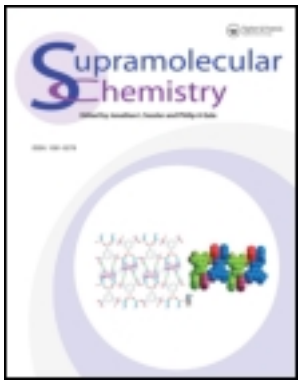

Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

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Version of record first published: 17 Dec 2012.

To cite this article: Francesco Yafteh Mihan , Silvia Bartocci , Alberto Credi , Serena Silvi & Antonella Dalla Cort (2013): Synthesis and photochemical behaviour of novel uranyl-salophen complexes bearing anthracenyl side arms, Supramolecular Chemistry, 25:2, 109-115

To link to this article: http://dx.doi.org/10.1080/10610278.2012.752089

Supramolecular Chemistry
Vol. 25, No. 2, February 2013, 109–115

Taylor & Francis
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Synthesis and photochemical behaviour of novel uranyl–salophen complexes bearing anthracenyl side arms†

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(*Received 13 August 2012; final version received 19 November 2012*)

In this paper, we report the synthesis and physico-chemical investigation of two uranyl–salophen receptors, bearing either one or two anthracenyl moieties appended to the salophen skeleton. Despite the presence of the anthracenyl fluorophores, no fluorescence emission was detected. Photophysical data and cyclic voltammetric experiments show that photoinduced electron transfer from the anthracene-localised first singlet excited state to the metal centre is strongly exergonic, thus suggesting that this is the main fluorescence quenching mechanism in these complexes. The investigated compounds are photoreactive upon UV irradiation, yielding either anthracene photooxidation or photodimerisation products depending on the specific complex and the experimental conditions.

Keywords: uranyl–salophen complexes; anthracenyl fluorophore; PET; cyclic voltammetry

Introduction

The condensation reaction between aldehydes and amines to give imines was firstly reported by Schiff (*1*) in 1864. From that time, such derivatives have been extensively used for a wide range of applications. Well-designed Schiff bases are known to behave as privileged ligands (*2*), able to stabilise different metals in various oxidation states, controlling their performances and tuning their properties. For instance, *N*,*N*′-bis(salicylaldehyde)-1,2-phenylenediimino (salophen) compounds deriving from the condensation of 1,2-phenylenediamine with two equiv. of salicylaldehydes are quite popular ligands in coordination chemistry as they form stable complexes with several transition and main group metals. In recent years, these metal complexes have emerged as antitumoural (*3*), antiviral and antibacterial agents (*4*), as building blocks in the formation of supramolecular assemblies (*5*), in the design of ion-selective membranes and ion-pair receptors (*6*), as sensors (*7*), and in the development of new materials showing nonlinear optical properties (*8*).

Among the metal centres that form robust, electrically neutral complexes with salophen ligands is the hexavalent uranyl ion, UO_2^{2+}. It is well known that uranyl exhibits a preference for a pentagonal bipyramidal coordination geometry (*9*) with the two metal-bound oxygen atoms in the apical positions and the salophen N_2O_2 donor atoms occupying four of the five equatorial coordination sites (Figure 1).

Hence, the fifth equatorial position is still available for coordination with monodentate ligands, e.g. enones and ketones (*10*), or anions such as halides (*11*), carboxylates, phosphates and nucleotides. Uranyl–salophen complexes can thus be regarded as strong Lewis acids capable of recognising hard Lewis bases, not only in organic solvents but, if properly derivatised, also in a more competitive solvent such as water (*12*). NMR and UV–vis absorption spectroscopies are commonly employed to measure the binding strength between such complexes and given guests, demonstrating that in many instances they behave as highly efficient and selective molecular receptors. In the last three decades, however, the supramolecular community has dedicated great attention to the development of receptors capable of generating changes in the fluorescence spectra upon guest recognition (*13–15*), expecially when dealing with anion sensing (*16*). Because of its simplicity and high sensitivity, fluorescence spectroscopy is a particularly attractive technique for analytical applications, and is highly recommended particularly for trace detection. Unfortunately, simple uranyl–salophen complexes do not show fluorescence emission properties (*17*). A feasible route to obtain fluorescent chemosensors based on this kind of receptors consists, therefore, in the

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†Dedicated to Professor A.P. de Silva for his 60th birthday.

ISSN 1061-0278 print/ISSN 1029-0478 online

http://dx.doi.org/10.1080/10610278.2012.752089
http://www.tandfonline.com

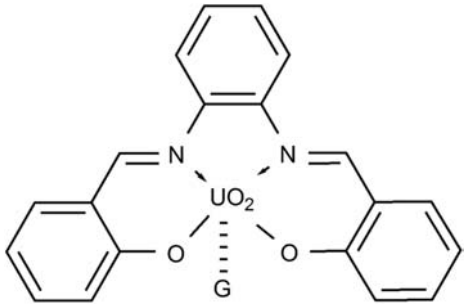


Figure 1. Chemical structure of the host–guest complex between a uranyl–salophen derivative and a guest, G.

incorporation of fluorescent fragments within the basic skeleton of the receptor.

