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Porphothionolactones: synthesis, structure, physical, and chemical properties of a chemodosimeter for hypochlorite†

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The conversion of the lactone functionality of porpholactones, porphyrin analogs in which a porphyrin β,β′-double bond was replaced by a lactone moiety, to a thionolactone functionality using Lawesson's reagent is described. The resulting novel thionolactones were spectroscopically characterized and their electronic structure defined using experimental (UV-vis, fluorescence, cyclic voltammetry) and theoretical methods (molecular modelling at the B3LYP/6-31G(d) level). The structures of two benchmark thionolactones were determined by single crystal X-ray diffractometry. The idealized planarity of the chromophores rationalize the bathochromically shifted optical spectra of the thionolactones when compared to the lactones on electronic grounds. The thionolactone moiety can be used as a synthetic handle in the preparation of oxazolochlorins using RANEY® nickel-induced hydrodesulfurization reactions. Importantly, the *meso*-pentafluorophenyl-based porphothionolactone fluoresces by at least a factor of 60 less compared to the corresponding lactone. The hypochlorite-selective conversion of the thionolactone to the lactone is the basis for the use of this thionolactone as a switch-on chemodosimeter for hypochlorite, a widely used disinfectant and molecule of biological significance in some inflammatory processes.

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Introduction

Porphyrin analogues in which at least one pyrrolic subunit was replaced by a non-pyrrolic moiety, such as a thiophene (**1**), a carbacycle, an oxazole, a morpholine (**2**), or in which a pyrrolic moiety is present in a 'confused' orientation (**3**), garnered great attention in recent years (Fig. 1).[1–3] *Inter alia*, they are tools for the fundamental study of the nature of the porphyrinoid aromatic π-system.[3] Moreover, they frequently possess different coordination properties, conformations, conformational flexibilities, or electronic structures compared to porphyrins and chlorins. For instance, morpholinochlorins **2** show a non-planar, twisted conformation that allows their chiral resolution.[4] Their altered conformational flexibility modulates also, for instance, the electrochemical outcome of their nickel(II) complexes.[5] Many pyrrole-modified porphyrins possess bathochromically shifted optical spectra that suggest their use in a number of applications, such as photodynamic therapy[6] or light harvesting.[7,8] Moreover, some pyrrole-modified porphyrins carry a functionality at their macrocycle periphery, such as N-confused porphyrins of type **3**.[2] This functionality can interact with its environment, resulting in a modulation of its electronic structure. This ability makes these

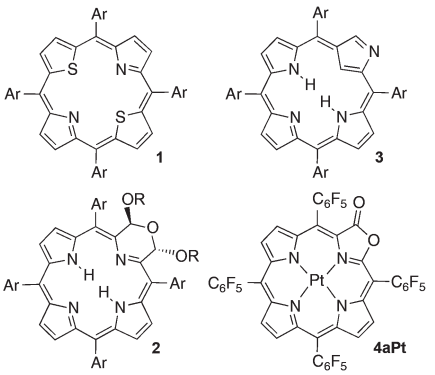

Fig. 1 Representative pyrrole-modified porphyrins.

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(and closely related β-functionalized)[9] systems suitable for utilization as chemosensors.[10,11]

Porpholactones are a particular class of pyrrole-modified porphyrins in which one porphyrin β,β′-double bond was replaced by a lactone moiety (or a pyrrole was replaced by an oxazolone).[12–17] While known for some time,[12,18] and occurring frequently as adventitious side products in reactions involving the (oxidative) transformation of porphyrin β,β′-bonds,[12,13,15,16,19] they have only more recently become readily available in synthetically useful scales along two complementary routes: (1) a one-step Ru-catalyzed direct oxidation of a porphyrin and,[20] (2), using a two-step route involving the OsO_4-mediated dihydroxylation of a porphyrin, followed by MnO_4^--oxidation of the dihydroxypyrroline moiety.[11,17,21]

Free base porpholactones possess porphyrin-like optical properties, while their metal complexes are metallochlorin-like.[13,17] Selected metalloporpholactones were shown to be, compared to the corresponding porphyrin complexes, better catalysts in atom transfer reactions.[22] Most prominently, the [porpholactonato]Pt(II) complex **4aPt** (Fig. 1) proved to be a particularly effective oxygen-sensing dye in pressure-sensing paints.[13,23] The sensing mechanism (phosphorescence quenching of the excited triplet state of the chromophore by triplet oxygen)[24] is only indirectly affected by the presence of the lactone moiety. This moiety is, however, the key functionality in the use of **4aPt** as a high pH indicator (the base attacks the lactone carbonyl group, causing an sp^2-to-sp^3-conversion of a β-carbon that causes a ~100 nm red-shift of the chromophore).[11]

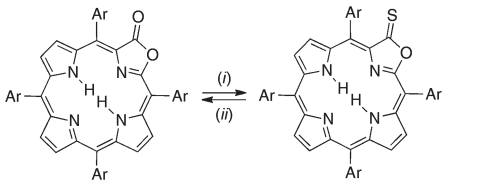
The lactone moiety was also used as a synthetic handle for further modifications. For instance, reductions of the lactone moiety allowed the preparation of oxazolochlorin- and oxazolobacteriochlorins with finely tuned optical spectra.[16,17,25,26] The conversion of the lactone to a lactam moiety was also shown, broadening the utilization of porpholactones for the synthesis of other pyrrole-modified porphyrin classes.[27]

The accessibility of porpholactones and the functionality at the periphery of the macrocycle that is strongly electronically coupled to the chromophore render the porpholactones to be enticing study objects. Herein we report the formation of a novel class of porpholactone derivatives, the porphothionolactones, in which the lactone moiety of porpholactones was replaced by a thionolactone group. This replacement affects the structure and electronic properties of the chromophore. It also allowed the utilization of the thionolactones as a starting point for further modifications. Most significantly, the thionoporpholactones can be used as a selective fluorescent 'switch-on' chemodosimeter for hypochlorite.

