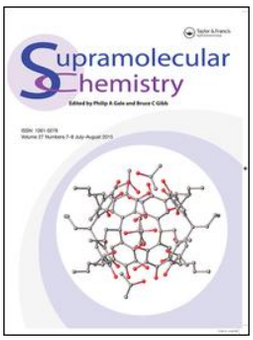

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Novel uranyl(VI) complexes incorporating ethynyl groups as potential halide chemosensors: an experimental and computational approach

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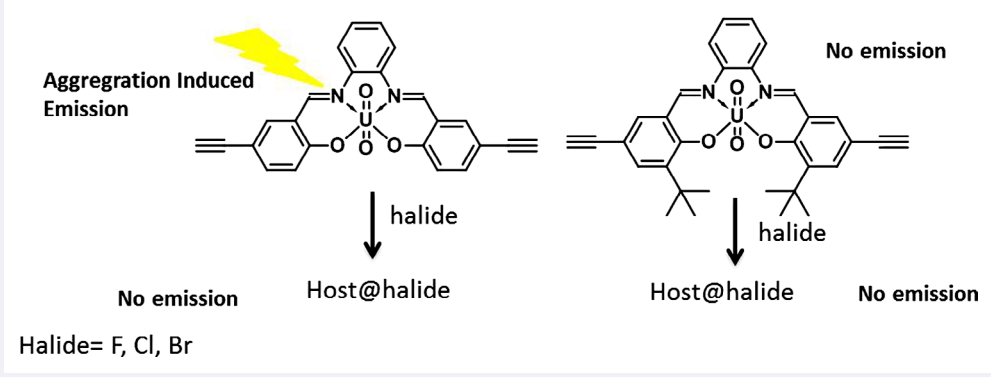
ABSTRACT

The synthesis of two novel Uranyl-salophen complexes, **1** and **2**, decorated with ethynyl substituents, and the study in chloroform of their binding properties toward three different tetrabutylammonium halide salts, i.e. fluoride, chloride, bromide, are here reported. Such derivatives proved to be efficient halide receptors. The presence of two ethynyl groups in the para position, with respect to the phenoxide oxygens, seemed to be accountable for the moderate emission shown by complex **1**. Surprisingly, instead, complex **2** does not show such property. The possibility of **1** to form dimers in non-coordinating solvents provides an explanation for such difference, since emission can be induced by the aggregation. This finding provides an unprecedented example of aggregation induced emission (AIE) for metal salophen derivatives. Moreover DFT calculations provide theoretical insight to the formation of host-guest complexes. Their stabilities were calculated in vacuum and in chloroform and the results are perfectly in agreement with the experimental data.



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Halide recognition; metal salophen; uranyl

Introduction

Nowadays a main focus of supramolecular chemistry is the design and study of luminescent and colorimetric sensors for anions (*1*). It is well known that anions play an essential role in many chemical and biological processes. Inorganic and biotic anions such as acetate, phosphate, and halide are involved in the activity of enzymes, transport of hormones, protein synthesis, and DNA regulation. Moreover, environmentally important anions such as nitrate and phosphate constitute a large part of current pollutants that cause eutrophication of rivers. For these reasons, over recent years, we have seen the development of a huge number of artificial anion receptors that can act as chemosensors, efficiently changing their photophysical properties in the presence of anions, and showing high sensitivity and low detection limit. Different types of non-covalent interactions are exploited to achieve recognition, ranging from hydrogen bond, anion-π interactions to hydrophobic effects etc. (*2–4*). Within these, an important binding motif is metal coordination, that has its roots in classical coordination chemistry (*5*).

Among the different metals that can be coordinated by these ligands, there is the hexavalent uranyl dication, UO_2^{2+} which displays a pentagonal bipyramidal coordination

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geometry in which the apical positions are occupied by the two oxygen atoms, while four of the five equatorial positions are engaged with the N_2O_2 donor atoms. Thus, an equatorial position remains available for substrates that can be complexed through Lewis acid-base interactions (*6*). It was found that such complexes behave as highly efficient receptors for anions. The recognition event can be easily detected by UV-vis or NMR spectroscopy following variations induced by the presence of the anion. Moreover uranyl cation and salophen ligands are fluorescent on their own, while the corresponding complexes hardly emits (*7*). Therefore only few examples of luminescent uranyl salophen complex based receptors have been reported till now (*8*).