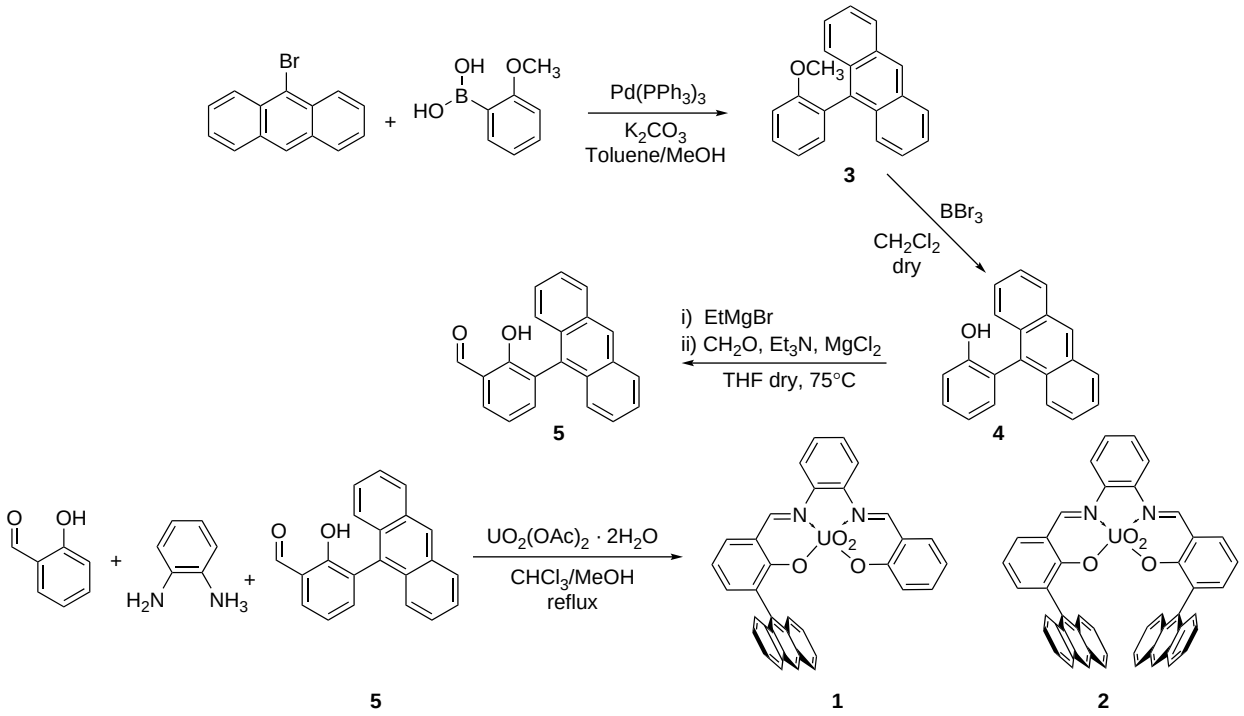
In this paper, we report the synthesis of two novel uranyl–salophen complexes (Scheme 1) bearing either one (**1**) or two (**2**) anthracenyl fluorogenic moieties appended to the salophen framework, and describe their photochemical and electrochemical properties.

Results and discussion

Compounds **1** and **2** were synthesised according to Scheme 1. Briefly, 3-methoxyphenylboronic acid and 9-bromoanthracene were used as starting materials for the synthesis of aldehyde **5**. By following the published procedures (*18*), intermediate **4** was obtained by standard Suzuki coupling followed by demethylation with a solution of BBr_3 in dichloromethane at room temperature. Formylation, performed on phenol **4**, led to 3-(anthracen-9-yl)-2-hydroxybenzaldehyde, **5**. The reaction is regioselective, affording the *ortho* derivative, thanks to the formation of an $MgCl^+$ chelating intermediate (*19*), and is performed in two steps: acid–base reaction of the phenol with 1 equiv. of EtMgBr, followed by the addition of $MgCl_2$, Et_3N and paraformaldehyde.

The final complexes **1** and **2** were directly synthesised by statistical condensation of an equimolar mixture of aldehyde **5**, salicylaldehyde and *o*-phenylendiamine in the presence of a slight excess of $UO_2(OAc)_2{\cdot}2H_2O$ as templating and metallating reagent. After chromatography, the pure compounds precipitated as bright orange solids.

