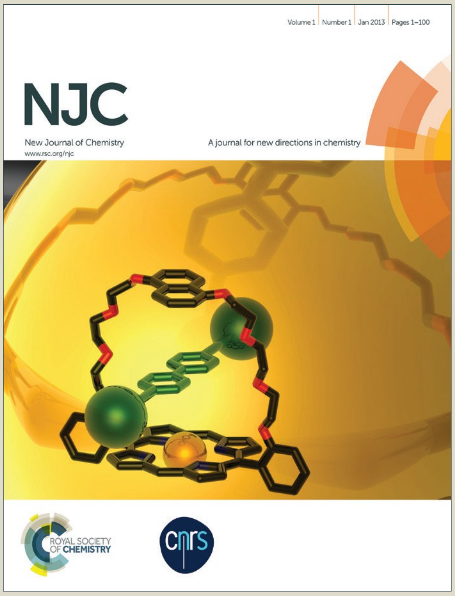
NJC

Accepted Manuscript



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Ternary assemblies comprising metal-salophen complexes and 4,4'-bipyridine

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Abstract

Two series of ternary assemblies comprising metal-salophen [salophen =N,N′-phenylenebis(salicylideneimine)] complexes (M = Zn^{2+} or UO_2^{2+}) and 4,4'-bipyridine have been synthesized. Their absorption and emission data have been compared with those of the corresponding mononuclear derivatives. The dinuclear zinc species present lower emission intensities than those corresponding to the mononuclear precursors while the emission of the analogous uranyl complexes is observed to increase. Absorption and emission titrations indicate that the ternary species are obtained in two independent coordination steps.

The important role of the electron donating/withdrawing properties of the substituents is analyzed regarding their photophysical properties and the association constants. A MLCT transition (recorded by emission spectra) is expected and supported by the increase on the emissive properties of the complexes containing the higher electron donating substituent (methoxy). Nevertheless, this electron donating character disfavors the coordination to the bipyridine as shown by the lower calculated association constants.

DFT calculations have been performed on the zinc derivatives in order to estimate the relative stability of the dinuclear complexes.

Keywords: salophen, uranyl, zinc, luminescence, absorption, DFT

Introduction

Metal salophen complexes are formed by transition and main group metals and the tetradentate salophen (a common abbreviation for N_2O_2 bis-Schiff-base bis-phenolates) ligands. Lately these structures have received considerable attention[1] due to their relative ease of synthesis, and to the ability to form stable complexes with many metals in a variety of oxidation states.[2-6] In general, the N_2O_2 ligands coordinate to the metal ion as a doubly deprotonated form in a tetradentate fashion. Hence, complexation with a d-block divalent transition metal ion affords a neutral metal complex. A variety of metal complexes can be formed in this way, some of which exhibit unique optical properties,[7] and valuable catalytic activity.[8-10]

In this context, sal(oph)en compounds can indeed be particularly useful and important for the development of cooperative multi-metal systems. Such kind of reactivity which involves multiple metal centers is commonly postulated for enzymatic systems.[11] The study of natural systems has provided hints for the synthesis of artificial catalysts including also Schiff-base complexes.[12,13] A main issue in the development of dimetallic analogues is how to connect the two metal-salophen complexes. The solution to this problem is strictly related to the nature of the metal centre and to its coordination geometry.[14]

An example of covalently linked dimeric complexes enforcing the cooperative catalytic mechanism is that reported by Jacobsen *et al.* about the use of a salen-Cr complex in the asymmetric ring opening (ARO) of meso epoxides with TMS-N_3. The two salen units were covalently linked by a tether connecting the two ligand skeletons leaving the metal centers free to coordinate the substrate.[12] More recently a number of well-defined, rigid and semirigid dinuclear complexes have been designed and applied in CO_2/epoxide copolymerization reactions.[15,16] The mechanism and the role played by binuclear compounds has also been investigated.

Different strategies should be adopted if the problem to be addressed is the development of new supramolecular architectures and new materials. The self-assembly of metal complexes of organic ligands into supramolecular architectures is an interesting field of research. In this case the metal becomes a hook to build up the auto-assembled systems and its affinity towards the potential linkers starts playing an important role.[17] The relative positions of the metal centers and the non-covalent interactions that drive the formation of the assemblies are fundamental.

The ability of several metal salophen complexes to form dimeric assemblies in the solid state via μ_2-O bridging has been often highlighted by X-ray diffraction. On the other hand, the presence of good donor ligands inhibits the dimerization leading to the formation of 1:1

complexes.[18] Organic molecules with donating groups or anions can coordinate to the metal center to give, accordingly to the metal coordination geometry, penta- or hexacoordinate complexes.[14,19,20] The formation of these aggregates is generally accompanied by enhancement of photoluminescence quantum yield.[21] A further possibility of using bifunctional guests can lead to the formation of 1-D nanostructures interesting for the development of new aggregates.[14,22] Moreover it can be expected that different molecular arrangements will give rise to differences in reactivity. For the sake of completeness, we should also add that in similar systems another property which is strongly influenced by the aggregation is the second-order nonlinear optical (NLO) response that is a characteristic feature of zinc-salophen complexes, as reported by Di Bella *et al.*[23]

In this context, we synthesized a series of uranyl-salophen complexes in which the salophen ligand is bearing different substituents in the 5,5' positions, *i.e.* OCH_3, Br, and NO_2. We used these newly synthesized derivatives as well as the corresponding Zn-complexes, available from a previous investigation,[24] to form ternary supramolecular assemblies through the combination of two metal salophen complexes with a ditopic nitrogen ligand, *i.e.* 4,4'-bipyridine. The photophysical characterization of such derivatives is herein reported. We should point out that Zn Schiff-base complexes present interesting responsive properties and are suitable candidates for the design and development of supramolecular architectures.