In the literature several approaches have been pursued to solve the problem of having very good receptors for specific targets, though weakly emissive, to use them in sensing. Different strategies have been adopted including for example the attachment to the ligand molecular framework of anthracene (*9*) and/or pyrene units (*10*) with high fluorescence quantum yields (Φ_F), or the extension of π-conjugation and the introduction of electron withdrawing groups (*11*) as substituents (*12*).

Such considerations have prompted us toward the synthesis of two new uranyl-salophen complexes, **1–2**, bearing ethynyl substituents as chromophoric groups. Here we report the synthesis of such derivatives and how the introduction of the ethynyl substituents on the ligand skeleton affects their association behavior toward a series of halides, fluoride, chloride and bromide, and their photoluminescent properties (Figure 1).

Results and discussion

Synthesis

The new compounds were obtained according to Scheme 1.

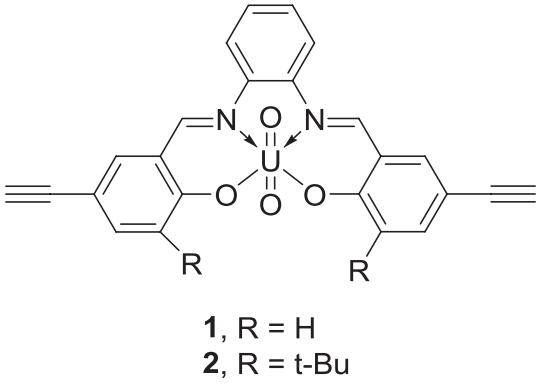


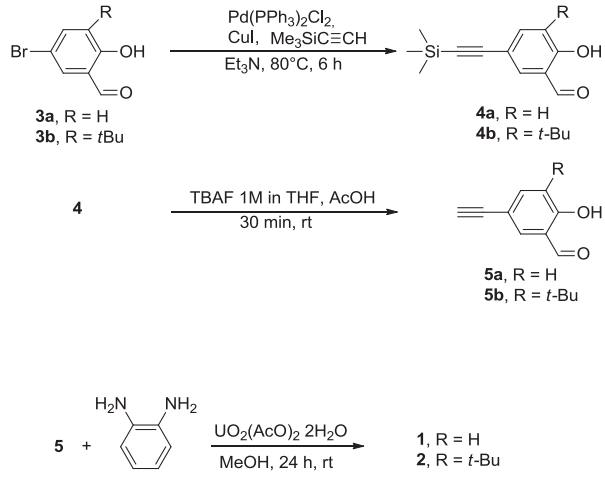
Figure 1. Structure of compounds **1** and **2**.

5-bromo-2-hydroxybenzaldehyde is commercially available, while 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde, **3b**, was prepared according to Scheme 2. Compounds **4a** and **4b** were obtained through Sonogashira coupling reactions (*13*) between the proper hydroxybenzaldehyde, **3a** or **3b**, ethynyltrimethylsilane in the presence of bis(triphenylphosphine)palladium(II) dichloride and copper iodide in triethylamine. After deprotection, derivatives **5a** and **5b** (*14*) were reacted with 1,2-phenylendiamine in the presence of $UO_2(OAc)_2{\cdot}2\ H_2O$ in methanol. After 24 h at room temperature, a bright orange powder, **1**, or a red powder, **2**, were obtained and isolated without further purification (SI).

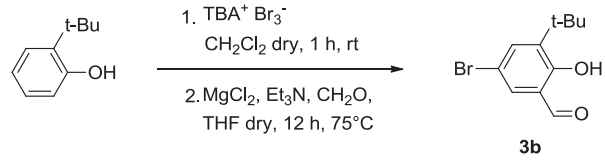
Results and discussion

Absorption spectra of the uranyl complexes display different bands between 300 and 450 nm which can be assigned to $\pi\rightarrow\pi^*$ transitions of the phenyl ring and of the azomethine chromophore. The farthest energy band is assigned to $n\rightarrow\pi^*$ transition involving the promotion of the lone pair electrons of nitrogen atom to the anti-bonding π^* orbital[6a].