Results and discussion

Synthesis of thionoporpholactones 5

Reaction of porpholactones **4a–d** with an excess of Lawesson's reagent under standard conditions (A or B)[28] each led to the formation of a major product in good to excellent yields



4a, Ar = C_6F_5
4b, Ar = Ph
4c, Ar = 2,4,6-Me_3-Ph
4d, Ar = 4-Cl-Ph

5a, Ar = C_6F_5 (50%, A)
5b, Ar = Ph (89%, A; 98%, B)
4c, Ar = 2,4,6-Me_3-Ph (89%, A)
4d, Ar = 4-Cl-Ph (69%, A)

Scheme 1 Formation of tetraarylporphothionolactone **5** by sulfurization of porpholactone **4**. *Reaction Conditions*: (i) Method A: 10 equiv. Lawesson's reagent, toluene, anoxic/anhydrous conditions, Schlenk tube, 100 °C, 3 d, dark, followed by column chromatography. Method B: 7 equiv. Lawesson's reagent, toluene, $NaHCO_3$–Na_2CO_3, anhydrous conditions, reflux, 12–24 h, followed by column chromatography. (ii) For **5a** only: **5a** (5.0×10^{-6} M) in MeCN–H_2O (9 : 1, v/v) and treated with 50 μM aq NaClO for 10 min.

(Scheme 1). Addition of base to the reaction mixture was found to be beneficial. The products could be identified as the corresponding thionolactones **5a–d**. All analytical data supported that only the desired ketone-to-thione conversion had taken place: The NMR spectra of the products were similar to those of the starting material, except for the low-field shift of the carbonyl signal in the ^{13}C NMR (*e.g.*, from 167.7 ppm in **4b**[17] to 197 ppm in **5b**) (all spectra are reproduced in the ESI†). Their IR spectra show that the $\nu_{C=O}$ band of the ketone (at 1774 and 1766 cm^{-1} for **4b**[17] and **4a**, respectively) is replaced by a strong $\nu_{C=S}$ band (at 1261 and 1262 cm^{-1} for **5b** and **5a**, respectively). The effects of the oxygen-to-sulfur exchange on the optical properties of the chromophores will be discussed below. HR-MS spectra confirmed the expected compositions. Their connectivities were ultimately proven by single crystal diffractometry (see below) (Fig. 6).

Optical spectra of thionoporpholactones 5

The rhodo-type UV-vis spectrum of the porpholactones converts to a phyllo-type and bathochromically shifted spectrum, with a significantly red-shifted (29 nm for **5a** and 35 nm for **5b**) Soret band and with an additional weak λ_{max} band at 682 nm (Fig. 2).[13,17] Thioketones generally possess red-shifted spectra compared to their parent ketones.[29] Thus, the strong electronic coupling of the thiono group with the chromophore is clearly reflected (see also below for the computational description of the chromophore electronics). Protonation reduces the number of Q-bands and further red-shifts the spectrum, as is generally observed upon protonation of the central nitrogens.[30]

Tetrakis(pentafluorophenyl)-substituted porphyrinoids show slightly altered electronic properties compared to their tetraphenyl-substituted congeners.[31] Thus, the optical spectrum of **5a** is slightly different from that observed for **5b**, but the general trends delineated above hold true.

The fluorescence emission spectra of the thionolactones are in terms of emission wavelengths and relative intensity of the I_{0-0} and I_{0-1} bands different from those of tetraphenylporphyrins and porpholactones but are still characterized by

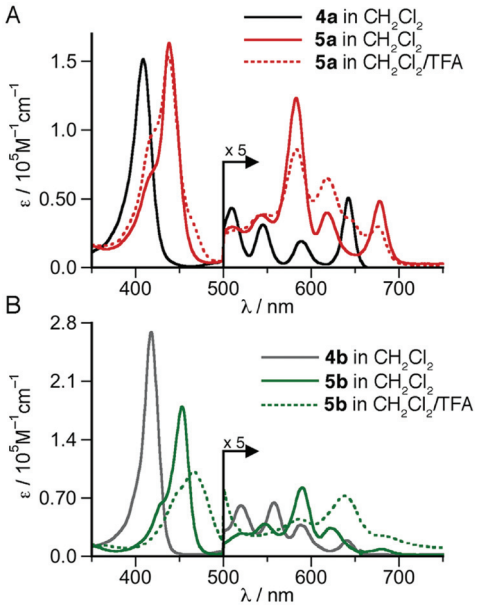


Fig. 2 UV-visible spectra of (A) *meso*-tetrakis(pentafluorophenyl)porpholactone **4a** (black), *meso*-tetrakis(pentafluorophenyl)porphothionolactone **5a** (red solid trace) in CH_2Cl_2, and **5a** (red broken trace) in CH_2Cl_2 + 2% TFA; (B) *meso*-tetraphenylporpholactone **4b** (grey) and *meso*-tetraphenylporphothionolactone **5b** (green) in CH_2Cl_2, and **5b** (green broken trace) in CH_2Cl_2 + 2% TFA.

