by flash chromatography over silica gel ($CHCl_3$/hexanes, 3:2). Porphyrin **5** was recrystallized from hexanes to give the pure product (35.2 mg, 0.051 mmol, 66%). UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 427 (5.28), 523 (4.17), 562 (3.89), 596 (3.77), 657 (3.32) nm. ^{1}H NMR (400.15 MHz, $CDCl_3$): δ = –2.67 (s, 2 H, N–H), 7.49–7.52 (m, 3 H, H-10^3, H-15^3, H-20^3), 7.84 (d, J = 4.0 Hz, 1 H, H-5^2), 7.86 (dt, J = 5.2, 1.3 Hz, 3 H, H-10^4, H-15^4, H-20^4), 7.92 (dd, J = 3.4, 1.2 Hz, 3 H, H-10^2, H-15^2, H-20^2), 8.31 (d, J = 4.0 Hz, 1 H, H-5^3), 8.96–9.14 (m, 8 H, β-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 108.4 (C5), 113.3–113.8 (C-10, C-15, C-20), 126.4 (C-10^3,C-15^3,C-20^3), 127.6 (C-5^3), 128.4 and 132.9 (C-5^2, C-10^4, C-15^4, C-20^4), 131.0–132.9 (β-C), 134.3 (C-10^2, C-15^2, C-20^2), 142.4 (α-C, C-10^1,C-15^1,C-20^1), 151.1 (C-5^1), 153.8 (C-5^4) ppm. HRMS-ESI-TOF: *m*/*z* calcd for $C_{36}H_{21}N_5O_2S_4$ [M + H]$^+$ 684.0656; found 684.0660.

5,10,15,20-Tetrakis(5′-nitrothien-2′-yl)porphyrin (6): Porphyrin **1** (101.4 mg, 0.159 mmol) was solubilized in $CHCl_3$ (10 mL) followed by the addition of $NaNO_2$ (162 mg, 2.35 mmol, 15 equiv.), and from 0.4 to 1.2 mM with additions of TFA (0.3 mL in 1 h periods). The mixture was stirred at –11 °C for 5 h, then the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (150 mL). The organic layer was washed with water (2 × 100 mL), dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum. The product was purified by flash chromatography in silica gel (CH_2Cl_2/MeOH, 99:1). Porphyrin **6** was recrystallized from hexanes to give the pure product (76.6 mg, 0.0935 mmol, 59%). UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 432 (5.39), 522 (4.27), 560 (3.92), 596 (3.87), 656 (3.45) nm. ^{1}H NMR (400.15 MHz, [D$_6$]DMSO): δ = –2.97 (s, 2 H, N–H), 8.21 (d, J = 4.2 Hz, 4 H, H-5^2, H-10^2, H-15^2, H-20^2), 8.63 (d, J = 4.0 Hz, 4 H, H-5^3, H-10^3, H-15^3, H-20^3), 9.32 (s, 8 H, H-β) ppm. HRMS-ESI-TOF: *m*/*z* calcd for $C_{36}H_{18}N_8O_8S_4$ [M + H]$^+$ 819.0203; found 819.0216.

