Anion Sensors

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Sn^{IV} Complexes of N-Confused Porphyrins and Oxoporphyrins—Unique Fluorescence "Switch-On" Halide Receptors**

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In recent years, novel porphyrin isomers and expanded porphyrins have attracted intensive interest, which is related to their novel structures and properties that cannot be realized in normal porphyrin systems.[1] One of the most interesting classes of porphyrin isomers is the N-confused porphyrin (ncp) which contains an α,β′ linkage of one pyrrole ring in the framework. Since the synthesis of such a porphyrin in 1994 by us and Latos-Grażyński's group,[2] research on its metal complexes has been expanding rapidly owing to its rich structural diversity and interesting properties, such as the stabilization of unusual metal oxidation states, outer coordination, and anion binding at the outer NH site.[3] The central metal ions have been extended from transition metals to main-group metals and lanthanides.[4] However, the corresponding complexes of tetravalent metals have still remained unknown, despite the fact that Sn^{IV} complexes of normal porphyrins (for example, **1**) are very well known.[5]

Herein, we report the synthesis of Sn^{IV} complexes of N-confused tetraphenylporphyrin [Sn(nctpp)Cl_2] (**2**) and N-confused oxoporphyrins [Sn(ncop)Cl] (**3a**–**c**). Complex **2** can bind halides at the outer NH site, and more interestingly, **3** can bind halides at the axial position of the Sn^{IV} center. This binding mode has not been observed until now for either Sn^{IV} complexes of normal porphyrins or other metal complexes of ncp ligands.

Anion binding by synthetic receptors has been investigated extensively in recent years owing to the importance of various anions in biological systems and the possibility of binding toxic anions in environmental science.[6] Fluorescence is one of the most important methods for sensing anions, as a result of its simplicity and high sensitivity. Most of the fluorescent anion-binding systems are based on fluorescence quenching mechanisms,[7] which has some inherent drawbacks.[8] Therefore, anion sensors based on fluorescence

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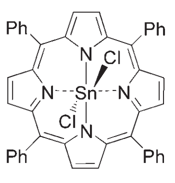
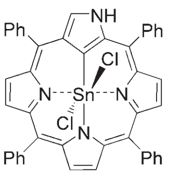
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



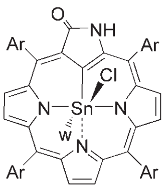
1

[Sn(tpp)Cl$_2$]



2

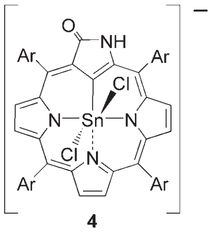
[Sn(nctpp)Cl$_2$]



3

[Sn(ncop)Cl(w)]

3a: Ar = Ph
3b: Ar = p-CF_3-C_6H_4
3c: Ar = p-CH_3-C_6H_4
w = H_2O



4

enhancement are highly desirable, but rather challenging to synthesize.[9] Herein, the fluorescence of the $\mathrm{Sn^{IV}}$ complexes of ncop is unexpectedly enhanced upon the unique axial binding to various halides, including F^-, Cl^-, Br^-, and even I^-. These complexes provide a novel prototype of fluorescence "switch-on" sensors for halides.

The complexes were synthesized in high yields by the reaction of nctpp with excess $SnCl_2$ in pyridine under aerobic conditions. In contrast to the trianionic form of nctpp in the corresponding $\mathrm{Ag^{III}}$ and $\mathrm{Sb^{V}}$ complexes,[10] **2** contains a dianionic nctpp ligand with an outer NH site, which gives a signal at $\delta = 10.67$ ppm in the ^{1}H NMR spectrum. In contrast, in **3a** the nctpp species has been converted to an N-confused tetraphenyloxoporphyrin (ncop),[11] which coordinates as a trianionic ligand as indicated by the crystal structure (Figure 1).[12] The axial positions of the $\mathrm{Sn^{IV}}$ center are occupied by a chloride and water ligand.