Experimental Section

General

Commercially available chemicals were used without further purification unless otherwise stated. Compounds **1A-3A** were synthesized according to previous methodology.[25]

Physical Measurements

Infrared spectra were recorded on a FT-IR 520 Nicolet Spectrophotometer. ^{1}H and ^{13}C NMR (δ(TMS) = 0.0 ppm) spectra were obtained on a Varian Unity 400. Elemental analyses of C, H and N were carried out at the Centres Científics i Tecnològics de la Universitat de Barcelona (CCiT-UB). ES(+) mass spectra were recorded on a Fisons VG Quatro spectrometer. Absorption spectra were recorded on a Varian Cary 100 Bio UV-spectrophotometer and emission spectra on a Horiba-Jobin-Yvon SPEX Nanolog spectrofluorimeter. Total luminescence quantum yields were measured at 298 K relatively to quinine sulphate in 1 N H_2SO_4 (ϕ = 0.54).[26]

Titrations were carried out at 25 ºC in air-equilibrated ethanol by addition of aliquots of 1x10^{-4} M or 1x10^{-3} M solution of 4,4'-bipyridyne to a 5x10^{-7} M solution of **1A-3A** and **1B-3B**.

The association constants were calculated using HypSpec 1.1.33 for Windows.[27]

Synthesis and Characterization

[N,N'-(o-Phenylene)bis(5-methoxysalicylideneiminato)zinc(II)]$_2$(4,4'-bipyridine), ***(1A)**$_2$bipy.*

A dichloromethane (15 mL) solution of *N,N'*-(*o*-Phenylene)*bis*(5-methoxysalicylideneiminato)zinc(II) (21.0 mg, 0.04 mmol) and 4,4'-bipyridine (3.6 mg, 0.02 mmol) was stirred for 1 hour. The solution was concentrated under reduced pressure until *ca*. 8 mL and precipitated by the addition of hexane (5 mL). The mixture was then filtered, and the final product was obtained as an orange solid in 83 % yield (17mg). IR (KBr, cm^{-1}): ν (C=N) = 1606. HRMS-ES (+): found 534.5 ([M + EtOH + 2H$^+$- CH_3] calcd. 534.4); found 558.1 ([M + 2CH_3CN + 2H$^+$] calcd. 558.1). Elemental analysis: calc. (%) for $C_{54}H_{44}N_6O_8Zn_2$: C, 62.62; H, 4.28; N, 8.11; found: C, 62.75; H, 4.35; N, 7.95.

[N,N'-(o-Phenylene)bis(5-bromosalicylideneiminato)zinc(II)]$_2$(4,4'-bipyridine) ***(2A)**$_2$bipy.*

The same procedure for the synthesis of (**1A**)$_2$bipy was also applied to the preparation of this compound but using N,N'-(*o*-Phenylene)bis(5-bromosalicylideneiminato)zinc(II) (21.0 mg, 0.04

mmol) as starting material. The final product was obtained as a yellow solid in 86 % yield (20 mg). IR (KBr, cm^{-1}): ν (C=N) = 1610. HRMS-ES(+): found 639.9 ([$M+3H_2O+2H^+$] calcd. 639.9). Elemental analysis: calc. (%) for $C_{50}H_{32}Br_4N_6O_4Zn_2$: C, 47.78; H, 2.62; N, 6.83; found: C, 47.92; H, 2.70; N, 6.92.

*[N,N'-(o-Phenylene)bis(5-nitrosalicylideneiminato)zinc(II)]$_2$(4,4'-bipyridine), (**3A**)$_2$bipy.*

The same procedure for the synthesis of (**1A**)$_2$bipy was also applied to the preparation of this compound but using *N,N'-(o*-Phenylene)*bis*(5-nitrosalicylideneiminato)zinc(II) (21.0 mg, 0.04 mmol) as starting material. The final product was obtained as a yellow solid in 91 % yield (20 mg). IR (KBr, cm^{-1}): ν (C=N) = 1621; (O=U=O) = 894 s. HRMS-ES (+): found 548.7 ([$M + 2H^+$] calcd. 548.8); found 560.3 ([$M + 2H^+ + Na$] calcd. 560.0). Elemental analysis: calc. (%) for $C_{50}H_{32}N_{10}O_{12}Zn_2$: C, 54.81; H, 2.94; N, 12.78; found: C, 54.94; H, 3.02; N, 12.86.

*[N,N'-(o-Phenylene)bis(5-methoxysalicylideneiminato)uranyl, **1B**.*

A solution of 2-hydroxy-5-methoxybenzaldehyde (0.145 g, 0.95 mmol), 1,2-diaminobenzene (0.060 g, 0.56 mmol), and $UO_2(OAc)_2{\cdot}2H_2O$ (0.256 g, 0.60 mmol) in MeOH (14 mL) was stirred for 24 h. The mixture was then filtered and the final product was obtained as yellow solid in 77% yield. ^{1}H NMR (300 MHz, DMSO -d_6) δ: 9.52 (s, 2H, N=C-H), 7.75 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 2H, CH (Ph)), 7.52 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 2H, CH (Ph)), 7.37 (d, J = 3.6 Hz, 2H, C=N-C-C*H*), 7.26 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 2H, O-C*H*), 6.90 (d, J = 9.2 Hz, 2H, O-CH-C*H*), 3.73 (s, 12H, CH_3) ppm. IR (KBr, cm^{-1}): ν (C=N) = 1595; (O=U=O) = 894 s. MS-ESI-TOF calc.: 645.17; found: 645.17 ($M+H^+$). Elemental analysis: calc. (%) for $C_{22}H_{18}N_2O_6U$: C, 41.00; H, 2.82; N, 4.35; found: C, 41.32; H, 2.93; N, 4.41.

*[N,N'-(o-Phenylene)bis(5-bromosalicylideneiminato)uranyl, **2B**.*

A solution of 2-hydroxy-5-bromobenzaldehyde (0.104 g, 0.52 mmol), 1,2-diaminobenzene (0.059 g, 0.55 mmol), and $UO_2(OAc)_2{\cdot}2H_2O$ (0.250 g, 0.59 mmol) in MeOH (15 mL) was stirred for 24 h. The mixture was then filtered and the final product was obtained as yellow solid in 75% yield. ^{1}H NMR (300 MHz, DMSO -d_6) δ: 9.60 (s, 2H, N=C-H), 8.00 (d, J = 2.4 Hz, 2H, CH (Ph)), 7.79 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H, CH (Ph)), 7.69 (dd, J_1 = 8 Hz, J_2 = 4.0 Hz, 2H, C=N-C-C*H*), 7.56 (dd, J_1 = 8 Hz, J_2 = 4.0 Hz, 2H, O-C*H*), 6.97 (d, J = 8.0 Hz, 2H, O-CH-C*H*) ppm. IR (KBr, cm^{-1}): ν (C=N) = 1605 s; (O=U=O) = 900 s. MS-ESI-TOF calc.: 743.16; found: 743.16 ($M+H^+$). Elemental analysis: calc. (%) for $C_{20}H_{12}Br_2N_2O_4U$: C, 32.37; H, 1.63; N, 3.77; found: C, 32.45; H, 1.72; N, 3.85.