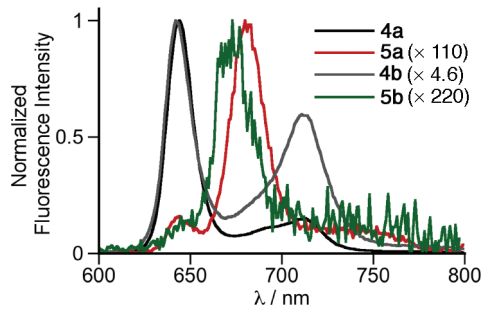


Fig. 3 Normalized fluorescence emission spectra of **4a** (black), **5a** (red), **4b** (grey) and **5b** (green) in CH_2Cl_2 at similar concentrations. $\lambda_{excitation} = \lambda_{Soret}$. The multiplication factors provided are only approximate as the large differences in fluorescence yields do not allow a good direct comparison using identical instrument settings.

the small Stokes shifts characteristic of most porphyrinoids (Fig. 3).[17,32] While the porpholactones are moderately strongly fluorescing ($\phi = 0.13$ for **4a**, $\phi = 0.04$ for **4b**),[17] the porphothionolactones are not ($\phi \ll 0.01$ for **5a** and **5b**). Thus, any reaction that induces the thiolactone-to-lactone conversion is accompanied by a strong fluorescence emission intensity enhancement, a property which can be utilized in a chemodosimeter for an oxidant (see below).

Electronic structure of thionoporpholactones

The computed molecular orbital diagrams of *meso*-tetrakis(pentafluorophenyl)porpholactone **4a** and the corresponding thionolactone **5a** rationalize the observed bathochromic shift upon oxygen-to-sulfur exchange (Fig. 4). The frontier molecular

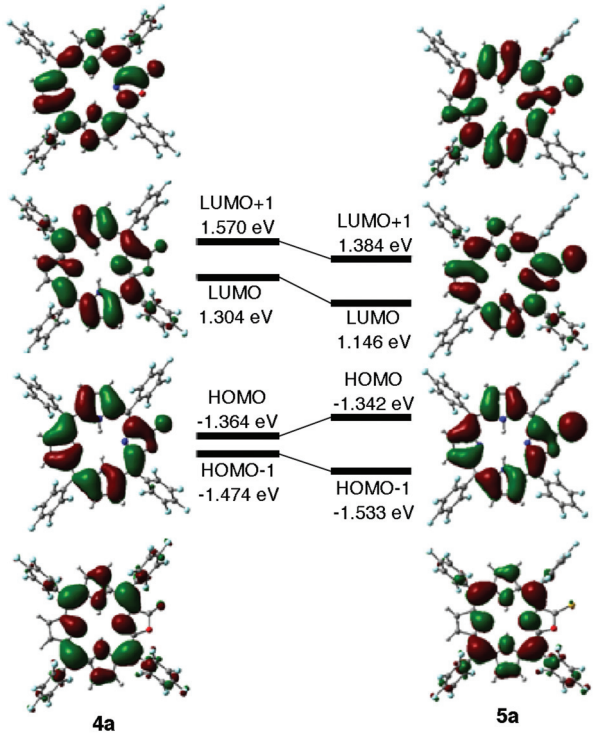


Fig. 4 Molecular orbital diagrams of **4a** and **5a** (optimized at B3LYP/6-31G(d) level using the Gaussian 09 software package).

orbitals of the thionolactone **5a** carry a larger coefficient on the sulfur when compared to the lactone analogue **4a**, showing the large influence of the thione. The LUMOs of the thionolactone are lowered and the HOMO elevated, thus narrowing the HOMO–LUMO gap. This finding is well reproduced experimentally in the bathochromically shifted optical spectra of the thionolactones as compared to their oxygen congeners.

Cyclovoltammetry of thionoporpholactones

Electrochemical studies further confirm the relative positions of the frontier orbitals of porpholactone **4a** and porphothionolactone **5a** (even though the absolute numbers vary from the computed numbers and the energy levels extracted from the UV-vis spectra; for details of the computations, see ESI†) (Fig. 5). Both compounds display two quasi-reversible reduction waves and an irreversible oxidation wave, whereby the porphothionolactone is, as predicted by the computations, easier to reduce and easier to oxidize compared to the oxo-analogue. In comparison, the corresponding redox potentials for the pentafluorophenylporphyrin are −0.80 V and −1.21 V.[33]

X-ray single crystal structure of the thionoporpholactones

The crystal structures of thionolactones **5a** and **5b** confirm their spectroscopically derived connectivity (Fig. 6). A comparison of the solid state structure of porpholactone **4b** with that of the thionolactone **5b** reveals that the oxazolthione moiety in **5b** is significantly more distorted from co-planarity with the remainder of the chromophore than the only little distorted

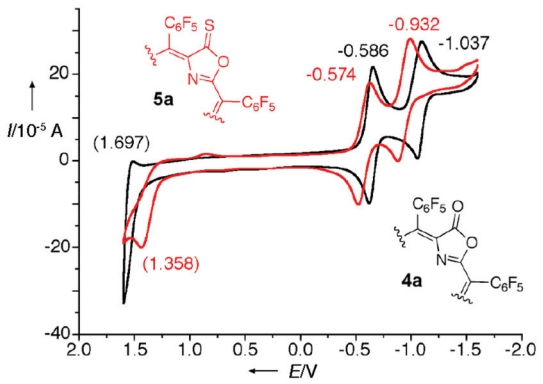


Fig. 5 Cyclic voltammograms of **4a** (black), **5a** (red) (1.0 mM in CH_2Cl_2 with 0.1 M $^tBu_4NPF_6$ as electrolyte); scan rate of 0.1 V s^{-1} and $E_{1/2}$ calculated based on peak position for the internal standard $FeCp_2$ ($E_{1/2}$ = 0.45 V *vs.* SCE).