5,10,15,20-Tetrakis(5′-nitrothien-2′-yl)porphyrinatozinc(II) (8): Porphyrin **6** (160 mg, 0.195 mmol) was solubilized in a mixture of CH_2Cl_2/MeOH (8:2, 80 mL), followed by the addition of $Zn(OAc)_2{\cdot}2H_2O$ (1.29 g, 5.86 mmol, 30 equiv.). The reaction mixture was stirred at 40 °C for 3 h, then the solvent was removed under vacuum and the remaining residue was extracted with CH_2Cl_2 and water. The organic layer was washed with water, dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum. The product was recrystallized from CH_2Cl_2 and hexanes to afford porphyrin **8** (147.8 mg, 0.168 mmol, 83%). UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 434 (5.04), 522 (3.51), 560 (4.16), 601 (3.50) nm. ^{1}H NMR (400.15 MHz, [D$_5$]pyridine): δ = 8.10 (d, J = 4.1 Hz, 4 H, H-5^2, H-10^2, H-15^2, H-20^2), 8.44 (d, J = 4.1 Hz, 4 H, H-5^3, H-10^3, H-15^3, H-20^3), 9.55 (s, 8 H, H-β) ppm. ^{13}C NMR (101 MHz, [D$_5$]pyridine): δ = 111.7 (C-5, C-10, C-15, C-20), 128.6 (C-5^3, C-10^3, C-15^3, C-20^3), 133.2 (C-β), 133.9 (C-5^2, C-10^2, C-15^2, C-20^2), 151.4 (C-1, C-4, C-6, C-9, C-11, C-14, C-16 and C-19), 151.6 (C-5^1, C-10^1, C-15^1, C-20^1), 153.9 (C-5^4, C-10^4, C-15^4, C-20^4) ppm. HRMS (ESI-TOF): *m*/*z* calcd for $C_{36}H_{16}N_8O_8S_4Zn$ [M + H]$^+$ 880.9344; found 880.9362.

General Procedure for the 1,3-Dipolar Cycloaddition Reactions with Benzyl-Azomethine Ylide: Porphyrin **6** (20.0 mg) was solubilized in monochlorobenzene (5 mL) followed by the addition of *N*-benzylglycine hydrochloride (30 equiv.) and 1,3,5-trioxane (30 equiv.). The mixture was stirred at 130 °C for 2 h, then an excess of the amino acid (30 equiv.) and trioxane (30 equiv.) was added in 2 h periods at the same temperature. The reaction was quenched after 48 h with an aqueous saturated solution of K_2CO_3 (60 mL), and the mixture was extracted with CH_2Cl_2 (2 × 100 mL) and the organic layer was washed with water, dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum. The product **9c** was purified by flash chromatography on silica gel (toluene with 1% of MeOH). Compound **9c** was obtained in trace amounts and the reaction was repeated several times to yield around 1–2 mg for characterization. UV/Vis (CH_2Cl_2): λ_{max} = 430, 520, 552, 610, 665 nm. ^{1}H NMR (400.15 MHz, $CDCl_3$): δ = –1.67 (s, 2 H, N–H), 2.73–2.76 (m, 2 H, H-pyrrolidine), 3.10–3.20 (m, 2 H, H-pyrrolidine), 3.41 (s, 2 H, H-2^2), 5.49 (br. s., 2 H, H-2, H-3), 6.94–7.01 (m, 2 H, Ph-H), 7.13–7.21 (m, 3 H, Ph-H), 7.57 (d, J = 9.4 Hz, 2 H, β-Th-H), 7.82 (d, J = 4.1 Hz, 2 H, β-Th-H), 8.22 (d, J = 4.0 Hz, 2 H, β-Th-H), 8.31 (d, J = 4.1 Hz, 2 H, β-Th-H), 8.55 (d, J = 5.0 Hz, 2 H, β-H), 8.70 (s, 2 H, β-H), 8.93 (d, J = 5.0 Hz, 2 H, β-H) ppm. HRMS (ESI-TOF): *m*/*z* calcd for $C_{45}H_{29}N_9O_8S_4$ [M + H]$^+$ 952.109447; found 952.109123.