The appearance of an emission band in the case of **1** with a maximum at 479 nm characterised by moderate quantum yield ($\Phi_F = 0.021 \pm 0.001$) in chloroform, Figure 2, let us think that this was due to the introduction of ethynyl groups.



Scheme 1. Synthetic route to Uranyl-salophen complex **1–2**.



Scheme 2. Synthetic route to 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde, **3b**.

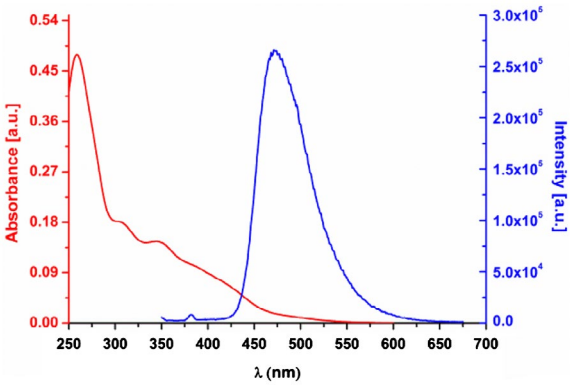


Figure 2. (Colour online) UV-vis (red) and emission (blue) spectra of compound **1**, c = 8.62 × 10^{-5} M, in $CHCl_3$.

Before starting an exploratory study of the affinity of **1** towards a series of halides based on emission variations, we performed standard UV-vis titrations measuring absorption variations in $CHCl_3$ using tetrabutylammonium (TBA) salts of fluoride, chloride and bromide.

The addition of increasing amount of standard solutions of the TBA salt in chloroform to the solution of **1**, caused variations of the absorbance spectrum, see Figure 3 due to the well known strong affinity of uranyl salophen complexes towards halides (*15*).

Typical titration experiments are reported in Figure 3. Reproducible absorbance changes in the 280–550 nm region caused by the enhancement of anion concentration at 25 °C were observed. The presence of sharp isosbestic points and the close adherence of titration data to the binding isotherm of a 1:1 complexation phenomenon lead to estimate association constants higher than 10^6 M^{-1} for fluoride and 10^5 M^{-1} for chloride. Instead in the case of TBABr, the titrations data were not reproducible and the values obtained appeared to be dependent on complex concentration, i.e. in the host concentration range of 5·10^{-5}–5·10^{-6} M, the calculated association constants assume values between 3·10^3 and 2·10^4 M^{-1}.

In 2007 Ikeda et al. reported that in non-coordinating solvents like chloroform, Uranyl-salophen complexes without substituents in the *ortho* position to the phenolic oxygens are present as dimeric complexes $[(UO_2(salophen)]_2$ even at low concentration (10^{-5}–10^{-6} M) (*16*). In the dimer, the two salophen units are held together through the coordination of the phenoxide oxygen of one salophen ligand to the fifth equatorial coordination site of the other Uranyl center. Likely, this occurs also in the case of complex **1**. This assumption is confirmed by the ^{1}H-NMR spectrum in $CDCl_3$ in which the aromatic signals appear quite broad. Indeed the addition of a small amount of a competitive guest, for example one or two drops of a coordinating solvent such as pyridine, leads to a well resolved spectrum characterised by sharp signals. To avoid dimerization, a likely reason for the irreproducibility of measurements in the case of weaker binders, we introduced two *tert*-butyl groups in the 3,3′ positions, **2**. UV-vis titrations with the three TBA halides, F^-, Cl^-, and Br^-, were performed using this time complex **2**. Very good affinities for fluoride and chloride, with association constants higher than 10^6 and 10^5 M^{-1}, respectively, were measured, Table 1, and accurate, although lower values, as expected, were obtained in the case of bromide, i.e. 7·10^3 M^{-1} (Figure 4). These data are perfectly reproducible and independent of host concentration. Moreover, unexpectedly no emission was observed in this case.