[N,N'-(o-Phenylene)bis(5-nitrosalicylideneiminato)uranyl, ***3B****.*

A solution of 2-hydroxy-5-nitrobenzaldehyde (0.100 g, 0.60 mmol), 1,2-diaminobenzene (0.053 g, 0.49 mmol), and $UO_2(OAc)_2 \cdot 2H_2O$ (0.255 g, 0.60 mmol) in MeOH (10 mL) was stirred for 24 h. The mixture was then filtered and the final product was obtained as yellow solid in 70% yield. ^1H NMR (300 MHz, DMSO -d_6) δ: 9.92 (s, 2H, N=C-H), 8.94 (d, J = 4.0 Hz, 2H, CH (Ph)), 8.46 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H, CH (Ph)), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H, C=N-C-C*H*), 7.66 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H, O-C*H*) 7.21 (d, J = 8.0 Hz, 2H, O-CH-C*H*) ppm. IR (KBr, cm^{-1}): ν (C=N) = 1606 s; ν (NO_2) 1570 s, 1499 s, 1466 s; (O=U=O) = 895 s. MS-ESI-TOF calc.: 675.12; found: 675.12 ($M+H^+$). Elemental analysis: calc. (%) for $C_{20}H_{12}N_4O_8U$: C, 35.62; H, 1.79; N, 8.31; found: C, 35.74; H, 1.84; N, 8.40.

[N,N'-(o-Phenylene)bis(5-methoxysalicylideneiminato)uranyl]$_2$(4,4'-bipyridine), ***(1B)$_2$****bipy.*

A dichloromethane (15 mL) solution of *N,N'-(o-*Phenylene)*bis*(5-methoxysalicylideneiminato)uranyl(II) (21.0 mg, 0.04 mmol) and 4,4'-bipyridine (3.6 mg, 0.02 mmol) was stirred for 1 hour. The solution was concentrated under reduced pressure until *ca*. 8 mL and precipitated by the addition of hexane (5 mL). The mixture was then filtered, and the final product was obtained as a brown solid in 90 % yield (26 mg). ^1H NMR (400 MHz, DMSO -d_6) δ: 9.57 (s, 4H, N=C-H), 8.73 (dd, J_1 = 4.6 Hz, J_2 = 1.8 Hz, 4H, bipyH_α), 7.84 (dd, J_1 = 4.6 Hz, J_2 = 1.8 Hz, 4H, bipyH_β), 7.76 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 4H, CH (Ph)), 7.54 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 4H, CH (Ph)), 7.39 (d, J = 3.6 Hz, 4H, C=N-C-C*H*), 7.28 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 4H, O-C*H*), 6.92 (d, J = 9.2 Hz, 4H, O-CH-C*H*), 3.76 (s, 12H, CH_3) ppm. IR (KBr, cm^{-1}): ν (C=N) = 1626 s; (O=U=O) = 902 s. MS-ES (+): found 1385.6 ([M – 2 OCH_3 + H^+] calcd, 1385.4). Elemental analysis: calc. (%) for $C_{54}H_{44}N_6O_{12}U_2$: C, 44.88; H, 3.07; N, 5.82; found: C, 44.96; H, 3.14; N, 5.95.

[N,N'-(o-Phenylene)bis(5-bromosalicylideneiminato)uranyl(II)]$_2$(4,4'-bipyridine), ***(2B)$_2$****bipy.*

The procedure for the synthesis of (**1B**)$_2$bipy was also applied to the preparation of this compound but using *N,N'-(o-*Phenylene)*bis*(5-bromosalicylideneiminato)uranyl(II) (21.0 mg, 0.04 mmol) as starting material. The final product was obtained as a yellow solid in 95 % yield (30 mg). ^1H NMR (400 MHz, DMSO -d_6) δ: 9.77 (s, 4H, N=C-H), 8.84 (dd, J_1 = 4.6 Hz, J_2 = 1.8 Hz, 4H, bipyH_α), 7.94 (dd, J_1 = 4.6 Hz, J_2 = 1.8 Hz, 4H, bipyH_β), 7.86 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 4H, CH (Ph)), 7.54 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 4H, CH (Ph)), 7.59 (d, J = 3.6 Hz, 4H, C=N-C-C*H*), 7.34 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 4H, O-C*H*), 7.05 (d, J = 9.2 Hz, 4H, O-CH-C*H*) ppm. IR (KBr, cm^{-1}): ν (C=N) = 1634 s; (O=U=O) = 910 s. MS-ES (+) found 661.9 ([**2B** – 2 Br + py + H^+] calcd: 661.5); found 1399.2 ([M – 3 Br + H^+] calcd. 1399.3). Elemental analysis: calc. (%) for $C_{50}H_{32}Br_4N_6O_8U_2$: C, 36.61; H, 1.97; N, 5.12; found: C, 36.49; H, 2.10; N, 5.24.