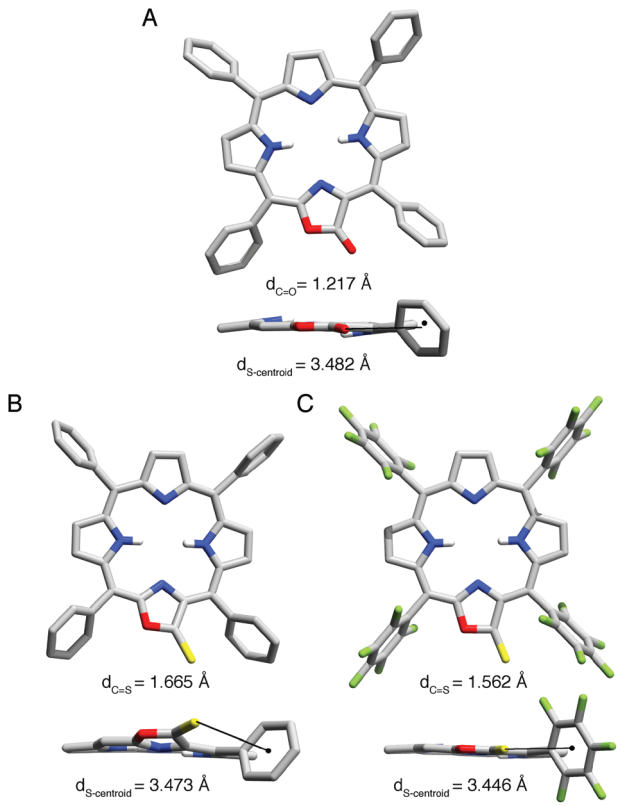


Fig. 6 Stick models of the single crystal X-ray structures of (B) **5b** and (C) **5a** in comparison to the structure of **4b**[17] (A), top and side views. All hydrogen atoms attached to carbon positions, disorder contributions, and the solvent molecules are omitted for clarity. All three aryl groups not adjacent to the lactone/thionolactone moiety are removed for clarity on the side views. For details to the X-ray structures, see ESI.†

oxazolone moiety in **4b**. This is presumably because of the larger size of the sulfur atom and the longer thiocarbonyl bond, thus leading to greater steric interaction with the flanking phenyl group.

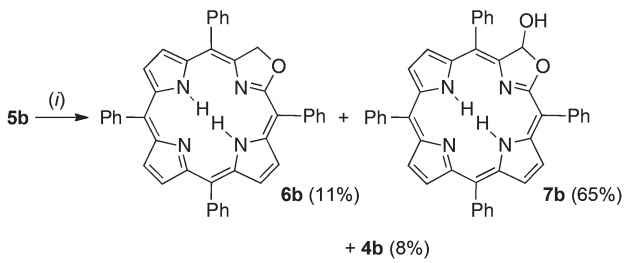
Remarkably, the crystal structure of the pentafluorophenyl derivative **5a** is much less distorted from planarity, yet the distance between the sulfur and the centroid of the flanking aryl group is shorter than in **5b**. This may indicate a stabilizing interaction between the negatively charged thioketone sulfur and the positively polarized center of the pentafluorophenyl group. A similar interaction was proposed for the stabilization of the anionic orthoester form of **4b** after nucleophilic attack by alkoxide or hydroxide.[11]

Reactivity of thionoporpholactones

Thioketones are susceptible to hydrodesulfurization reactions using RANEY® nickel.[34] When tetraphenylporphothionolactone **5b** was subjected to the classic reaction conditions (large excess RANEY® nickel slurry, THF, ambient temperature with and without the presence of 1 bar H_2), we observed the formation of three known compounds in varying yields (Scheme 2; yields listed are typical yields; the actual yields depend on the dryness of the conditions, reaction time, and temperature). The desired oxazolochlorin **6b** is formed invariably in mediocre yields, and the corresponding 3-hydroxy-derivative **7b** (porpholactol) is the major product. Some porpholactone **4b** is also formed. We previously reported the formation of the chlorin-like oxazolochlorins **6b** and **7b** by direct reduction of porpholactone **4b**.[17,25] We also noted the profound oxidation sensitivity of the parent oxazolochlorin and have observed the facile formation of the hemiacetal **7b** from oxazolin **6b**.[17,35] Thus, we surmise that the hydrodesulfurization took place as intended but that subsequent oxidation reactions generated hemiacetal **7b** and **4b**. The direct (metal-catalyzed) hydrolysis of thione-to-ketone conversion is a known reaction.[36] Thus, this pathway for the formation of porpholactone **4b** also cannot be excluded (see also below). In certain cases, the ketone-to-alkane conversion was facilitated by the intermediacy of a thione.[37] However, we must conclude that this route is inefficient in the preparation of oxazolochlorin **6b** when compared to the direct reduction route.[17,25]

Thionoporpholactones as chemodosimeter for hypochlorite

To elucidate the sensitivity of the thionolactone toward oxidative hydrolysis that regenerates the lactone functionality, we attempted to use the standard method for converting thiones to ketones by oxidations, such as H_2O_2,[36] but failed to observe any reaction. Upon screening oxidants, we noted that



Scheme 2 Hydrodesulfurization of porphothionolactone **5b**. *Reaction Conditions*: (i) Excess RANEY® nickel slurry (washed with EtOH and THF), THF, anhydrous conditions, r.t., 24 h, dark, with or without 1 bar H_2, followed by preparative plate chromatography.