The general design of a good fluorescent chemosensor relies on an efficient mechanism for either quenching or reviving the fluorescence upon recognition of the substrate (*13*, *14*). A series of receptors utilising photoinduced electron transfer (PET) (*20*), intramolecular charge transfer (*21*), excited-state proton transfer (*22*), excimer/exciplex formation, competitive binding (*23*) and metal-to-ligand charge transfer (*24*) as mechanisms to transduce the binding event into a luminescence change have been reported in the literature (*25*). Among the mechanisms listed above, PET is often exploited for the construction of sensors, because the thermodynamic and kinetic aspects of this phenomenon can be reliably rationalised and hence predicted (*26*), and a large amount of literature data is available on PET processes in



Scheme 1. Synthetic route to uranyl–salophen complexes **1** and **2**.

multicomponent molecular systems (*13*, *20*, *27–29*). This was also the idea behind the development of our systems: we thought that the presence of the anthracenyl fragments in the *ortho* position with respect to the phenolic oxygen, i.e. proximal to the incoming guest, could eventually maximise the fluorescence sensing response.

Unfortunately, despite the presence of the fluorescent units, both **1** and **2** resulted to be not luminescent both in chloroform solution at room temperature and in a solvent glass matrix at 77 K. Only a very weak fluorescence band at around 500 nm was detected and ascribed to a residual emission of the bound salophen ligand (*30*). We, therefore, decided to perform photochemical and electrochemical experiments in order to investigate the interplay between the various subunits of our systems, and eventually understand their luminescence.

We know from the work of Kunkler and Vogler (*17*) that the lack of fluorescence in simple uranyl–salophen complexes is due to the occurrence of a ligand-to-metal charge-transfer (LMCT) process involving lower energy salophen^{2-} states. They reported that an analogous intermolecular quenching mechanism can take place between uranyl salts and suitable electron donors present in solution (*31*). An intramolecular version of such an LMCT phenomenon may indeed happen also in our systems, which contain anthracenyl moieties potentially capable of playing the role of electron donors. To verify this hypothesis, we analysed the electrochemical behaviour of compounds **1** and **2** in chloroform solution. Cyclic voltammetry measurements showed that in both complexes, a quasi-reversible reduction process at -1.5 V versus ferrocene (Fc) occurs (Figure 2), while an irreversible oxidation process at potential higher than $+0.6$ V versus Fc is observed.

The reduction process found for **1** and **2** takes place at a potential value consistent with that reported in the literature for the one-electron reduction of the uranyl dication in salophen complexes (*32*). The process observed in the positive potential region is assigned to the monoelectronic oxidation of the anthracenyl units. These data, together with the energy of the first singlet excited state (S_1) of the anthracenyl chromophore, suggest that an intramolecular PET process from the anthracenyl S1 state to the metal centre may occur in our complexes (Equation (1)):

$$*\mathrm{Ant}(S_1) + U^{VI} - \mathrm{Sal} \rightarrow \mathrm{Ant}^{\cdot+} + U^{V} - \mathrm{Sal}. \quad (1)$$

The overall free energy change associated with the PET ($\Delta G^\circ_{\mathrm{PET}}$) can be estimated by Equation (2):

$$\Delta G^\circ_{\mathrm{PET}} \cong \left[E^\circ\left(\frac{D^+}{D}\right) - E^\circ\left(\frac{A}{A^-}\right)\right] - E_{0-0}, \quad (2)$$

in which $E^\circ(D^+/D)$ and $E^\circ(A/A^-)$ are the redox potentials for oxidation of the donor (anthracenyl unit) and reduction of the acceptor (uranyl–salophen moiety), respectively, and E_{0-0} is the energy of the excited state involved in the reaction (the S_1 level of the anthracenyl unit, about 3.3 eV) (*33*). On the basis of the redox potentials we have found, a $\Delta G^\circ_{\mathrm{PET}}$ value of *ca.* -1.2 eV can be estimated. Therefore, a PET process involving the anthracenyl pendant units and the metal centre is thermodynamically feasible, considering also the close proximity of these moieties, and PET is most likely the cause of the very efficient fluorescence quenching of the anthracene substituents in **1** and **2**. A further experimental evidence in support of the intramolecular quenching mechanism comes from the emission spectra of **1** and **2** recorded in $CHCl_3$ after the addition of a small amount of triflic acid which catalyses and promotes the hydrolysis of the imine bond. The rupture of the imine bond causes the detachment of the anthracenyl unit (as the corresponding salicylaldehyde) from the metal–salophen