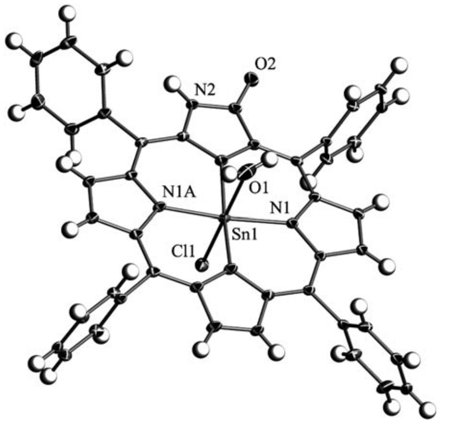
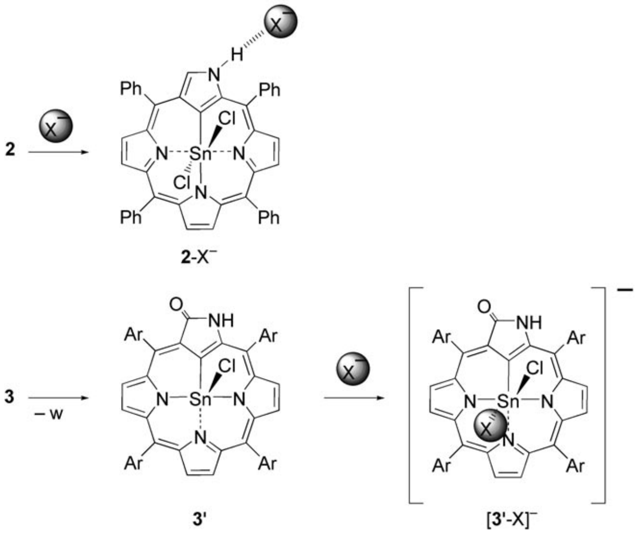


Figure 1. Perspective view of the X-ray crystal structure of **3a**. Selected bond length (Å): Sn1–Cl1 2.405(2). The thermal ellipsoids are scaled to the 30% probability level.

The binding of halides with the $\mathrm{Sn^{IV}}$ complexes was checked by changes in the electronic spectra (Supporting Information). Interestingly, the binding constants and UV/Vis changes for complex **3a** are much larger than those for complex **2**. This observation can be explained by the different binding modes of **2** and **3a** (Scheme 1). For complex **2**, chloride binds at the peripheral NH site, and the signal of the outer NH proton in the ^{1}H NMR spectrum was shifted significantly to lower field from $\delta = 10.67$ to 12.22 ppm upon adding one equivalent of Bu_4NCl (Supporting Information). Compared with NH, other proton signals were only slightly shifted. In contrast, **3a** is dissociated in $CDCl_3$ to give a pentacoordinate species, with the absence of signals for coordinated H_2O in the ^{1}H NMR spectrum. Then the vacant axial position of the $\mathrm{Sn^{IV}}$ center can bind a halide to afford an octahedral complex anion, resulting in a significant change in the electronic state of $\mathrm{Sn^{IV}}$, and consequently, a significant change in its UV/Vis spectra. Meanwhile, all the ^{1}H NMR signals are shifted similarly to higher field. For the NH proton, the signal is shifted from $\delta = 8.80$ to 8.62 ppm upon adding one equivalent of Bu_4NCl.



Scheme 1.

The axial binding of Cl^- with complex **3a** was also clearly evidenced by the crystal structure of complex **4** (Figure 2),[13] which was obtained from the recrystallization of **3a** in the presence of Me_4NCl. The axial $\mathrm{Sn^{IV}}$–Cl bond length in **4** (2.498(1) Å) is longer than that in **3a** (2.405(2) Å), thus indicating the weakening of the $\mathrm{Sn^{IV}}$–Cl bond by the additional coordination of Cl^-. For different halides, the binding constants decrease in the sequence $F^- > Cl^- > Br^- > I^-$, and the values for F^- are too large to be precisely measured (Table 1).