*[N,N'-(o-Phenylene)bis(5-nitrosalicylideneiminato)uranyl]$_2$(4,4'-bipyridine), (**3B**)$_2$bipy.*

The procedure for the synthesis of (**1B**)$_2$bipy was also applied to the preparation of this compound but using *N,N'-(o*-Phenylene)*bis*(5-nitrosalicylideneiminato)uranyl(II) (21.0 mg, 0.04 mmol) as starting material. The final product was obtained as a yellow solid in 95 % yield (30 mg). ^{1}H NMR (400 MHz, DMSO -d_6) δ: 9.92 (s, 4H, N=C-H), 8.94 (d, J = 3.2 Hz, 4H, CH (Ph)), 8.73 (dd, J_1 = 4.6 Hz, J_2 = 1.8 Hz, 4H, bipyH_α), 8.46 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 4H, CH (Ph)), 7.94 (dd, J_1 = 6.0 Hz, J_2 = 3.3 Hz, 4H, C=N-C-C*H*), 7.84 (dd, J_1 = 4.6 Hz, J_2 = 1.8 Hz, 4H, bipyH_β), 7.66 (dd, J_1 = 6.0 Hz, J_2 = 3.3 Hz, 4H, O-C*H*) 7.21 (d, J = 9.2 Hz, 4H, O-CH-C*H*) ppm. IR (KBr, cm^{-1}): ν (C=N) = 1634; ν (NO_2) = 1572 s, 1439 s, 1413 s; (O=U=O) = 898 s. MS-ES (+) found 1460.9 ([M – NO_2 + H^+] calcd. 1459.9). Elemental analysis: calc. (%) for $C_{50}H_{32}N_{10}O_{16}U$: C, 39.91; H, 2.14; N, 9.31; found: C, 40.08; H, 2.26; N, 9.40.

Computational methods

All calculations were carried out with the Gaussian 03[28] package of programs at the B3LYP computational level.[29] The basis set was chosen as follows: for Zn, the LANL2DZ basis, where an effective core potential was used to replace the 10 innermost electrons[30] was used. For carbon, hydrogen, bromine, oxygen and nitrogen the 6-31G(d) basis including polarization functions for the non-hydrogen atoms[31] was used. Geometries have been optimized in vacuum, without including any symmetry constraints.

Results and Discussion

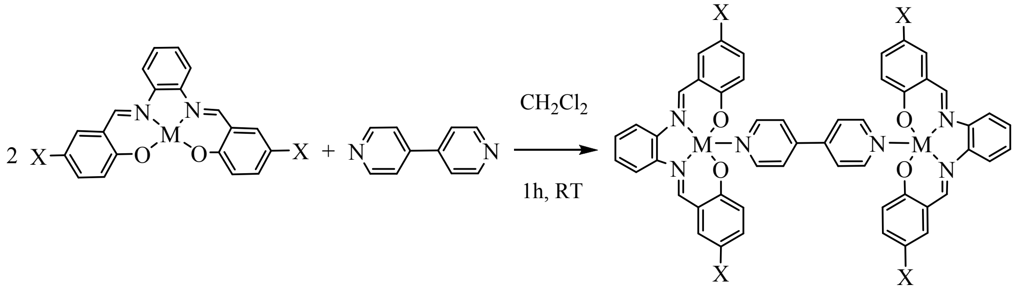
Mono- and dinuclear zinc and uranyl salophen complexes have been synthesized in this work. The differences on the observed properties regarding their nuclearity have been carefully explored.

It is worthwhile to remind that the two metal centres display different coordination geometries. Uranyl dication typically adopts a pentacoordinate geometry, thus the tetradentate salophen ligand in these complexes leaves one site available for the coordination of another guest molecule that occupies the fifth equatorial site. Instead, zinc is usually tetrahedrally coordinated, but can be also found pentacoordinated and, rarely, hexacoordinated. Upon equatorial coordination with the salophen ligand, zinc generally accommodates an additional guest in the apical position. These differences can give origin to supramolecular structures with different features and topological orientations.

Synthesis and Characterization

Compounds **1B - 3B** were prepared using 5-X-salicylaldehyde, X = methoxy (**1B)**, bromo (**2B**) and nitro (**3B**)) and 1,2-diaminobenzene as starting materials and the stoichiometric amount of uranyl acetate salt. The reactants were refluxed in methanol for 1 h, and the products precipitated as yellow-orange solids in pure form and in high yields (70-80%). Characterization by different techniques verified the correct formation of the products. In the solid state, IR spectra show the typical C=N stretching vibration bands of the imine bond at ca. 1630 cm^{-1} together with the C=C of the aromatic rings at *ca*. 1400 cm^{-1}. The typical U=O vibration at *ca*. 900 cm^{-1} is also recorded in all cases. On the other hand, in solution, ^{1}H-NMR shows the typical C*H*=N proton at 9.5-9.9 ppm as the main proof of the correct formation of the product and the molecular peak was observed in all cases by ES-MS spectrometry.

The formation of larger assemblies was obtained by the reaction of the different monometallic derivatives with 4,4'-bipyridine in 2:1 ratio to obtain the ternary complexes as yellow-brown solids in very high yields (Scheme 1). Dinuclear complexes containing Zn(II) as metal centre, (**1-3A**)$_2$bipy, present lower solubility than their precursors. Attempts to perform ^{1}H-NMR experiments gave rise to very broad and weak signals that precludes the use of this technique as a good characterization method. The low solubility prevented also the possibility to obtain single crystals to perform X-ray analysis.



M = Zn^{2+}; X = OMe (**1A**)
M = Zn^{2+}; X = Br (**2A**)
M = Zn^{2+}; X = NO_2 (**3A**)
M = UO_2^{2+}; X = OMe (**1B**)
M = UO_2^{2+}; X = Br (**2B**)
M = UO_2^{2+}; X = NO_2 (**3B**)

M = Zn^{2+}; X = OMe (**1A**)$_2$bipy
M = Zn^{2+}; X = Br (**2A**)$_2$bipy
M = Zn^{2+}; X = NO_2 (**3A**)$_2$bipy
M = UO_2^{2+}; X = OMe (**1B**)$_2$bipy
M = UO_2^{2+}; X = Br (**2B**)$_2$bipy
M = UO_2^{2+}; X = NO_2 (**3B**)$_2$bipy

Scheme 1. Experimental procedure for the synthesis of the ternary species.

On the contrary, the higher solubility of the dinuclear uranyl species allowed us to record ^{1}H-NMR spectra. They show the expected peaks corresponding to the H_α and H_β protons of the bipyridine apart from those corresponding to the salophen ring, which are slightly affected (0.05-0.1 ppm downfield shifted) by the coordination with the bridging ligand (Figure 1).