General Procedure for the 1,3-Dipolar Cycloaddition Reactions with 2,6-Dichlorobenzonitrile Oxide: Synthesis of the 2,6-Dichlorobenzonitrile Oxide Precursor 10: A solution of 2,6-dichlorobenzaldehyde (17.1 mmol, 3.0 g), hydroxylamine hydrochloride (34.2 mmol, 2.44 g, 2 equiv.), and pyridine (51.4 mmol, 4.3 mL, 3 equiv.) in ethanol (24 mL) was heated to reflux for 3 h. The solvent was then removed under vacuum and the remaining residue was extracted with EtOAc and water. The organic layer was washed with brine, dried with Na_2SO_4, filtered, and the solvents evaporated to dryness. The product was collected by filtration and washed with cold hexane (3 × 50 mL). White crystals of the oxime were intermediate obtained (2.77 g, 14.6 mmol, 83%). ^{1}H NMR (400.15 MHz, $CDCl_3$): δ = 7.32–7.40 (m, 3 H, Ph-H), 8.57 (s, 1 H, H-3), 8.39 (s, 1 H, H-1) ppm. A solution of 2,6-dichlorobenzaldehyde oxime (2.0 g, 10.5 mmol) and *N*-chlorosuccinimide (1.40 g, 10.5 mmol) in DMF (24 mL) was stirred at room temperature for 2 h. The product was extracted with diethyl ether and the organic layer was washed with water and brine, and dried with anhydrous $MgSO_4$. The solvent was removed under vacuum to obtain 2,6-dichlorophenylhydroximic chloride **10** (2.29 g, 10.2 mmol, 95%). ^{1}H NMR ($CDCl_3$, 400.15 MHz): δ = 7.26–7.43 (m, 3 H, Ph-H), 8.41 (s, 1 H, H-1) ppm.

1,3-Dipolar Cycloaddition Reaction: Porphyrin **1**, **6**, **7** or **8** (50 mg) were solubilized in distilled monochlorobenzene (5 mL), followed by the addition of 2,6-dichlorophenylhydroximic chloride (**10**; 20 equiv.) and *N*,*N*,*N*-triethylamine (25 equiv.). The reaction mixture was stirred at 80 °C under an argon atmosphere for 24–48 h. The reaction was monitored by UV/Vis and TLC until no further progress of the reaction was observed. After this time, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to give the cycloadducts. The conditions of purification of the products varied depending on the porphyrin used as starting material. Using this procedure, compounds **11a**, **11b**, **11c**, **11d**, **12c** and **13c** were prepared.

Compound 11a: The purification of chlorin **11a** was carried out by flash column chromatography using toluene as eluent. The residue was reapplied in preparative silica-gel TLC using mixture of toluene/hexanes, 4:6 as eluent and the chlorin derivative was crystallized from ethyl acetate and pentane giving **11a** (8.6 mg, 10.4 μmol, 13%). UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.09), 523 (4.02), 556 (4.08), 603 (3.84), 656 (4.29) nm. ^{1}H NMR (400.15 MHz, CD_2Cl_2): δ = –1.71 (s, 1 H, NH), –1.77 (s, 1 H, NH), 6.85 (dd, J = 8.0, 1.2 Hz, 1 H, Ph-H), 7.00 (s, 1 H, Th-H), 7.19 (t, J = 8.0 Hz, 1 H, Ph-H), 7.26 (dd, J = 8.0, 1.2 Hz, 1 H, Ph-H), 7.36 (d, J = 10.0 Hz, 1 H, H-3), 7.44–7.53 (m, 3 H, Th-H), 7.58 (d, J =

5.3 Hz, 1 H, Th-H), 7.81 (dd, *J* = 5.3, 1.1 Hz, 1 H, Th-H), 7.83–7.85 (dd, *J* = 1.2, 0.3 Hz, 1 H, Th-H), 7.85–7.88 (m, 3 H, Th-H), 7.98 (d, *J* = 10.0 Hz, 1 H, H-2), 8.32 (dd, *J* = 4.9, 1.4 Hz, 1 H, β-H), 8.63 (dd, *J* = 4.9, 1.4 Hz, 1 H, β-H), 8.65–8.72 (d AB, *J* = 4.6 Hz, 2 H, β-H), 8.82 (dd, *J* = 4.9, 1.4 Hz, 1 H, β-H), 8.92 (dd, *J* = 4.9, 1.4 Hz, 1 H, β-H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): *δ* = 62.1 (C-3), 92.2 (C2), 106.5–116.6 (C-5,C-10,C-15,C-20), 125.2–134.3 (β-CH, Th-CH, Ph-CH), 135.9–142.9 (α-Cq, Th-Cq, Ph-Cq), 153.8–163.2 (α-Cq, C-1,C-4, C-3[1]) ppm. HRMS (ESI-TOF): *m/z* calcd for $C_{43}H_{25}Cl_2N_5OS_4$ $[M + H]^+$ 826.0397; found 826.0414.