Thus, the absence of substituents close to the metal center in complex **1** favors the formation of dimers even in diluted solution. Since fluoride and chloride bind very strongly to uranyl, their additions immediately disrupt dimeric aggregates shifting the equilibrium completely toward the monomeric species. This leads to reliable and reproducible data for titrations as the model we apply

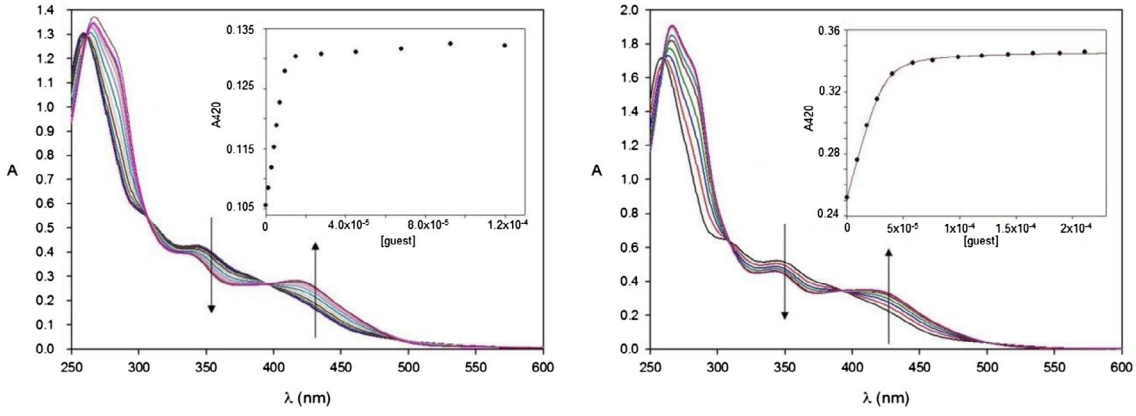


Figure 3. (Colour online) UV-vis titration curves in $CHCl_3$ at 25 °C of host **1** with TBAF ([**1**] = 1.02·10^{-5} M) left, and TBACl ([**1**] = 2.98·10^{-5} M) right.
Insets: variation of the absorption at 420 nm against concentration; points are experimental, curves are calculated.

is that of a 1:1 complexation phenomenon (*17*). Instead for bromide, that has a lower affinity for the metal, at least three orders of magnitude less, the equilibrium between monomeric and dimeric species, Equation (1), is more important and concentration starts playing a crucial role. Indeed for complex **1** the binding constant with bromide decreases upon increasing complex concentration while for complex **2**, in which dimer formation is prevented, the host-halide complex is formed immediately, and concentration is not influencing the measurements.

$$HOST_{dimer} \rightleftharpoons HOST_{monomer} \quad (1)$$

$$HOST_{monomer} + Anion \rightarrow HOST@Anion$$

The unexpected finding that complex **2** does not show emissive properties suggests that the fluorescence that we observe for **1** should be ascribed to aggregation. Such phenomenon is known as aggregation-induced emission (AIE) and originates from the restriction of intramolecular rotation (*18*).

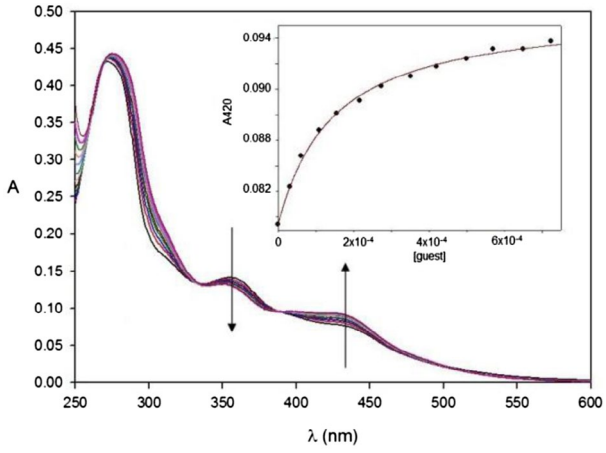


Figure 4. (Colour online) UV-vis titration curve in $CHCl_3$ at 25 °C of complex **2** (inset, points are experimental, curve is calculated) and corresponding spectral variation with TBABr ([**2**] = $9.36 \cdot 10^{-6}$ M).