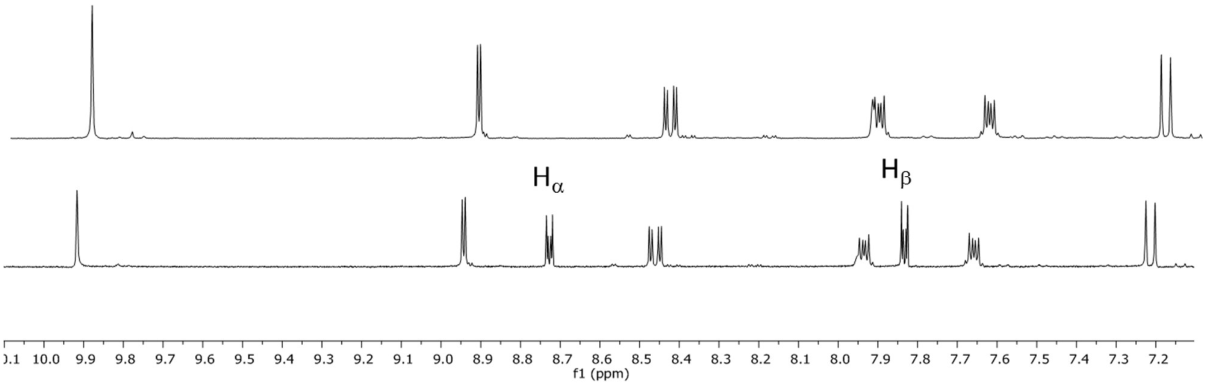


Figure 1. ^{1}H-NMR spectra of **3B** (up) and (**3B**)$_2$bipy (bottom) in dmso-d_6.

IR and mass spectra confirmed the unequivocal formation of the desired complexes in all cases. IR spectra showed a shift of pyridyl C=N vibration of *ca.* 20 cm^{-1} towards higher wavenumbers as a consequence of the coordination of this unit to the metal atom. Molecular peaks present in ES-MS(+) spectra confirmed the formation of all derivatives.

Photophysical Characterization

Absorption and emission characterization was carried out in ethanol solutions at *ca.* 10^{-5} M concentrations. The corresponding spectra were recorded for the mononuclear uranyl complexes **1B-3B** and for all the ternary species (the corresponding data for the mononuclear **1A-3A** zinc complexes were already available from a previous investigation[25]). The results are summarized in Table 1.

The absorption spectra for the mononuclear uranyl derivatives, **1B-3B**, exhibit the same fine structure that is commonly observed for analogous uranyl-salophen complexes in organic solvents (Figure 2).[32] The corresponding emission data collected for the same solutions display only luminescence (not very intense) in the case of the methoxy substituted compound (**1B**). This result is in agreement with a metal-to-ligand charge-transfer transition (MLCT) since the higher the electro-donating density to the metal atom the higher is the probability for the observed emission.

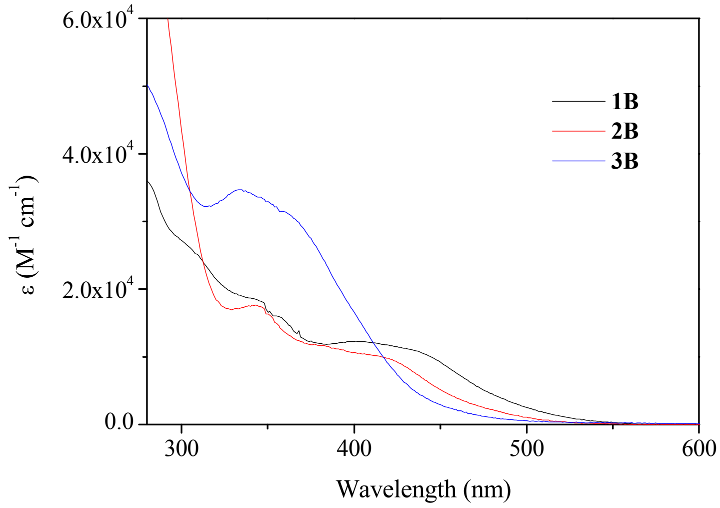


Figure 2. Absorption spectra of *ca.* $9\cdot10^{-6}$ M solutions of **1-3B** in ethanol.

Spectroscopic data for the larger assembled complexes (**1-3A**)$_2$bipy and (**1-3B**)$_2$bipy) display absorption profiles similar to those of the corresponding mononuclear precursors. The luminescence of the dinuclear zinc species resembles the corresponding data retrieved from the mononuclear species, with lower intensity (Table 1). Very low emission was recorded for the dinuclear uranyl derivatives.

Table 1. Absorption and emission data of zinc and uranyl ternary derivatives (**1-3A**)$_2$bipy and (**1-3B**)$_2$bipy), together with the data of their mononuclear precursors, at 25 ºC in air-equilibrated ethanol. λ_{exc} = 340 nm.

Compound	**Absorption (nm)** **(εx10^{-3}, M^{-1}·cm^{-1})**	**Emission (nm)^{a}**	**QY^{c}**
1A^{b}	300 (10.4), 432 (7.2) ^{b}	551^{b}	0.130 ^{b}
2A^{b}	290 (24.9), 400 (19.7) ^{b}	507 ^{b}	0.016 ^{b}
3A^{b}	295 (37.1), 380 (39.6) ^{b}	476 ^{b}	0.009 ^{b}
1B	351 (20.6), 401 (16.2)	540	0.001
2B	341 (21.7), 422 (14.1)	-	-
3B	337 (34.7)	-	-
(**1A**)$_2$bipy	427 (10.95), 476 (6.84)	556	0.070
(**2A**)$_2$bipy	405 (21.0), 441 (14.35)	507	0.011
(**3A**)$_2$bipy	370 (20.8), 420 (14.24)	467	0.008
(**1B**)$_2$bipy	338 (32.8), 429 (22.6)	-	-
(**2B**)$_2$bipy	343 (31.8), 420 (20.9)	-	-
(**3B**)$_2$bipy	339 (51.3)	-	-

[a] λ_{exc} = 420 nm; [b] Data retrieved from ref.25; [c] Quantum yields referred to quinine sulphate in H_2SO_4 1N as reference (ϕ = 0.54).

As expected, the donor/acceptor electronic character of the substituents is reflected in the energy of both the absorption and emission bands.[33] The recorded energy trend is similar to that previously observed for **1A-3A**,[25] (λ(OMe) > λ(Br) > λ(NO_2)), *i.e.*, the higher the electrodonating character, the lower the energy of the observed transitions (longer wavelength). This trend was observed both for zinc and uranyl derivatives. Luminescence quantum yields recorded for all the complexes follow the same trend previously displayed by the mononuclear precursors, being the stronger the electron donating capability, the higher calculated quantum yield. Thus, the methoxy-substituted derivatives show the higher values, while nitro derivatives are the less emissive.