Upon binding of Cl^- with **3a**, the intensity of fluorescence was enhanced significantly (Figure 3). This observation can be ascribed mainly to the better rigidity and planarity of the anion-bound octahedral complex anion compared with the neutral complex, as can be evidenced from the crystal structure data. In the neutral complex **3a**, the $\mathrm{Sn^{IV}}$ center is

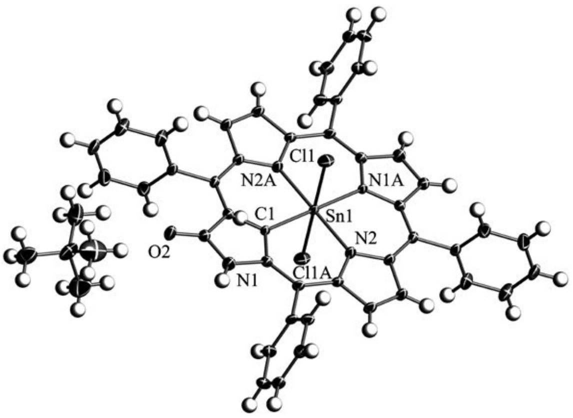


Figure 2. Perspective view of the X-ray crystal structure of **4**. Selected bond length (Å): Sn1–Cl1 2.498(1). The thermal ellipsoids are scaled to the 30% probability level.

Table 1: Anion binding constants (M^{-1}) of the Sn^{IV} ncp complexes.

	Cl	Br	I
2	$4.2(2)\times10^3$	$1.09(8)\times10^3$	40(5)
3a (Ar = C_6H_5)	$1.15(7)\times10^5$	$2.1(1)\times10^4$	$6.1(3)\times10^2$
3b (Ar = p-CF_3-C_6H_4)	$2.2(3)\times10^6$	$1.2(1)\times10^5$	$1.1(1)\times10^4$
3c (Ar = p-CH_3-C_6H_4)	$1.4(2)\times10^4$	$2.7(3)\times10^3$	$3.8(4)\times10^2$

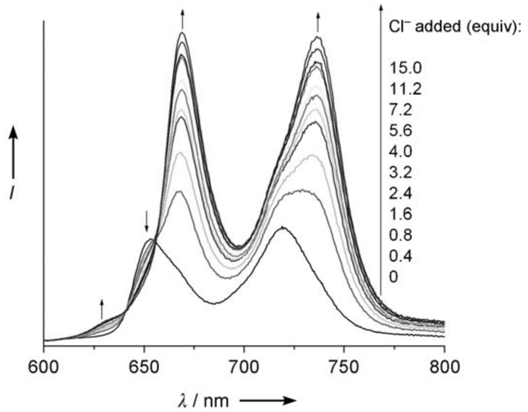


Figure 3. Fluorescence changes during the titration of **3a** with Bu_4NCl in CH_2Cl_2. Excitation wavelength was fixed at 465 nm (one of the isosbestic points) during titration. $[\textbf{3a}] = 6.63\times10^{-6}\,\text{M}$.

displaced 0.170 Å towards the Cl^- ion from the least-squares plane defined by the coordinated C and N atoms of the porphyrin ring, which can be ascribed to the stronger coordination of Cl^- compared with that of water at the other axial site (Sn–O 2.364(5) Å). It can be inferred that this displacement becomes more pronounced in solution when the coordination bond of Sn–OH_2 is disrupted.[14] In contrast, in the crystal structure of the anionic complex **4**, the bonding of Sn–Cl is weakened upon Cl^- binding, and owing to the symmetrical axial ligation, the Sn^{IV} center is located exactly within the porphyrin plane. Consequently, the fluorescence quenching is also weakened. Finally, the quenching through collision between the complex anion and the free halide anions in solution may also be negligible, owing to their electrostatic repulsion, as supported by the observation that when even a large excess of Br^- or I^- is added, the fluorescence intensity is not decreased (Supporting Information).