Molecular modelling

In order to provide more theoretical insight into the geometry of the host-guest complexes as well as into the energy of their formation, molecular modelling studies were performed at the DFT level, using the B3LYP functional (*19*, *20*) (see below). The minimum energy geometries of receptors **1** and **2** are displayed in Figure 5.

As previously reported, the U–O distance, is significantly longer than the one corresponding to the axial oxygens (U=O) due to the overlap between the 6d and 5f orbitals of the uranium atom and the three p orbitals (or two p and one hybrid sp orbitals) of each axial oxygen providing the linear structure (*21*).

The O=U=O moiety is almost linear, Table 2. The two derivatives, **1–2**, are expected to be folded with the aromatic substituted rings with a torsion angle of 43–45° with respect to the main plane of the $U–N_2O_2$ atoms (see Figure S1). This conformation would favour the coordination with guest molecules as no steric hindrance is expected around the fifth equatorial binding site of the metal.

Calculations on the halide complexes were also performed and the resulting structures and main distances and angles are shown in Figures 6, S2 and Table 3.

Coordination with halides affects the environment around the metal atom and induces a slight deviation from O=U=O linearity (the angle becomes less than 180°). It should be noted that the U···X (X = F^-, Cl^-, Br^-) calculated distances reproduce quite nicely those obtained from X-ray crystal diffraction in analogous host-guest uranyl-halide complexes (*22*, *23*).

The energies for the formation of the adducts with the different halides (fluoride, chloride and bromide) were calculated by DFT in the gas phase and in chloroform. The results are summarised in Table 4.

Inspection of Table 3 confirms the experimental data. The affinity for fluoride anion is the highest for both receptors, following the general trend $F^- > Cl^- > Br^-$ and indeed, the predicted energy for the complex formation with the bromide anion is clearly lower in all cases. The energies predicted for the host: guest interactions with receptor **2** are larger than those calculated for **1**. This is in

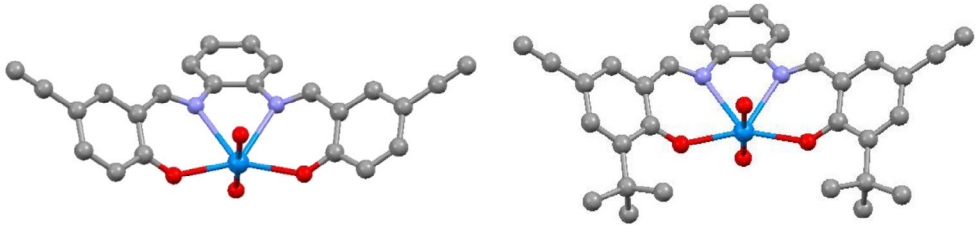


Figure 5. (Colour online) Optimised structures of **1** (left) and **2** (right).
Notes: Carbon (grey); oxygen (red); uranium (cyan); nitrogen (blue). Hydrogens are omitted for clarity.

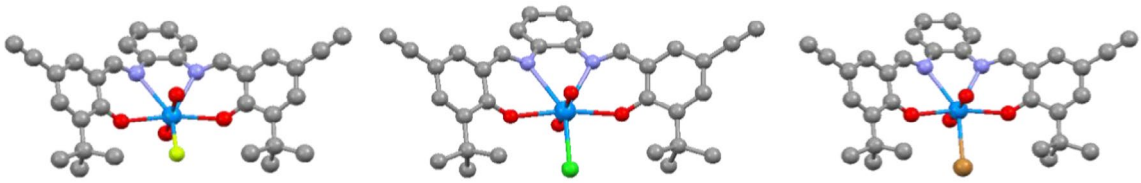


Figure 6. (Colour online) Molecular modelling structure of **2**-F (left), **2**-Cl (middle) and **2**-Br (right).
Notes: Hydrogens are omitted for clarity. Carbon (grey); oxygen (red); uranium (cyan); nitrogen (blue); fluoride (yellow); chloride (green) and bromide (brown).