Compound 11b: The crude reaction product was purified by flash column chromatography (dichloromethane/hexane, 6:4). The fraction of interest was concentrated and reapplied in preparative silica-gel TLC and eluted with toluene/hexanes, 7:3. Subsequently, the product was purified over Sephadex LH-20 using a mixture of dichloromethane/methanol, 1:1 as eluent. Finally, chlorin **11b** (4.9 mg, 5.5 μmol, 8%) was crystallized from chloroform and methanol and obtained. UV/Vis (CH_2Cl_2): λ_{max} (log*ε*) = 424 (5.31), 484 (3.77), 523 (3.85), 593 (4.07), 622 (4.52) nm. ^{1}H NMR (CD_2Cl_2, 400.15 MHz): *δ* = 6.87 (d, *J* = 1.5 Hz, 1 H, Ph-H or Th-H), 6.88 (d, *J* = 1.6 Hz, 1 H, Ph-H or Th-H), 7.15–7.22 (m, 3 H, Ph-H, H-3), 7.33–7.40 (m, 3 H, Th-H), 7.43 (d, *J* = 5.3 Hz, 1 H, Th-H), 7.68 (d, *J* = 4.9 Hz, 1 H, Th-H), 7.69–7.74 (m, 4 H, Th-H), 7.77 (d, *J* = 10.4 Hz, 1 H, H-2), 8.06 (d, *J* = 4.5 Hz, 1 H, β-H), 8.35 (d, *J* = 4.7 Hz, 1 H, β-H), 8.56 (d, *J* = 4.5 Hz, 2 H, β-H), 8.63 (d, *J* = 4.7 Hz, 1 H, β-H), 8.72 (d, *J* = 4.7 Hz, 1 H, β-H) ppm. ^{13}C NMR (CD_2Cl_2, 101 MHz): *δ* = 61.2 (C-3), 90.8 (C-2), 106.6–118.0 (C-5,C-10,C-15,C-20), 126.6–133.6 (β-CH, Th-CH, Ph-CH), 136.0–156.4 (α-C, Th-C, Ph-C) ppm. HRMS (ESI-TOF): *m/z* calcd for $C_{43}H_{23}Cl_2N_5OS_4Zn$ $[M]^+$ 886.9454; found 886.9463.

Compounds 11c, 12c and 13c: The crude reaction product was purified by flash column chromatography (toluene/ethyl acetate, 9.5:0.5). Two fractions were collected, where the less polar was identified as compound **11c** and the more polar was as a mixture of compounds **12c** and **13c**. The latter mixture was separated by preparative silica-gel TLC using dichloromethane/hexane, 7:3 as eluent. The compounds were reapplied in silica Sephadex LH-20 using dichloromethane/methanol, 1:1 and then crystallized with chloroform and methanol. Compound **11c** was obtained in 15% yield (9.4 mg, 9.34 μmol), **12c** in 14% yield (10.0 mg, 8.39 μmol) and **13c** in 13% yield (9.7 mg, 8.14 μmol).

Compound 11c: UV/Vis (CH_2Cl_2): λ_{max} (log*ε*) = 430 (5.09), 521 (4.20), 554 (4.19), 609 (3.93), 662 (4.46) nm. ^{1}H NMR (400.15 MHz, CD_2Cl_2): *δ* = –1.80 (s, 1 H, NH), –1.86 (s, 1 H, NH), 6.91 (dd, *J* = 7.3, 1.8 Hz, 1 H, Ph-H), 7.24–7.34 (m,3 H, Ph-H, Th-H), 7.38 (d, *J* = 9.9 Hz, 1 H, H-3), 7.85 (d, *J* = 4.1 Hz, 1 H, Th-H), 7.86 (d, *J* = 4.1 Hz, 1 H, Th-H), 7.94 (br. d., *J* = 24.5 Hz, 2 H, Th-H), 8.04 (d, *J* = 9.9 Hz, 1 H, H-2), 8.28–8.35 (m, 3 H, Th-H), 8.52 (dd, *J* = 5.0, 1.3 Hz, 1 H, β-H), 8.74–8.80 (m, 3 H, β-H), 8.93 (dd, *J* = 5.0, 1.3 Hz, 1 H, β-H), 9.05 (dd, *J* = 5.0, 1.3 Hz, 1 H, β-H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): *δ* = 62.2 (C-3), 92.1 (C-2), 105.4–115.0 (C-5, C-10, C-15, C-20), 125.8–134.2 (β-CH, Th-CH, Ph-CH), 136.1–163.6 (α-C, Th-C, Ph-C) ppm. HRMS (ESI-TOF): *m/z* calcd for $C_{43}H_{21}Cl_2N_9O_9S_4$ $[M + H]^+$ 1005.9795; found 1005.9793.