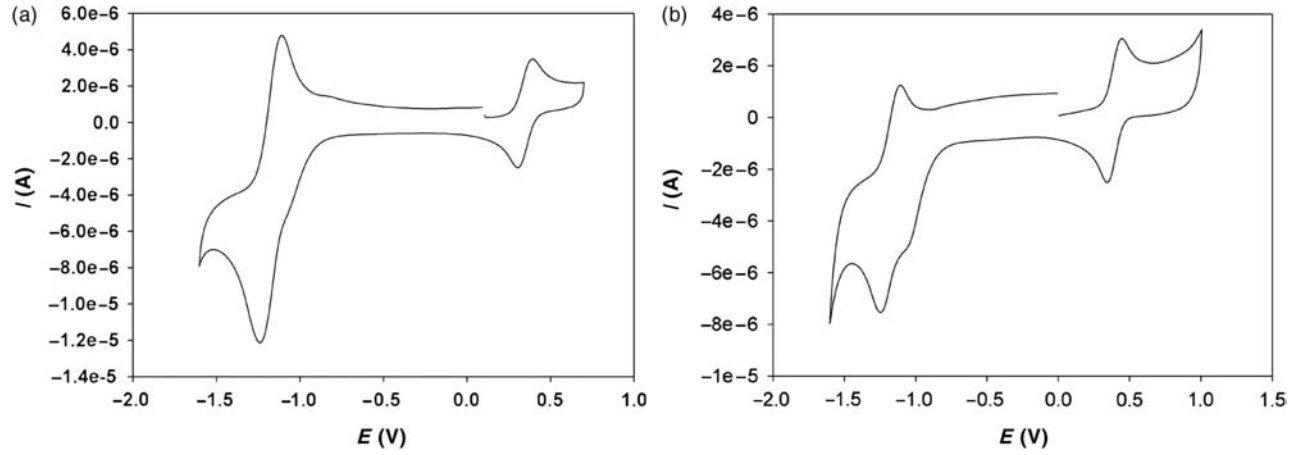


Figure 2. Cyclic voltammetric scans upon reduction of (a) **1** (6.8×10^{-4} M) and (b) **2** (5.3×10^{-4} M). Conditions: argon purged $CHCl_3$, 0.067 M tetrabutylammonium hexafluorophosphate, scan rate 200 mV/s. The wave at around $+0.4$ V is that of Fc used as an internal standard.

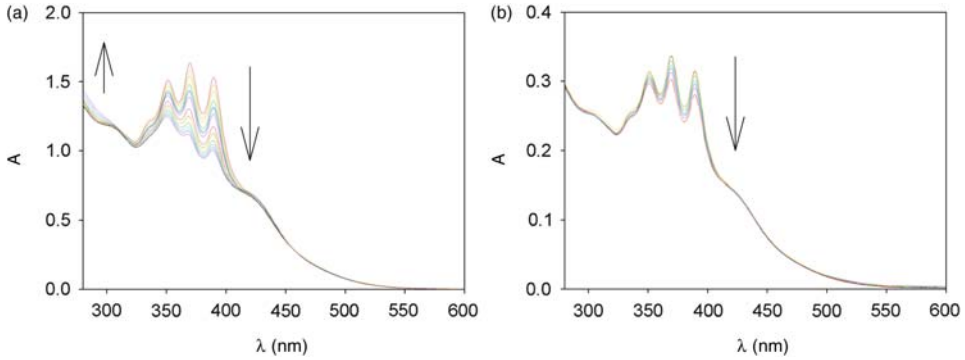


Figure 3. Absorption spectral changes observed upon exhaustive UV irradiation of (a) **2** (5.6×10^{-5} M) in air-equilibrated $CHCl_3$ (left; total irradiation time, 220 min) and of (b) **2** (1.1×10^{-5} M) in carefully deoxygenated $CHCl_3$ (right; total irradiation time, 90 min).

moiety, resulting in the appearance of the typical structured fluorescence band of anthracene.

It is well known that anthracene derivatives undergo photochemical reactions upon UV (S_1) excitation (*34*, *35*). Specifically, UV irradiation in solution in the presence of oxygen affords oxidation products (usually, the bridged 1,10-endoperoxide) because singlet oxygen produced by photosensitisation from the lowest triplet state of anthracene reacts with the anthracene itself. Conversely, in oxygen-free solutions photooxidation reactions are prevented and, if the anthracene concentration is high enough, photodimerisation can take place via the S_1 state (*34*, *35*). Both photooxidation and photodimerisation reactions cause a decrease in the structured absorption band between 300 and 400 nm region, as a result of the disruption of the anthracene aromatic system.

The above experiments indicate that in our complexes the anthracene S_1 state is strongly quenched; to investigate whether this excited state can still evolve along a reactive path, we subjected solutions of **1** and **2** to UV irradiation in the presence and absence of oxygen. Chloroform solutions of **2** in the concentration range of 10^{-5} M were irradiated using a cut-off filter at 350 nm, under continuous stirring, both in aerated and disaerated conditions; the corresponding UV–vis absorption changes are reported in Figure 3.