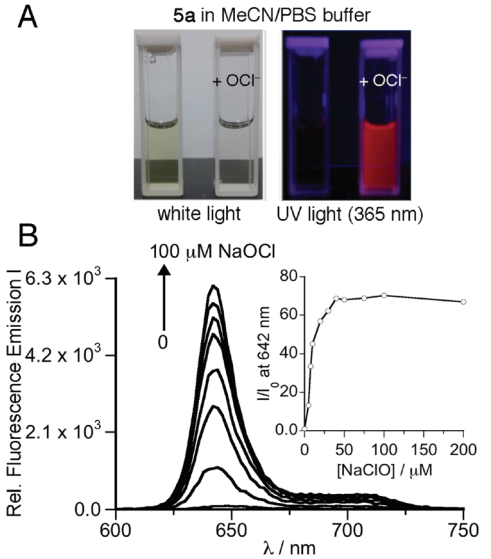


Fig. 7 A. Visible changes in the color and fluorescence of a solution of **5a** upon addition of NaOCl. B. Change of the fluorescence emission spectrum of a solution of **5a** (5.0×10^{-6} M in MeCN–PBS buffer at pH = 7.4, 9 : 1, v/v) upon titration with NaClO. [NaClO] ranging from 5 μM to 200 μM; $\lambda_{excitation}$ = 410 nm. Insert: Relative fluorescent intensity increase (at 642 nm) *vs.* [NaClO].

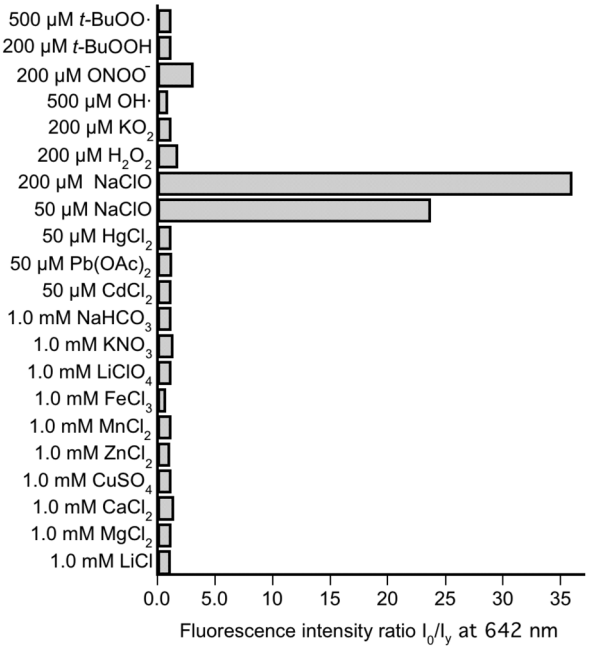


Fig. 8 Relative fluorescent intensity (at $\lambda_{emission}$ = 642 nm and $\lambda_{excitation}$ = 410 nm) of a solution of **5a** (5.0×10^{-6} M in MeCN–PBS buffer at pH = 7.4, 9 : 1, v/v) upon addition of a range of biologically relevant oxidants and ions. All data recorded after 20 min equilibration time at ambient temperature.

hypochlorite (in the from of NaOCl, bleach) was well suited to convert the pentafluorophenylthionoporpholactone **5a** to the corresponding lactone **4a** rapidly and quantitatively (Scheme 1). Since the thionolactone possesses only a very dim fluorescence emission but the lactone is brightly fluorescing, the addition of an aqueous solution of NaOCl to a MeCN–PBS buffer solution of porphothiolactone **5a** switches the fluorescence on (enhances it ~60-fold at $\lambda_{emission}$ = 642 nm) within 10 min at ambient conditions (Fig. 7B). Even a hypochlorite concentration of 5 μM elicits a larger than 10-fold fluorescence enhancement within 20 min at ambient temperature. This switching on of the fluorescence is readily observed with the unaided eye (Fig. 7A).

This conversion reaction is highly selective for the oxidant hypochlorite. Particularly no other common reactive oxygen species (ROS) of biological relevance affects this transformation (Fig. 8), nor do chloride, chlorite, chlorate (not shown), or perchlorate. Also, no other common non-oxidizing anions or cations (alkaline metals, hard, borderline hard, or soft metal ions and/or mildly oxidizing ions) added to the solution of **5a** induced any fluorescence increase over a time period of 20 min. The reaction is, however, pH-dependent (see ESI†). Acidic to neutral conditions (pH 1 through 7.4 as measured in a 9 : 1 MeCN–aqueous PBS buffer solution) are required for the conversion of **5a** by ClO^- (within 10 min). At low pH values, the prevalent species in solution is HOCl, in equilibrium with chlorine and hydrochloric acid.[38] Above pH 7.4, the reaction begins to slow considerably and no change is observed at a pH value above 10. In none of the reactions did we find any evidence for the occurrence of ring-opened products. The summation of these findings gives rise to the potential utilization of porphothiolactones as chemodosimeters for hypochlorite under physiological conditions.