It should be noted that the luminescence quantum yields of the ternary zinc systems are much lower than those obtained for the monometallic precursors. This is not surprising since it was already reported that solution-phase emission quantum yields for salophen derivatives vary extensively in response to molecular structure.[34] On the contrary, some emission could be recorded for the dinuclear uranyl derivatives (see below titration experiments), but not enough to be able to calculate their luminescent quantum yields rigorously.

Spectrophotometric and spectrofluorimetric titrations of the salophen complexes **1-3A** and **1-3B** with different amounts of 4,4'-bipyridine were performed in order to monitor the formation of the 2:1 adduct. No significant changes were recorded by absorption titrations carried out with the zinc complexes. This is in agreement with what we have previously observed in other complexes, where absorption changes were attributed to π−π stacking of a guest molecule interacting with the Zn-salophen host (process that is not possible in the present work).[24,35] Similar experiments carried out with **1B-3B** complexes display a progressive hypochromic effect on the absorption of the uranyl host molecule upon addition of the ditopic ligand as displayed in Figures 3, S1 and S2. Two different inflection points were observed as expected from two independent binding sites (inset Figure 3).

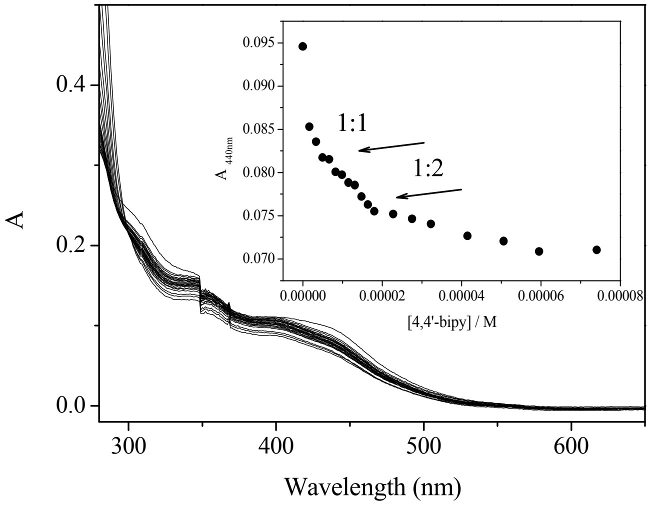


Figure 3. Absorption spectra of **3B** in the presence of increasing amounts of 4,4'-bipyridine. Inset: Plot of A(440 nm) vs [bipyridine].

Quenching of the emission spectra of the complexes was observed for the formation of (**1-3A**)$_2$bipy in the presence of the ditopic ligand while an enhance of this property was exhibited by the respective formation of (**1-3B**)$_2$bipy (Figures 4, 5 and S3-S6). The recorded changes on emission are well fitted for a 2:1 complexation.

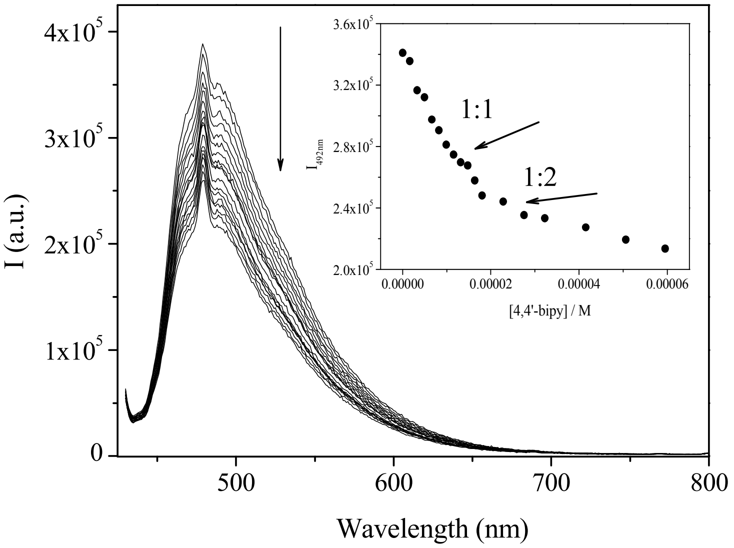


Figure 4. Spectrofluorometric titration of compound **3A** in the presence of increasing amounts of 4,4’-bipyridine (left); Inset: Emission intensity maxima of compound **3A** vs. concentration of 4,4’-bipyridine (right).

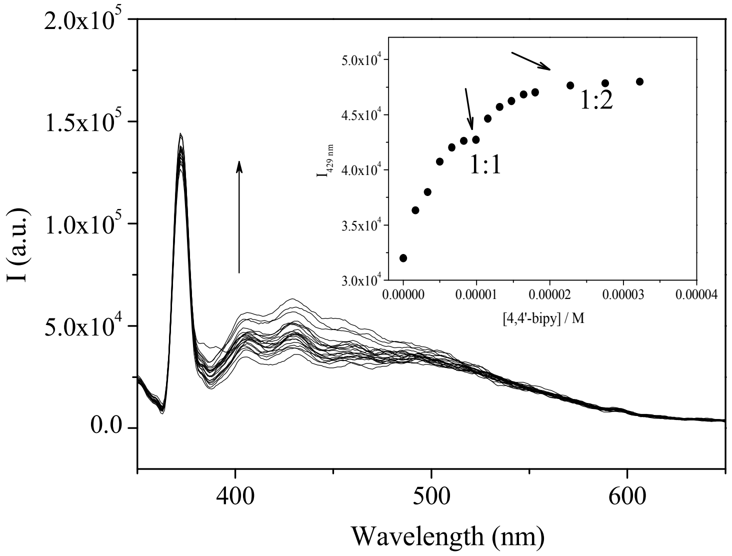


Figure 5. Spectrofluorometric titration of compound **3B** in the presence of increasing amounts of 4,4’-bipyridine (left); Inset: Emission intensity maxima of compound **3B** vs. concentration of 4,4’-bipyridine (right).