The loss of the structured absorption band in the 300–400 nm region observed upon irradiation of an air-equilibrated solution indicates that **2** undergoes the anthracene photooxidation reaction. Qualitatively similar spectral changes were detected also upon irradiation of **2** in an oxygen-free solution. Since the oxidation reaction cannot occur under these conditions, the disappearance of the anthracene absorption band has to be ascribed to a photodimerisation process. Intermolecular dimerisation, however, can be ruled out because of the short lifetime of the S_1 excited state (a few nanoseconds for anthracene, but in our case it may be much shorter because of the PET quenching process) and the low concentration of the compound. Therefore, we believe that UV irradiation of **2** in the absence of oxygen causes the intramolecular dimerisation of the two anthracenyl pendant units. To confirm this hypothesis, similar irradiation experiments were performed with complex **1** that has only one anthracenyl pendant unit. The corresponding absorption changes (Figure 4) indicate that for this compound, the decrease in the anthracene absorption band takes place only in an air-equilibrated solution because of the photooxidation process. No absorption changes could be detected upon irradiation of **1** in oxygen-free solution even after 50 min of continuous irradiations, suggesting that anthracene photodimerisation

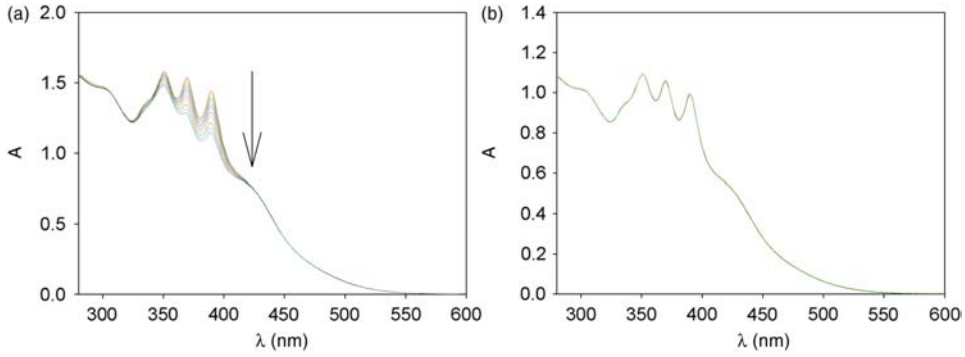


Figure 4. Absorption spectral changes observed upon exhaustive UV irradiation of (a) **1** (7.1×10^{-5} M) in air-equilibrated $CHCl_3$ (left; total irradiation time, 300 min) and of (b) **1** (4.7×10^{-5} M) in carefully deoxygenated $CHCl_3$ (right; total irradiation time, 50 min).

does not occur. These observations strongly indicate that the photoreaction observed for compound **2** in deoxygenated conditions is in fact the intramolecular dimerisation of the two anthracenyl units.

Conclusions

We have described the synthesis of two new uranyl–salophen complexes, **1** and **2**, bearing, respectively, one and two anthracenyl units appended to the ligand skeleton. The absence of fluorescence emission in the two derivatives, despite the presence of the anthracenyl fluorophore, is most likely due to a PET process from the lowest singlet excited state of the anthracenyl unit to the metal centre. The redox potentials measured for **1** and **2** by cyclic voltammetry are indeed in agreement with such an interpretation. Although the anthracenyl unit in the investigated complexes is strongly quenched by PET, it is still capable of exhibiting the typical light-induced reactions of anthracene in solution, namely photo-oxidation and photodimerisation. Both **1** and **2** undergo photo-oxidation when irradiated in the UV in an air-equilibrated solution, whereas only **2**, which bears two anthracenyl units, is photoreactive upon UV irradiation in the absence of oxygen. We therefore inferred that such a photoreaction is the intramolecular dimerisation of the two anthracenyl units, which is obviously impossible in compound **1**. In principle, such a process could be used as a tool to control the access of guests to the free coordination site on the uranyl moiety. Further studies in this direction are underway in our laboratories.

Experimental

General methods and materials

^{1}H NMR spectra were recorded on a Bruker AC-200 and AC-300 MHz. High-resolution mass spectra (HR-MS) were performed by an ESI-TOF spectrometer. Salicylaldehyde, 2-methoxyphenylboronic acid, 9-bromoanthracene, EtMgBr solution in hexane and the BBr_3 solution in CH_2Cl_2 were purchased from Aldrich Co. (Milan, Italy) Anhydrous $MgCl_2$ and K_2CO_3 were obtained by Fluka Co (Milan, Italy). Other reagents were of analytical grade and were used without further purification. Solvents and solutions used in the Suzuki coupling have been degassed for 30 min by Argon bubbling.