Table 1. Binding constants, K (M^{-1}) of **1** and **2** toward TBAX salts (X = F^-, Cl^-, Br^-) in $CHCl_3$ at 25 °C.

Complex	F^-	Cl^-	Br^-
1	$>10^6$	$>10^6$	–
2	$>10^5$	$>10^5$	7×10^3

Table 2. Main distances calculated for optimised geometries of compounds **1** and **2**.

	Distance (Å)			Angle (°)		
Complex	U=O	U-O	U-N	O=U=O	U-O-C	U-NH-C
1	1.787	2.271	2.579	179	135.36	125.06
2	1.787	2.274	2.563	179	137.69	124.86

Table 3. Main distances calculated for optimised geometries of complexes **1** and **2** with fluoride, chloride and bromide.

	Distance (Å)				Angle (°)		
Complex	U-X	U=O	U-O	U-N	O=U=O	U-O-C	U-NH-C
1·F	2.115	1.797	2.380	2.757	172.26	136.16	125.08
1·Cl	2.708	1.788	2.345	2.748	172.51	136.44	125.11
1·Br	2.923	1.787	2.336	2.740	172.91	136.45	125.11
2·F	2.141	1.798	2.372	2.713	173.46	137.16	124.31
2·Cl	2.726	1.787	2.368	2.696	173.44	141.24	126.96
2·Br	2.936	1.786	2.369	2.689	173.63	141.52	126.34

Table 4. ΔE values (kcal/mol) calculated for the formation of **1** and **2**:halide adducts in gas phase and in $CHCl_3$.

	Gas	$CHCl_3$
1-F	−129.76	−71.42
1-Cl	−59.01	−15.93
1-Br	−44.87	−7.04
2-F	−135.35	−83.73
2-Cl	−61.71	−24.94
2-Br	−46.12	−14.83

agreement with the more stable monomeric species of complex **2**, where the presence of the *tert*-butyl group precludes dimer formation. Additional non common halide···H hydrogen bonding interactions, that could be established between the different halides and the *tert*-butyl groups, may favor the stability of the resulting adducts (*24*).

Conclusions

Here, we reported the synthesis of two novel Uranyl-salophen complexes, **1** and **2**, and the study in chloroform of their binding properties toward three different tetrabutylammonium halide salts, i.e. fluoride, chloride, bromide.

The presence of two ethynyl groups in the *para* position with respect to the phenoxide oxygens, seemed to be accountable for the appearance of moderate emission in **1**. UV-vis titration experiments highlighted the good affinity for TBAF ($K > 10^6\ M^{-1}$) and TBACl ($K > 10^5\ M^{-1}$) salts, while for TBABr measurements resulted to be not reproducible, depending on host concentration.

The possibility for **1** to form dimeric species in non-coordinating solvents provides an explanation for the irreproducibility as well as for the observed emission that can be induced by aggregation (AIE).

These considerations are supported by the fact that complex **2**, in which the presence of two *tert*-butyl groups in the *ortho* position with respect to the phenoxide oxygens prevents dimer formation, shows association constants for fluoride and chloride, comparable with those obtained for **1**. The binding affinity of **2** toward TBABr, $K = 7{\cdot}10^3\ M^{-1}$, was, in this case, reproducibly measured and proved to be independent of receptor concentration. Moreover complex **2** did not have any emission spectrum confirming that the moderate fluorescence shown by **1** is indeed due to dimerization.

DFT calculations provided theoretical insight into the formation of host-guest complexes. Their stabilities were calculated in vacuum and in chloroform and the results are in agreement with the experimental data since the energies for the host:guest interactions calculated in the case of receptor **2** are higher than those calculated for **1** where the different affinity strength towards halides, $F^- > Cl^- >> Br^-$, influences the efficiency of dimer dissociation.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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