Bright optical sensors for hypochlorite (ClO^- or HOCl) are important as these species play a crucial role in biological systems. For instance, activated neutrophils generate HOCl by myeloperoxidase-mediated peroxidation of chloride ions, thereby aiding, like a number of other ROS,[39] in the destruction of bacteria.[40] Hypochlorite is also a widely used disinfectant in the food industry, the medical sector, the household, and in drinking water treatment; it is also used in the oxidative removal of cyanide from industrial waste streams.[41] As hypochlorite does not have a native spectroscopic signature in the visible or NIR range of the electromagnetic spectrum, it prompted the search for optical sensors and chemodosimeters.

chemodosimeters for hypochlorite were recently reported.[42] The hypochlorite-mediated removal of a fluorescence quenching sulfur atom from a chromophore is a popular and effective approach. Most of these dosimeters are based on rhodamine-, coumarin-, BODIPY-, and pyrene-based chromophores.[42] Porphyrins have not been used as chromophores in hypochlorite sensors even though they possess a number of advantageous properties: particularly the *meso*-pentafluorophenyl-substituted derivatives combine high oxidative stability with high extinction coefficients and high fluorescence quantum yields.

The oxidative conversion of thiones to ketones using a wide range of possible oxidants is common.[36] Where studied, the reaction mechanism is believed to proceed *via* sulfines (C═S═O). The C═S bond in these species is being oxidized/

epoxidized to form transient sultines that, however, cannot be isolated as they produce the final ketone and sulfur oxide (that is generally quickly oxidized to sulfur dioxide).[43]

Conclusions

In conclusion, we have shown the conversion of the lactone moiety in porpholactones to a thionolactone moiety. The effects on its electronic structure were examined using a number of spectroscopic (among others, UV-vis and fluorescence spectroscopy and cyclic voltammetry) and theoretical methods. The subtle effects of the exchange of the smaller ketone oxygen to a larger thione sulfur on the solid state conformation of the macrocycle was demonstrated using single crystal diffractometry. By and large, the thionoporpholactones follow the expected general trends: their frontier molecular orbitals are lowered, their HOMO–LUMO gaps are narrowed, and they are less fluorescent. The thionoporpholactones can, in principle, also be used as intermediates in the synthesis of oxazolochlorins, even though this route toward these chlorin analogues is not competitive to the direct reduction route. A thione-to-ketone conversion can be effected by hypochlorite, converting the dimly fluorescing porphothionolactone to a relatively much stronger fluorescing porpholactone. Thus, we have demonstrated how a peripherally modified porphyrinoid can be tuned to become a bright fluorescence chemodosimeter for hypochlorite, suitable to detect this oxidant at slightly acidic to neutral pH values in aqueous media.

Methods recently reported by us to generate freely water-soluble pentafluorophenyl-substituted porphyrinoids promise the evaluation of the chemodosimeters in biological settings;[44] the results of these experiments will be reported in due time.

Experimental section

X-ray single crystal diffractometry

The crystallographic data for the single crystal of thionolactone **5a** (0.46 × 0.30 × 0.24 mm) were collected at room temperature on a Bruker SMART 1000 CCD diffractometer using graphite monochromated Mo source Kα radiation (λ = 0.71073 Å). A single crystal of thionolactone **5b** (0.51 × 0.34 × 0.13 mm) was mounted on a MiTeGen micromesh mounts with the help of a trace of mineral oil, mounted on a pin and placed a goniometer head under a stream of cold nitrogen. Intensity data were collected on a Bruker APEX CCD diffractometer with Mo source Kα radiation (λ = 0.71073 Å) using ω scans. The frames of both compounds were integrated with the Bruker SAINT software package using a narrow frame algorithm. Data were corrected for absorption effects using the multiscan method (SADABS). The structures were solved by direct methods and refined using the Bruker SHELXTL Software Package until the final anisotropic full-matrix, least-squares refinement on F^2 converged. The structure of **5a** exhibits disorder of the thionolactone moiety with the pyrrole unit at two possible positions related by a two-fold symmetry axis. The structure of **5b** exhibits severe disorder of the thionolactone moiety with the three pyrrole units, and two fold disorder of two of the phenyl rings. For the details of the disorder model applied, see ESI.†

Data collection and structural parameters for the structure elucidations can be found in Table 1 and the ESI.†

Table 1 Crystal data[a]

	5a	5b
Formula	$C_{45}H_8F_{20}N_4OS{\cdot}2CH_3CN$	$C_{43}H_{28}N_4OS$
M/g mol^{-1}	1090.70	648.75
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/n$
a, b, c/Å	11.9116(6), 15.8442(9), 22.7764(13)	14.4595(18), 16.894 (2), 14.8193(18)
α, β, γ (°)	90, 90, 90	90, 117.621(2), 90
V/Å^3	4298.6(4)	3207.5(7)
T/K	296(2)	100(2)
Z	4	4
Reflections measured	21 610	43 496
Unique (R_{int})	4234 (0.0221)	7139 (0.0480)
Data/parameters/restraints	4234/344/0	7139/608/481
Goodness-of-fit on F^2	1.167	1.034
$R(F)$ [all data]	0.0744	0.1358
$R(F)$ [$I > 2\sigma(I)$]	0.0676	0.0744
w$R(F_2)$ [all data]	0.1879	0.1916
w$R(F_2)$ [$I > 2\sigma(I)$]	0.1833	0.1609
CCDC Number	932831	932832

[a] For details, particularly with respect to the disorder models used, see ESI.