Cyclic voltammetry

Cyclic voltammetric experiments were performed with an Autolab 30 multipurpose equipment interfaced to a PC, using a three electrode cell composed of a glassy carbon working electrode, a platinum spiral counter electrode and a pseudo-reference silver electrode. Spectrophotometric grade chloroform, deoxygenated by argon bubbling, was employed as the solvent, and the sample concentration was on the order of 5×10^{-4} M, and tetrabutylammonium hexafluorophosphate (0.067 M) was the supporting electrolyte. The reversible oxidation wave of Fc ($E_{1/2} = +0.51$ V versus SCE) (*36*) was employed as an internal reference for the potential measurements.

Photochemical reactions

Photochemical reactions were performed by irradiation with a Xenon lamp projector using a cut-off filter at 350 nm. Deoxygenation was performed by five freeze–pump–thaw cycles. The reactions were monitored by UV–vis absorption spectrophotometry using a Perkin-Elmer λ18 spectrophotometer.

*9-(2′-Methoxyphenyl)anthracene (**3**)*. Under argon atmosphere, a solution of 9-bromoanthracene (3.00 g, 11.7 mmol) and $Pd(PPh_3)_4$ (130 mg, 0.117 mmol) in 40 ml of toluene was added to a solution of 2-methoxyphenylboronic acid (2.13 g, 11.4 mmol) in 35 ml of ethanol absolute followed by addition of K_2CO_3 (2.40 g, 17.4 mmol). The mixture was stirred and heated to reflux for 20 h under inert atmosphere, and then allowed to cool to room temperature. Then 90 ml of 0.5 M NaOH solution was added to the reaction mixture, which was extracted with CH_2Cl_2 (two portions of 90 ml). The organic phases were combined, dried over anhydrous $MgSO_4$ and filtered. After flash chromatographic purification on a silica gel (petroleum ether 40–70°C: CH_2Cl_2, 9:1), 3.55 g of product was obtained as an off-white solid. Yield 76%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.47 (s, 1H), 8.02 (d, 2H, $J = 8.4$ Hz), 7.61–7.49 (m, 3H), 7.46–7.43 (m, 2H), 7.42–7.29 (m, 2H), 7.15 (t, 2H, $J = 8.4$ Hz), 3.60 (s, 3H).

*9-(2′-Hydroxyphenyl)anthracene (**4**)*. Under argon atmosphere in a dry flask, a solution of BBr_3 (1.0 M in CH_2Cl_2) (18 ml, 18 mmol) was added dropwise over a period of 20 min to a stirring solution of **3** (1.05 g, 3.68 mmol) dissolved in 50 ml of CH_2Cl_2 and cooled in an ice bath. Once the addition was complete, the mixture was stirred for an additional hour at room temperature. While cooling with an ice bath, the reaction was quenched with 100 ml of H_2O, and the mixture was extracted with two portions of 50 ml of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to give the crude product. After recrystallisation from hot toluene, 0.890 g of yellow crystals was obtained with a yield of 94%. GC–MS *m/z* (+) 270 (M, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.62 (s, 1H), 8.75 (d, 2H, $J = 8.4$ Hz), 7.68–7.65 (m, 2H), 7.52–7.37 (m, 6H), 7.18–7.01 (m, 2H), 4.53 (s, 1H).

*3-(Anthracen-9-yl)-2-hydroxybenzaldehyde (**5**)*. In a two-necked flask, previously flamed under flux of argon, 6 ml of dry tetrahydrofuran (THF) freshly distilled on sodium and phenol **4** (234 mg, 0.856 mmol) was added. Then EtMgBr (0.285 ml, 0.856 mmol) was slowly added. The mixture was stirred for 45 min and then paraformaldehyde (570 mg, 18.98 mmol) and anhydrous $MgCl_2$ (187 mg, 1.96 mmol) were added. The reaction mixture was stirred at 75°C for 4 h. Then, AcOEt (50 ml) was added to the mixture and the organic phase was washed with three portions of 1 M (40 ml) HCl. The organic phase was then washed once with saturated NaCl solution and twice with portions of 50 ml of water. The organic phase was dried over anhydrous Na_2SO_4. The crude product was purified by chromatographic column on flash silica gel ($CHCl_3$:petroleum ether (40–70°C), 4:6). One hundred and nineteen milligrams of pure product as bright yellow solid have been obtained with a yield of 46%. GC–MS *m/z* (+) 298 (M, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.15 (s, 1H), 10.07 (s, 1H), 8.54 (s, 1H), 8.06 (dd, 2H, $J = 6$ Hz, $J = 1.8$ Hz), 7.78 (dd, 1H, $J = 7.8$ Hz, $J = 1.8$ Hz), 7.62–7.56 (m, 3 H), 7.50–7.20 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.39, 140.00, 133.59, 131.16, 130.02, 128.39, 127.21, 125.75, 125.51, 124.89, 119.62 ppm. MS-ESI-TOF for $C_{21}H_{14}NaO_2$ calcd 321.0886, found 321.0877 *m/z* $^+$.