Compound 12c: UV/Vis (CH_2Cl_2): $\lambda_{máx}$ (log*ε*) = 392 (4.98), 540 (4.52), 668 (3.79), 728 (4.79) nm. ^{1}H NMR (CD_2Cl_2, 400.15 MHz): *δ* = –1.82 (s, 2 H, NH), 6.84 (dd, *J* = 8.8, 2.0 Hz, 2 H, Ph-H), 7.18–7.32 (m,5 H, Ph-H, Th-H), 7.22 (d, *J* = 9.9 Hz, 2 H, H-3, H-13), 7.66–8.13 (m, 5 H, Th-H), 7.95 (d, *J* = 9.9 Hz, 2 H, H-2, H-12), 8.29 (d, *J* = 4.0 Hz, 2 H, Th-H), 8.33 (d, *J* = 2.0 Hz, 2 H, β-H), 8.48 (dd, *J* = 4.9, 1.8 Hz, 2 H, β-H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): *δ* = 61.8 (C-3, C-13), 92.0 (C-2, C-12), 108.0 (C-5,C-10, C-15, C-20), 125.6–132.3 (β-CH, Th-CH, Ph-CH), 135.8–155.5 (α-C, Th-C, Ph-C) ppm. HRMS (ESI-TOF): *m/z* calcd for $C_{50}H_{24}Cl_4N_{10}O_{10}S_4$ $[M + H]^+$ 1192.9387; found 1192.9419.

Compound 13c: UV/Vis (CH_2Cl_2): λ_{max} (log*ε*) = 393 (5.00), 542 (4.55), 667 (3.92), 728 (4.85) nm. ^{1}H NMR (400.15 MHz, CD_2Cl_2): *δ* = –1.82 (s, 1 H, NH), –1.76 (s, 1 H, NH), 6.95–7.02 (m, 2 H, Ph-H), 7.23 (d, *J* = 9.9 Hz, 2 H, H-3, H-12), 7.26–7.34 (m, 5 H, Ph-H, Th-H), 7.89 (d, *J* = 9.9 Hz, 2 H, H-2, H-13), 7.92–8.0 (s.l., 4 H, Th-H), 8.16 (s.l., 2 H, Th-H), 8.31 (d, *J* = 4.1 Hz, 2 H, β-H), 8.63 (d, *J* = 2.0 Hz, 2 H, β-H) ppm. ^{13}C NMR (CD_2Cl_2, 101 MHz): *δ* = 61.82 (C-3, C-12), 91.1 (C-2,C-13), 107.8–108.6 (C-5, C-10, C-15, C-20), 123.8–132.3 (β-CH, Th-CH, Ph-CH), 136.0–161.2 (α-C, Th-C, Ph-C) ppm. HRMS (ESI-TOF): *m/z* calcd for $C_{50}H_{24}Cl_4N_{10}O_{10}S_4$ $[M + H]^+$ 1192.9387; found 1192.9416.