The emission spectrum of (**3B**)$_2$bipy shows different peaks in the range of 450-600 nm, characteristic for UO_2^{2+} units, as observed for uranyl organic extended structures.[36] Nevertheless, depending on compositions and structures of the uranyl-organic derivatives, sometimes the fine feature of the emission peaks does not appear clearly,[37,38] and only a broad emission band in the 450-600 nm range is observed. This seems to be the case of (**1B**)$_2$bipy and the residual emission of (**2B**)$_2$bipy. In some cases, if no emissions characteristic of free ligands is observed upon excitation at the ligand absorption wavelengths, it is possible that an efficient energy transfer from the ligand to the central metal atoms occurs.[36] The enhance on the emission of the dinuclear uranyl species may be attributed to this factor, where energy transfer comes from both salophen units together with a possible contribution of the bipyridine group. Moreover, the emissive properties recorded for the mononuclear complex **1B** (and not observed for **2B** and **3B**) are expected to be due to the presence of a ligand rich of electron density (methoxy substituent).

As observed in the absorption intensity variations, two different inflection points were observed in emission titrations, as expected for two independent binding sites. The association constant values of the formation of the ternary species were calculated by using Hypspec v1.1.0.16 program[27] and are summarized in Table 2. The binding curve was fitted with a 2:1 model showing a global preference for the formation of the dinuclear complex reflected in the similar or higher association constant values of K_2 with respect to K_1.

Table 2. Association constant values calculated for the formation of the ternary species.
[a] Approximate value due to the very low intensity of emission recorded.

Compound	log β_1	log β_2
(1A)$_2$bipy	3.3	8.4
(2A)$_2$bipy	5.3	8.9
(3A)$_2$bipy	4.5	9.2
(1B)$_2$bipy	4.2	9.8
(2B)$_2$bipy[a]	5.0	10.1
(3B)$_2$bipy	4.3	10.0

Inspection of Table 2 let us to retrieve more information about the effect of the electron donating/withdrawing character of the substituents of the salophen ligands on the resulting formation of the ternary species. As expected, the methoxy group (both in the case of the zinc and of the uranyl mononuclear complexes) provides increased electron density to the aromatic ring coordinated to the metal atom and hinders the additional coordination with the ditopic bipyridine. This is reflected in the lower association constant values calculated for (**1A**)$_2$bipy and (**1B**)$_2$bipy in each series.

The average values of log*K* ~ 5 is in agreement with those calculated for analogous dinuclear salophen complexes and reported in the literature with the corresponding X-ray crystal structure evidence.[22]

Theoretical studies

In order to rationalize the experimental results we have performed some theoretical calculations at the DFT level, using the B3LYP functional.[29] In a first step we have optimized the geometries corresponding to the mononuclear and dinuclear zinc complexes, and afterwards we have calculated the reaction energy corresponding to the formation of the dinuclear derivatives.

The minimum energy geometries of all zinc complexes and the corresponding non substituted model are displayed in Figures 6, 7 and S7.

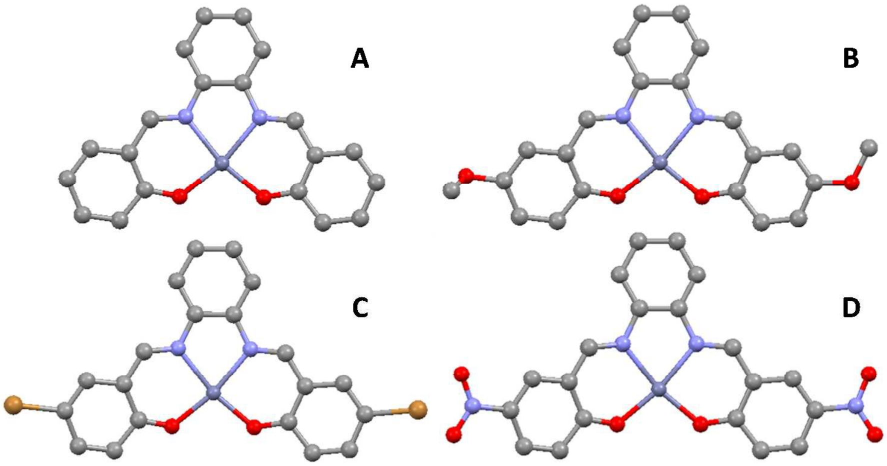


Figure 6. Minimum energy geometries calculated for the mononuclear Zn model (A), **1A** (B), **2A** (C) and **3A** (D) (hydrogen atoms have been omitted from the figure).

The Zn-N and Z-O distances retrieved for the mononuclear complexes do not seem to be affected by the presence of the different substituents being 2.122 Å (Zn-N) and 1.951 Å (Zn-O) for the model compound, methoxy (**1A**) and bromo- substituted (**2A**) derivatives and slightly different for the nitro, **3A** (Zn-N: 2.120 Å and Zn-O: 1.955 Å) as a possible effect of the electrowithdrawing effect of this group (Table 3). These distances are in the same order than those obtained from the X-ray crystal structure resolution of other zinc salophen complexes reported in the literature.[19] The two symmetric units coordinated to the metal atom are not in the same plane with a distortion of *ca*. 15º (Figure S8), in agreement with the expected location of the Zn atom above the N_2O_2 plane.[39]

Table 3. Main distances retrieved from the calculated geometries of the mononuclear and dinuclear complexes.

Distance	**Model**	**1A**	**2A**	**3A**	**Dinuclear model**	**(1A)₂**bipy	**(2A)₂**bipy	**(3A)₂**bipy
Zn-N	2.122	2.122	2.122	2.120	2.174	2.180	2.175	2.173
Zn-O	1.951	1.951	1.951	1.955	1.988	1.984	1.989	1.995
Zn-N(bipy)	-	-	-	-	2.219	2.221	2.213	2.204

The two salophen units in the dinuclear complexes are located in a perpendicular position due to the torsion of *ca*. 40º of the two pyridyl units of the bridging ligand (Figure 7).