*Complexes **1** and **2***. 0.450 g (1.51 mmol) of aldehyde **5** was dissolved in 20 ml of MeOH absolute. The mixture was stirred and refluxed until dissolution of the solid, then salicylaldehyde (158 µl, 1.51 mmol) and, after 2 min, 1,2-diaminobenzene (0.158 g, 1.46 mmol) was added and the solution was stirred for 20 min. After this, uranyl acetate dihydrate (0.725 g, 1.71 mmol) was added. The reaction mixture was then stirred and refluxed for 1 h 30 min. After cooling at room temperature, the precipitated red solid was filtered and then purified by chromatographic column in flash silica gel using $CHCl_3$ as eluent. From the column, two fractions were collected containing, respectively, complexes **1** and **2**. Addition of acetone resulted in the precipitation of the compounds that were isolated as orange powders. Yields 27% (**1**) and 10% (**2**).

*Complex **1***. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.53 (s, 1H), 9.38 (s, 1H), 8.45 (s, 1H), 8.07 (d, 2H, $J = 8.4$ Hz), 7.90–7.78 (m, 3H), 7.70–7.50 (m, 5H), 7.38 (dd, 3H, $J = 7.2$ Hz), 7.2–7.1 (m, 2H), 7.17 (t, 1H, $J = 1.2$ Hz), 6.98 (d, 1H, $J = 1.2$ Hz), 6.81 (t, 1H, 1.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.72, 165.63, 138, 136.25, 135.46, 135.08, 131.14, 130.38, 128.84, 138.73, 128.22, 126.98, 126.32, 125.25, 124.96, 121.17, 119.55, 117.96, 117.52 ppm. MS-ESI-TOF for $C_{34}H_{22}N_2O_4NaU$ calcd 783.1985, found 783.1967 *m/z* $^+$.

*Complex **2***. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.49 (s, 2H), 8.43 (s, 2H), 8.01 (d, 4H, $J = 8.7$ Hz), 7.83–7.79 (m, 3H), 7.70 (d, 4H, $J = 1.8$ Hz), 7.70–7.53 (m, 4H), 7.53–7.39 (m, 6H), 7.13–6.93 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 165.47, 138.89, 135.42, 131.04, 130.28, 128.69, 128.04, 127.01, 126.10, 125.00, 124.97, 124.05, 119.54, 117.43 ppm. MS-ESI-TOF for $C_{48}H_{30}N_2O_4NaU$ calcd 959.2611, found 959.2617 *m/z* $^+$.

Acknowledgement

We thank the Ministero dell'Istruzione, Università e Ricerca (PRIN 2008), for financial support.

References

(1) Schiff, H. *Liebigs. Ann. Chem. Suppl.* **1864**, *3*, 343–345.
(2) Cozzi, P.G. *Chem. Soc. Rev.* **2004**, *33*, 410–421.
(3) Campbell, N.H.; Abd Karim, N.H.; Parkinson, G.N.; Gunaratnam, M.; Petrucci, V.; Todd, A.K.; Vilar, R.; Neidle, S. *J. Med. Chem.* **2012**, *55*, 209–222.
(4) Hille, A.; Ott, I.; Kitanovic, A.; Kitanovic, I.; Alborzinia, H.; Lederer, E.; Wölfl, S.; Metzler-Nolte, N.; Schäfer, S.; Sheldrick, W.S.; Bischof, C.; Schatzschneider, U.; Gust, R. *J. Bio. Inorg. Chem.* **2009**, *14*, 711–725.
(5) Hui, J.K.H.; Zhen, J.; MacLachlan, M.J. *Angew. Chem. Int. Ed.* **2007**, *46*, 7980–7983.
(6) Dalla Cort, A. In *In Ion-Pair Receptors in Supramolecular Chemistry: From Molecules to Nanomaterials*. Steed, J.W., Gale, P.A., Eds.; Wiley: Chichester, 2012; pp. 1281–1308.
(7) Dalla Cort, A.; De Bernardin, P.; Forte, G.; Yafteh Mihan, F. *Chem. Soc. Rev.* **2010**, *39*, 3863–3874.
(8) Di Bella, S. *Chem. Soc. Rev.* **2001**, *30*, 355–366.
(9) Engbersen, J.F.; Harkema, S.; Reinhoudt, D.N. *J. Am. Chem. Soc.* **1992**, *114*, 9671–9673.
(10) Van Axel Castelli, V.; Dalla Cort, A.; Mandolini, L.; Pinto, V.; Reinhoudt, D.N.; Ribaudo, F.; Sanna, C.; Schiaffino, L.; Snellink-Ruël, B.H.M. *Supramol. Chem.* **2002**, *14*, 211–219.
(11) Cametti, M.; Nissinen, M.; Dalla Cort, A.; Mandolini, L.; Rissanen, K. *J. Am. Chem. Soc.* **2007**, *129*, 3641–3648.
(12) Dalla Cort, A.; Forte, G.; Schiaffino, L. *J. Org. Chem.* **2011**, *76*, 7569–7572.
(13) de Silva, A.P.; Gunaratne, H.Q.N.; Gunnlaugsson, T.; Huxley, A.J.M.; McCoy, C.P.; Rademacher, J.T.; Rice, T.E. *Chem. Rev.* **1997**, *97*, 1515–1566.
(14) Prodi, L. *New J. Chem.* **2005**, *29*, 20–31.
(15) Credi, A. *New J. Chem.* **2012**, *36*, 1925–1930.
(16) Zapata, F.; Caballero, A.; White, N.G.; Claridge, T.D.W.; Costa, P.J.; Felix, V.; Beer, P.D. *J. Am. Chem. Soc.* **2012**, *134*, 11533–11541; Sun, S.-S.; Lees, A.J. *Coord. Chem. Rev.* **2002**, *230*, 171–192; Raad, F.S.; El-Ballouli A.O.; Moustafa, R.M.; Al-Sayah, M.H.; Kaafarani, B.R. *Tetrahedron* **2010**, *66*, 2944–2952.
(17) Kunkler, H.; Vogler, A. *Verlag Z. Naturforsh.* **2002**, *57b*, 301–304.
(18) Flegel, M.; Lukeman, M.; Huck, L.; Wan, P. *J. Am. Chem. Soc.* **2004**, *126*, 7890–7897.
(19) Hofsølkken, N.; Skattebøl, L. *Acta Chem. Scand.* **1999**, *53*, 258–262.
(20) Fabbrizzi, L.; Marcotte, N.; Stomeo, F.; Taglietti, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 3811–3814.