For derivatives of complex **3a**, when the electron-withdrawing group CF_3 is introduced (**3b**), the Sn^{IV} center has more positive charge; thus, larger binding constants are observed. In contrast, the constants become smaller when the electron-donating group CH_3 is introduced (**3c**; Table 1).

As shown above, in solution the neutral ncop complex has a vacant coordination site and the Sn center has a high valency of +4. Thus, it has a strong tendency to bind an additional anion to form an octahedral complex anion. The carbonyl group in the ncop ligand also creates a favorable situation for axial anion binding owing to the electron-withdrawing effect. Such a unique axial binding mode has not yet been observed for N-confused porphyrin complexes of other metals. For the divalent[15] and trivalent[10a] metal complexes of N-confused porphyrins, the tendency for the central ion to bind an additional anionic ligand is weaker compared to Sn^{IV} owing to the lower valence. In contrast, for the complexes of higher valence metals, such as Sb^{V}, no additional axial position is available because both the coordination sites are already occupied by the anionic ligands.[4a,10b] In the case of normal porphyrin Sn^{IV} complexes, such as $[\text{Sn(tpp)Cl}_2]$, the tpp ligand binds in a dianionic form, and thus, the axial positions of the Sn^{IV} center are occupied by the two chloride ligands. Therefore, further binding of the halide at the axial position is only possible by anion exchange or substitution.[16] On the other hand, transition-metal complexes of normal porphyrins have been well-known to serve as anion receptors in polymeric membrane electrodes.[17,18] However, no fluorescent anion receptors based on these metalloporphyrins have been reported, which may be partly a result of the strong fluorescence quenching by the transition metals.

In conclusion, Sn^{IV} complexes of nctpp and ncop ligands were synthesized in high yields. The nctpp and ncop species coordinate in the dianionic and trianionic forms, respectively. The nctpp complex binds halides at the outer NH site, whereas the ncop complexes bind halides at the axial position with larger binding constants and more pronounced fluorescence enhancement. These complexes can thus be regarded as a novel prototype of fluorescence "switch-on" halide sensors. Such a feature results from a vacant site for the axial coordination of external anions, which seems to originate from the combination of a tetravalent (nontransition) metal and the trianionic nature of the ligand. Similar types of porphyrin-based fluorescent anion receptors could be expected from the porphyrin analogues including corroles.[19]

Experimental Section

2: A mixture of nctpp (61 mg, 0.1 mmol) and $SnCl_2$ (3.8 g, 20 mmol) was heated at reflux in pyridine (15 mL) for 5 min, poured into hexane (50 mL), and filtered, and the solid was washed with CH_2Cl_2. The resulting CH_2Cl_2 solution was rotary evaporated to dryness, and the residue was purified by a silica gel column using CH_2Cl_2/MeOH (4% MeOH) as the eluent to afford a dark purple crystalline solid of **2**

(55 mg, 69 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta = 10.69$ (br, 1 H, outer NH), 8.90 (s, 1 H, α-H), 8.48 (d, $J = 5.1$ Hz, 1 H, β-H), 8.44 (d, $J = 4.2$ Hz, 1 H, β-H), 8.24 (s, 2 H, β-H), 8.12 (t, $J = 4.8$ Hz, 2 H, β-H), 8.01 (s, 8 H, *o*-Ph), 7.67–7.74 (m, 12 H, *m*-Ph, *p*-Ph); MALDI-MS: m/z: 767 $[M{-}Cl]^+$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 353 (22 600), 460 (132 000), 571 (4600), 662 (3700), 716 (6100), 788 nm (11 800 $mol^{-1} dm^3 cm^{-1}$).