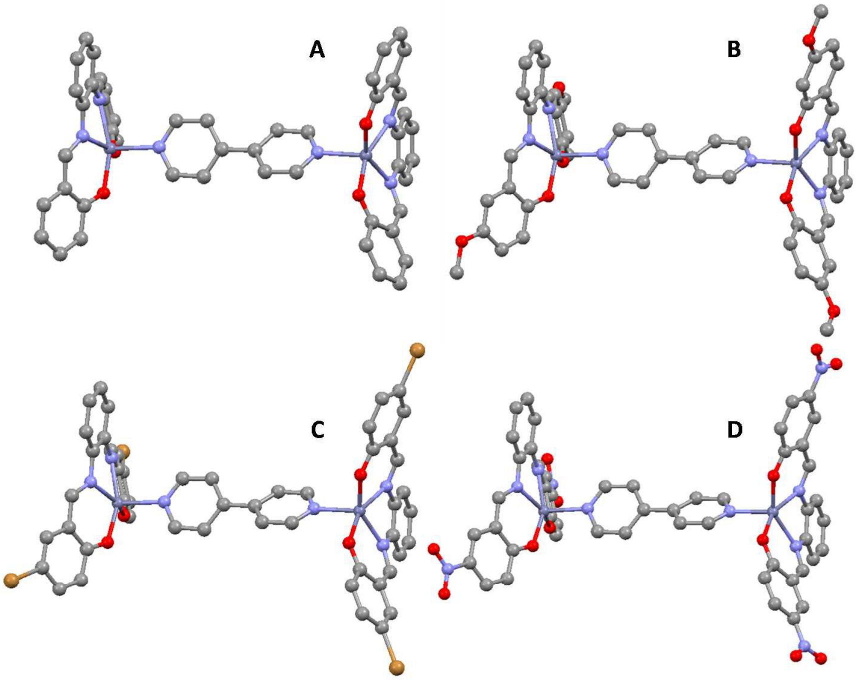


Figure 7. Minimum energy geometries calculated for the dinuclear Zn model (A), **$(1A)_2$**bipy (B), **$(2A)_2$**bipy (C) and **$(3A)_2$**bipy (D).

Interestingly, the calculated N(bipy)-Zn distance in **$(3A)_2$**bipy (Table 3) is shorter than that of the other complexes which is in agreement with a stronger binding process.

Once the geometries have been optimized, we have calculated the energies corresponding to the formation of the dinuclear complexes, from the corresponding monomeric compounds and 4,4'-bipyridine. The results are shown in Table 4. In all cases the reactions are exothermic; all the substituents produce an increment in the energy released with respect to the unsubstituted reference model. The values calculated in vacuum are similar, around 40 kcal/mol, and it is observed that the more exothermic parameter has been observed for the nitro-substituted complex (**3A**)$_2$bipy. This is in agreement with the largest logβ_2 value obtained for the titration experiments and with the fact that coordination is more favoured when the metal atom is more electron deficient due to the presence of an electron withdrawing substituent in the salophen structure.

Table 4. Calculated energies corresponding to the formation of the dinuclear zinc derivatives (kcal/mol).

Compound	**Energies (kcal/mol)**
Reference (R=H)	-37.7
$(1A)_2$bipy	-41.3
$(2A)_2$bipy	-39.6
$(3A)_2$bipy	-42.5

Conclusions

The reaction of the ditopic 4,4’´-bipyridine ligand with mononuclear zinc and uranyl salophen complexes gives rise to the formation of ternary assemblies.

The presence of different substituents on the salophen ligand skeleton influences the absorption features of the derivatives, *i.e.* the higher the electrodonating character, the lower the energy of the observed transitions (longer wavelength) in all cases. The luminescence quantum yields of the ternary systems for the series of zinc complexes, result much lower than those obtained for the monometallic precursors. Thus, this property is definitely influenced by the coordination to a ditopic ligand and can become a useful tool to detect the formation of supramolecular architectures with interesting responsive properties. On the other hand, the behavior displayed by the corresponding uranyl derivatives is the contrary showing an increase of the emission for the ternary species. The presence of an electron donating group (methoxy) induces a positive effect on the emissive properties in both series, being higher than those of the other substituted derivatives. This is in agreement with a MLCT character of the transition.

Absorption and emission titrations let us expect that the ternary species are formed in two independent steps. The corresponding fitting of the recorded variations is in agreement with this fact and leading to lower association constant values for the methoxy substituted species. This could be due to the fact that the metal center is less deficient on electronic density and thus, the coordination to the bipyridyl unit is less favored.

The largest estimated energy value for the formation of (**3A**)$_2$bipy, containing the nitro substituent, is in agreement with the presence of a more electron deficient zinc metal atom that favors the process.

Acknowledgements

The support and sponsorship provided by COST Action CM1005 is acknowledged. Authors are also grateful to the Ministerio de Ciencia e Innovación of Spain (Project CTQ2012-31335). A.D.C. and I. G. aknowledge “Ricerca scientifica di Ateneo 2014” and MIUR “PRIN 2010CX2TLM”. This research was supported by a Marie Curie Intra European Fellowship within the 7th European Community Framework Programme (R.G.).

Supporting Information

Absorption spectra of *ca*. 9·10^{-6}M solutions of **2B** in ethanol in the presence of increasing amounts of 4,4’-bipyridine (Figure S1); Absorption spectra of *ca*. 9·10^{-6}M solutions of **2C** in ethanol in the presence of increasing amounts of 4,4’-bipyridine (Figure S2); Emission spectra of *ca*. 9·10^{-6}M solutions of **1A** in ethanol in the presence of increasing amounts of 4,4’-bipyridine (Figure S3); Emission spectra of *ca*. 9·10^{-6}M solutions of **2A** in ethanol in the presence of increasing amounts of 4,4’-bipyridine (Figure S4); Emission spectra of *ca*. 9·10^{-6}M solutions of **1B** in ethanol in the presence of increasing amounts of 4,4’-bipyridine (Figure S5); Emission spectra of *ca*. 9·10^{-6}M solutions of **2B** in ethanol in the presence of increasing amounts of 4,4’-bipyridine (Figure S6); Side view of the minimum energy geometry calculated for the mononuclear Zn model (A), **1A** (B), **2A** (C) and **3A** (D) (Figure S7).

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Ternary assemblies comprising metal-salophen complexes and 4,4’-bipyridine

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Table of Contents Entry

The formation of ternary species containing zinc or uranyl salophen complexes has been explored and analyzed in this work.