(21) Beer, P.D. *Acc. Chem. Res.* **1998**, *31*, 71–80.
(22) Gale, P.A.; Anzenbacher, Jr, P.; Sessler, J.L. *Coord. Chem. Rev.* **2001**, *222*, 57–102.
(23) Leung, K.C.-F.; Nguyen, T.D.; Stoddart, J.F.; Zink, J.I. *Chem. Mater.* **2006**, *18*, 5919–5928.
(24) Zhao, S.-B.; McCormick, T.; Wang, S. *Inorg. Chem.* **2007**, *46*, 10965–10967.
(25) Jiasheng, W.; Weimin, L.; Jiechao, G.; Hongyan, Z.; Pengfei, W. *Chem. Soc. Rev.* **2011**, *40*, 3483–3495.
(26) Balzani, V., Ed. *Electron Transfer in Chemistry*; Wiley-VCH: Weinheim, 2001.
(27) Fabbrizzi, L.; Gatti, F.; Pallavicini, P.; Parodi, L. *New J. Chem.* **1998**, *22*, 1403–1407.
(28) Magri, D.C.; Brown, G.J.; McClean, G.D.; de Silva, A.P. *J. Am. Chem. Soc.* **2006**, *128*, 4950–4951.
(29) de Silva, A.P.; Moody, T.S.; Wright, G.D. *Analyst* **2009**, *134*, 2385–2393.
(30) Shen, Y.Z.; Pan, Y.; Wang, L.Y.; Dong, G.; Jin, X.P.; Huang, X.Y.; Hu, H. *J. Organomet. Chem.* **1999**, *590*, 242–247.
(31) Burrow, H.D.; Kemp, T.J. *Chem. Soc. Rev.* **1974**, *3*, 139–165; Azenha, E.M.D.G.; Burrows, H.D.; Fermosinho, S.J.; Miguel, Maria de Graça M. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2625–2634.
(32) Nocton, G.; Horeglad, P.; Vetere, V.; Pe'caut. J.; Dubois, L.; Maldivi, P.; Eldstein, N.M. *J. Am. Chem. Soc.* **2010**, *132*, 495–508; Hardwick, H.C.; Royal, D.S.; Helliwell, M.; Pope, S.J.A.; Ashton, L.; Goodacre, R.; Sharrad, C.A. *Dalton Trans.* **2011**, *40*, 5939–5952.
(33) Gilbert, A.; Baggott, J. In *Essentials of Molecular Photochemistry*; Blackwell Science Ltd: Oxford, 1991; p 161.
(34) Turro, N.; Scaiano, J.C.; Ramamurthy, V. *Modern Molecular Photochemistry of Organic Molecules*; University Science Books: Herndon, VA, 2008.
(35) (a) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2000**, *29*, 43–55; (b) Bouas-Laurent, H.; Castellain, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2001**, *30*, 248–263.
(36) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M.T.; Kadish, K.M. *J. Phys. Chem.* **1992**, *96*, 7137–7145.