Compound 11d: The crude product was purified by flash column chromatography (dichloromethane/toluene, 1:1). The fraction of interest was concentrated under vacuum and reapplied in preparative silica-gel TLC using toluene/ethyl acetate, 9:1 as eluent. Subsequently, the product was eluted over Sephadex LH-20 with a mixture of dichloromethane/methanol, 1:1 and crystallized from chloroform and methanol to give **11d** (13.5 mg, 12.6 μmol, 22%). UV/Vis (CH_2Cl_2): λ_{max} (log*ε*) = 429 (4.94), 527 (3.87), 596 (3.97), 630 (4.44) nm. ^{1}H NMR (400.15 MHz, CD_2Cl_2): *δ* = 6.95 (dd, *J* = 16.0, 12.0 Hz, 1 H, Ph-H), 7.21–7.35 (m, 3 H, H-3, Th-H, Ph-H), 7.73–7.89 (m, 4 H, H-2, Th-H), 8.23 (td, *J* = 9.6, 4.8 Hz, 3 H, Th-H), 8.29 (s, 1 H, β-H), 8.52 (dd, *J* = 7.4, 4.8 Hz, 1 H, β-H), 8.68–8.75 (m, 2 H, β-H), 8.78 (t, *J* = 4.4 Hz, 1 H, β-H), 8.87 (t, *J* = 5.0 Hz, 1 H, β-H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): *δ* = 61.21 (C-3), 90.62 (C-2), 105.02–116.23 (C-5, C-10, C-15, C-20), 128.16–133.93 (β-CH, Th-CH, Ph-CH), 136.05–159.29 (α-Cq, Th-Cq, Ph-Cq) ppm. HRMS (ESI-TOF): *m/z* calcd for $C_{43}H_{19}Cl_2N_9O_9S_4Zn$ $[M + H]^+$ 1067.89298; found 1067.89393.

Singlet Oxygen ($^1O_2$) Generation Quantum Yield (Φ_Δ): Singlet oxygen ($^1O_2$) generation, quantum yield (Φ_Δ) and $^1O_2$ lifetimes were determined by using the phosphorescence detection method. Two different laser equipment were used as excitation sources: a Continuum Surelite III Nd:YAG laser (532 nm; pulse duration: 5 ns; frequency of pulsation: 10 Hz, Q-switch: 350 μs – Santa Clara, USA), which was also used to pump a Continuum Jaguar dye laser with (2-{2-[4-(dimethylamino)phenyl]ethenyl}-6-methyl-4*H*-pyran-4-ylidene)propanedinitrile in ethanol (635 nm; pulse duration: 5 ns; frequency of pulsation: 10 Hz, Q-switch: 240 μs – Santa Clara, USA). The 1270 nm radiation emitted from singlet oxygen was detected at right angles with an Edinburgh Analytical Instruments time-resolved NIR fluorometer (Livingston, UK) equipped with a liquid-nitrogen cooled Hamamatsu R55009 photomultiplier (Bridgewater, NJ) and a fast acquisition MSA-300 board (Becker & Hickl – Berlin, Germany). For quantum yield measurements, a 5,10,15,20-tetraphenylporphyrin (TPP, **2**) solution in chloroform was used as a standard (Φ_Δ = 0.50)[28] and both standard and PSs had absorbances around 0.25 at the excitation wavelength. Lifetime measurements were performed by accumulation of 1000 decays. The value of Φ_Δ was obtained by comparing the absorbances and higher intensity emissions of samples and standard as published before.[24] Phosphorescence decay curves at 1270 nm were fitted to second-order exponential decays for the determination of $^1O_2$ lifetime using the Origin 8.0 software (OriginLab – Northampton, MA).

Fluorescence Quantum Yield (Φ_{fl}): Fluorescence spectra were recorded in the 550–800 nm range using 515 nm as excitation wavelength, 10 nm excitation slit and 20 nm emission slit with a Cary

50 Fluorescence Spectrophotometer (VARIAN – Victoria, Australia). All chlorin chloroform solutions were prepared with absorbance at the excitation wavelength below 0.1 to avoid inner filter effects. The quantum yield was obtained by using the equation published before.[32] Tetraphenylporphyrin was used as standard both in toluene and chloroform. The TPP toluene Φ_{fl} (0.11)[33] was used to calculated the TPP chloroform Φ_{fl}, considering refractive indexes of both solvents (toluene = 1.4967; and chloroform = 1.4476).[34]