Materials and instrumentation

Solvents and reagents were used as received. The *meso*-tetraarylporpholactones **4** were synthesized as reported in the literature.[17,20]

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX 400 instruments. High and low resolution mass spectra were provided by the Mass Spectrometry Facilities at the University of Connecticut and Peking University. UV-vis spectra were recorded on a Varian Cary 50 spectrophotometer or an Agilent 8453 UV/Vis spectrometer equipped with an Agilent 89090A thermostat. Fluorescence spectra were recorded on an Edinburgh Instruments Ltd. FLS920 lifetime and steady state spectrometer at 293 K or on a Cary Eclipse spectrophotometer at ambient temperature. IR spectra were acquired on a JASCO FT-IR-410 using an ATR (ZnSe) unit or in KBr pellets using a Bruker VECTOR22 FT-IR spectrometer. Cyclic voltammetry experiments were recorded on a Shanghai Chenhua CHI660C electrochemical workstation; a glassy carbon electrode was selected as working electrode, the auxiliary electrode was a platinum wire, and a SCE (saturated calomel electrode) served as reference electrode.

***meso*-Tetrakis(pentafluorophenyl)-2-oxa-3-thionoporphyrin (5a).** In a Schlenk tube, porpholactone **4a** (0.10 mmol, 100 mg) was dissolved in toluene (8 mL). In a glove box, 10 equiv. of Lawesson's reagent (1.0 mmol, 400 mg) were

added and the tube was sealed and heated to 100 °C for 3 days. After this time, the mixture was dried by rotary evaporation and the residue was purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether 60–90 1 : 5). Light should be excluded during the reaction and purification to prevent photolysis of the product. Yield: 89% (89.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 2H), 8.78 (m, 1H), 8.75 (m, 1H), 8.59 (d, J = 4.4 Hz, 1H), 8.51 (d, J = 4.7 Hz, 1H), −1.35 (s, 1H), −1.65 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.3, 159.0, 157.8, 155.2, 147.4, 145.4, 142.3, 141.3, 139.7, 138.8, 137.6, 135.4, 133.9, 130.1, 128.6, 127.9, 127.3, 114.8, 114.3, 112.6, 111.2, 111.0, 108.6, 105.0, 103.1, 85.8, 32.0, 29.7, 22.7, 1.1, 0; ^{19}F NMR (470 MHz, $CDCl_3$): δ −136.99 (d, J = 7.4 Hz, 1H), −137.44 (d, J = 7.4 Hz, 1H). −137.48 (d, J = 7.4 Hz, 1H), −137.53 (d, J = 7.4 Hz, 1H), −137.60 (d, J = 7.4 Hz, 1H), −137.64 (d, J = 7.4 Hz, 1H), −139.14 (d, J = 7.4 Hz, 1H), −139.19 (d, J = 7.4 Hz, 1H), −151.10 (m, 3H), −152.76 (m, 1H), −161.48 (m, 5H), −162.04 (m, 3H); UV-vis (CH_2Cl_2) λ_{max}, nm (log ε): 438 (5.21), 508 (3.83), 543 (3.88), 582 (4.37), 618 (3.91), 677 (4.17); UV-vis (CH_2Cl_2 + 2% TFA) λ_{max}, nm (log ε): 438 (5.19), 545 (3.89), 582 (4.23), 618 (4.11), 675 (3.77); IR (cm^{-1}): 713, 764, 924, 991, 1502, 2939; HR-MS (ESI^+, CH_2Cl_2, TOF) m/z $[M + H]^+$: Calcd for 1009.0178, found 1009.0172.

***meso*-Tetraphenyl-2-oxa-3-thionoporphyrin (5b).** Method A: Prepared in 80% yield (52 mg) from **4b** (0.10 mmol, 63.3 mg) as described for **5a**. Method B: In a 50 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser topped with a drying tube, porpholactone **4b** (110 mg, 1.74 × 10^{-4} mol) was dissolved in toluene (18 mL), solid anhydrous $NaHCO_3$ and Na_2CO_3 (3 small scoops each) and Lawesson's reagent (450 mg, 1.2 × 10^{-3} mol, ~ 7 equiv.) were added, and the mixture was heated to reflux for 1 d. When the starting material was consumed (reaction monitoring by TLC), the reaction mixture was allowed to cool and was evaporated to dryness by rotary evaporation. The residue was taken up in CH_2Cl_2, mixed with little silica gel, and the slush was loaded onto a flash silica gel chromatography column (CH_2Cl_2–petroleum ether 30–60 7 : 3). Yield: 98% (110 mg). R_f (silica-CH_2Cl_2) 0.86. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (dd, ^3J = 5.1, ^4J = 1.8 Hz, 1H), 8.73 (dd, ^3J = 5.1 Hz, ^4J = 1.6 Hz, 1H), 8.61 (dd, ^3J = 4.9, ^4J = 1.9 Hz, 1H), 8.55 (dd, ^3J = 5.0, ^4J = 2.0 Hz, 1H), 8.53 (d, ^3J = 4.7 Hz, 1H), 8.47 (d, ^3J = 4.7 Hz, 1H), 8.17–8.04 (m, 6H), 7.84 (dd, ^3J = 7.6, ^4J = 1.7 Hz, 2H), 7.81–7.65 (m, 12H), −1.29 (s, 1H), −1.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 158.8, 157.9, 155.0, 141.7, 141.4, 141.4, 141.1, 140.5, 139.6, 139.3, 138.3, 137.5, 135.5, 134.5, 134.4, 134.3, 133.9, 132.4, 130.2, 128.8, 128.7, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.3, 127.1, 125.2, 121.4, 120.5, 101.8. UV-vis (CH_2Cl_2) λ_{max}, nm (log ε): 453 (5.25), 519 (3.72), 547 (3.87), 589 (4.19), 622 (3.81), 680 (3.16). UV-vis (CH_2Cl_2 + 2% TFA) λ_{max}, nm (log ε): 465 (5.01), 588 (3.95), 639 (4.16), 685 (3.68). IR (cm^{-1}): 696, 798, 1184, 1265, 2924, 3341. HR-MS (ESI^+, cone voltage = 30 V, 100% CH_3CN, TOF) m/z calcd for $C_{43}H_{29}N_4OS^+$ 649.2057 ($[M + H]^+$), found 649.2114.