3a: The reaction and work-up procedure are the same as those for **2**, except that the reaction mixture was stirred at room temperature for 3 days instead of heating, and the eluent for the column contained 2 % MeOH. A dark purple shiny solid of **3a** (63 mg, 79 %) was collected. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta = 9.02$ (d, $J = 3.9$ Hz, 1 H, β-H), 8.99 (d, $J = 3.3$ Hz, 1 H, β-H), 8.87–8.91 (m, 4 H, β-H), 8.80 (d, $J = 4.8$ Hz, 1 H, outer NH), 8.20–8.30 (m, 3H *o*-Ph), 8.05–8.15 (m, 3 H, *o*-Ph), 7.72–7.89 (m, 14 H, Ph); MALDI-MS: m/z: 782 $[M{-}H_2O]^+$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 388 (15 100), 446 (172 000), 458 (146 000), 560 (11 600), 597 (10 600), 647 nm (4100 $mol^{-1} dm^3 cm^{-1}$).

Compounds **3b**,**c** were synthesized by a procedure similar to that of **3a** in yields of 96 % and 72 %, respectively. **4** was obtained from the recrystallization of **3a** with one equivalent of Me_4NCl in $CHCl_3$/hexane by the vapor-diffusion method. **3b**: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta = 8.91$ (d, $J = 4.8$ Hz, 1 H, β-H), 8.80–8.87 (m, 4 H, β-H), 8.75 (d, $J = 4.8$ Hz, β-H), 8.68 (s, 1 H, outer NH), 7.95–8.40 (m, 16 H, *o*-, *m*-Ph); MALDI-MS: m/z: 1054 $[M{-}H_2O]^+$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 387 (16 500), 445 (195 000), 457 (161 000), 559 (12 700), 597 (11 200), 647 nm (5600 $mol^{-1} dm^3 cm^{-1}$). **3c**: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta = 8.99$ (d, $J = 4.8$ Hz, 1 H, β-H), 8.96 (d, $J = 5.1$ Hz, 1 H, β-H), 8.85–8.91 (m, 4 H, β-H), 8.80 (d, $J = 4.5$ Hz, 1 H, outer NH), 8.09–8.12. (m, 3 H, *o*-Ph), 7.92–8.00 (m, 3 H, *o*-Ph), 7.72–7.79 (m, 2 H, *o*-Ph), 7.50–7.65 (m, 8 H, *m*-Ph), 2.65–2.70 (m, 12 H, *p*-CH_3); MALDI-MS: m/z: 838 $[M{-}H_2O]^+$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 390 (16 900), 448 (185 000), 458 (160 000), 561 (12 900), 597 (12 200), 647 nm (4100 $mol^{-1} dm^3 cm^{-1}$).

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[12] Crystallographic data for **3a**: $C_{44}H_{29}ClO_2N_4Sn$, $M_r = 799.85$, monoclinic, space group $C2/c$, $a = 13.546(1)$, $b = 19.522(2)$, $c = 13.239(1)$ Å, $\beta = 91.119(2)°$, $V = 3500.2(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.518$ g cm^{-3}, $T = -150$ °C, 12 858 measured reflections, 4222 unique reflections ($R_{int} = 0.0543$), 3249 with $I \geq 2\sigma(I)$ used in refinement, $R = 0.0541$, $R_w = 0.1141$, GOF = 1.052.

[13] Crystallographic data for **4**: $C_{48}H_{39}Cl_2N_5OSn$, $M_r = 891.43$, monoclinic, space group $C2/c$, $a = 18.752(1)$, $b = 13.409(1)$, $c = 19.757(1)$ Å, $\beta = 116.607(1)°$, $V = 4441.9(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.333$ g cm^{-3}, $T = -150$ °C, 15 962 measured reflections, 5295 unique reflections ($R_{int} = 0.0329$), 4421 with $I \geq 2\sigma(I)$ used in refinement, $R = 0.0440$, $R_w = 0.0992$, GOF = 1.084. CCDC-271378 (**3a**) and 271380 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] When the axial H_2O ligand of **3** was replaced with an EtOH molecule, ^{1}H NMR signals of unbound EtOH were detected in the solution.

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