Aggregation Studies: The self-aggregation of porphyrinoid compounds is a natural tendency due to the strong attractive interactions between π-systems of the polyaromatic compounds. It is already known that the aggregation degree increases with concentration. UV/Vis analyses were used to evaluate the aggregation of compounds **11a–d**, **12c** and **13c**. The UV/Vis spectra were acquired in different concentrations using dichloromethane as solvent. Chemical shift variations for each sample were the analyzed parameters. Changes in the λ_{max} from the bands in UV/Vis spectra were monitored.

Fluorescence Measurements: Performed using toluene as solvent. Chlorins **11a–d**, bacteriochlorins **12c** and **13c** had their absorbances adjusted to 0.05 and 0.1, respectively. Excitation of both were performed at 417 nm and the emission spectra were recorded.

Photobleaching Studies: A solution of new chlorins and bacteriochlorins **11a–d**, **12c** and **13c** in CH_2Cl_2 with an absorbance value around 1 was prepared, and irradiated for 1 min using 50 mW as laser potency. The absorbance spectra were always recorded after the irradiation and 10 further irradiations (1 min) were performed, each one followed by a spectrum registration to observe possible photobleaching by reduction of the photosensitizer concentration.

Supporting Information (see footnote on the first page of this article): Aggregation studies by UV/Vis analyses, photobleaching study by UV/Vis analyses, fluorescence emission spectra and singlet oxygen emission spectra of compounds **11ad**, **12c** and **13c**, UV/Vis spectra of compounds **9c**, **11a–d**, **12c** and **13c**, ^1H, ^{13}C and 2D NMR spectra of compounds **1**, **5**, **7**, **8**, **9c**, **10**, **11a–d**, **12c** and **13c**, and mass spectra of compounds **1**, **5**, **6**, **7**, **8**, **9c**, **11a–d**, **12c**, **13c**, **13d**.

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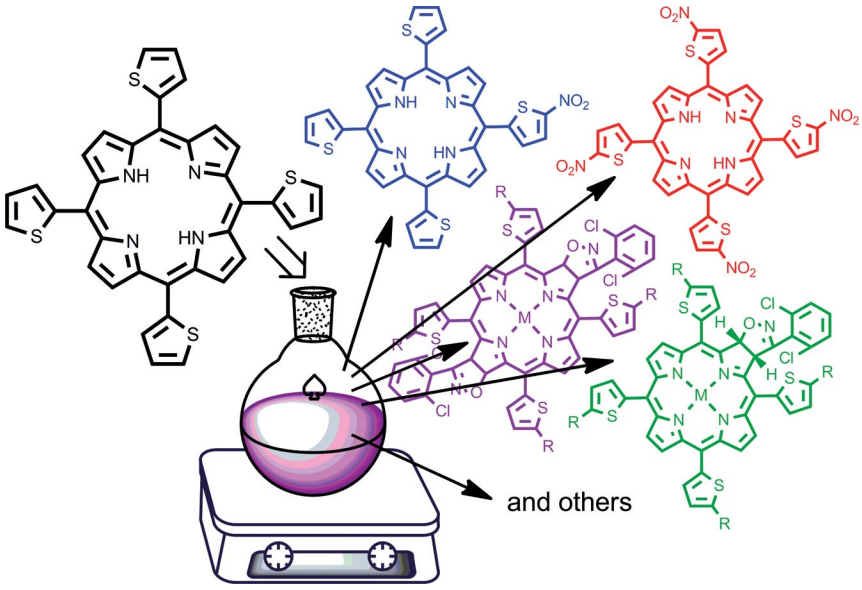
Porphyrinoids



The chemistry of *meso*-tetrathienyl-substituted porphyrin derivatives was explored, including synthesis and subsequent metalation, nitration, and 1,3-dipolar cycloaddition reactions. The products were characterized in detail and their photophysical properties were evaluated.

Keywords: Porphyrinoids / Photophysics / Sensitizers / Cycloaddition / Metalation