***meso*-Tetramesityl-2-oxa-3-thionoporphyrin (5c).** Prepared in 89% yield (73 mg) from **4c** (0.10 mmol, 80 mg) as described for **5a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (m, 1H), 8.47 (m, 1H), 8.43 (s, 2H), 8.36 (m, 1H), 8.28 (m, 1H), 7.24 (m, 8H), 2.59 (m, 12H), 1.92 (s, 6H), 1.88 (d, J = 5.9 Hz, 12H), 1.74 (s, 6H), −1.05 (s, 1H), −1.45 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.8, 196.6, 158.8, 157.8, 154.7, 141.1, 140.7, 139.4, 139.2, 139.1, 139.0, 138.3, 138.1, 138.1, 138.1, 137.9, 137.8, 137.5, 137.4, 136.9, 135.1, 134.7, 133.4, 133.0, 129.1, 128.0, 127.8, 126.9, 126.8, 122.9, 118.7, 118.7, 65.9, 53.5, 30.9, 29.7, 21.6, 21.5, 21.4, 20.8, 15.3, 14.1, 7.9, 1.1, 0.1; UV-vis (CH_2Cl_2) λ_{max}, nm (log ε): 453 (5.43), 518 (3.86), 547 (4.00), 590 (4.38), 622 (4.00), 681 (3.32); IR (cm^{-1}): 723, 802, 968, 1188, 1265, 2920; HR-MS (ESI^+, DCM, TOF) m/z $[M + H]^+$: Calcd for $C_{55}H_{53}N_4OS$ 817.3940, found 817.3935.

***meso*-Tetrakis(4-chlorophenyl)-2-oxa-3-thionoporphyrin (5d).** Prepared in 69% yield (54 mg) from **4d** (0.10 mmol, 77 mg) as described for **5a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (m, 1H), 8.74 (m, 1H), 8.61 (m, 1H), 8.57 (m, 1H), 8.52 (m, 1H), 8.47 (m, 1H), 8.03 (m, 6H), 7.73 (m, 10H), −1.37 (s, 1H), −1.73 (s, 1H). UV-vis (CH_2Cl_2) λ_{max}, nm (log ε): 454 (5.40), 518 (3.94), 548 (4.06), 590 (4.36), 623 (3.97), 682(3.29); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.8, 196.6, 158.8, 154.6, 157.6, 141.1, 140.7, 139.4, 139.2, 139.1, 139.0, 138.3, 138.1, 137.8, 137.5, 137.4, 136.9, 135.1, 134.7, 133.4, 133.0, 129.1, 128.5, 128.0, 127.9, 127.8, 126.9, 126.7, 122.9, 118.7, 65.9, 53.5, 30.9, 29.7, 21.6, 21.5, 21.4, 20.8, 15.3, 14.1, 1.0, 0. 1; IR (cm^{-1}): 796, 1016, 1092, 1265, 2926; HR-MS (ESI^+, DCM, TOF) m/z $[M + H]^+$: Calcd for $C_{43}H_{25}Cl_4N_4OS$ 785.0503, found 785.0498.

RANEY® nickel-mediated desulfurization of 5b

A ~2–3 mL sample of a commerical 50% slurry of RANEY® nickel in water of >pH 9 was placed into a centrifuge tube and washed with absolute EtOH (10×), followed by anhydrous THF (10×). Thionolactone **5b** (5 mg, 7.7 × 10^{-6} mol) was dissolved in anhydrous THF (5 mL) under anhydrous conditions, the flask was closed with a septum and magnetically stirred. The slurry of RANEY® nickel in THF (~2.0 mL) was added and a balloon filled with H_2 gas was attached to the flask *via* a hypodermic needle and the mixture was vigorously stirred at r.t. under exclusion of light for 1 d. When the starting material was consumed (reaction monitoring by TLC), the reaction mixture was transferred into centrifuge tubes, the RANEY® nickel was spun down and washed with CH_2Cl_2 (careful with the disposal of this potentially pyrophoric solid!). The supernatant and washing solutions were combined, dried over anhydrous Na_2SO_4, and reduced to dryness using rotary evaporation. The residue was separated using flash column chromatography (silica gel, petroleum ether 30–60–ethyl acetate 9 : 1), providing oxazolochlorin **6b** in 10%, porpholactone **4b** in 10%, and hemiacetal **7b** in 65% yield. All compounds showed the expected spectroscopic data.[17]

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