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Photochromic crowned spirobenzopyrans: Quantitative metal-ion chelation by UV, competitive selective ion-extraction and metal-ion transportation demonstration studies

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Abstract

Following our publication of the synthesis of the new 5-substituted crowned spirocyclic benzopyrans (**3a**–**c**), and the fact that suitably placed substituents can be used to influence their metal-ion chelating properties [Roxburgh, CJ, Sammes, PG. Dyes Pigments 1995;28:317.], we now report the results of an extensive quantitative study to demonstrate that these systems selectively and photoreversibly chelate a variety of metal-ions *i.e.* Li^+, Na^+, Ca^{2+}, Ba^{2+}, and Mg^{2+}. Experiments were conducted at seven different spiropyran concentrations, for each of the three crowned spiropyrans, and with the five different metal-ions (above). The 5-trifluoromethyl-substituted system produced the most pronounced effects and was thus chosen as the best system for further selective investigations which include: (1) competitive relative selective metal-ion chelating capability – investigated by devising a 'matrix' series of experiments, in order to ascertain which metal-ions, under dual competition (two metal-ions simultaneously present) were relatively more chelated (a priority order for the relative selectivity was consequently deduced), and (2) a system and experiments were devised to demonstrate that metal-ions could reversibly, under photodynamic control, be transported across a barrier (an immiscible layer of 1,2-dichloroethane and water: metal-ion concentrations were measured before and after photoirradiations using inductively coupled plasma mass spectrophotometry (ICP-MS) a powerful and accurate analytical technique for the quantification of metal-ions) to establish the levels of transportation.
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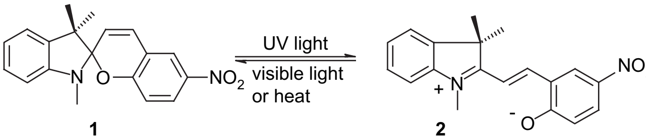
Keywords: Crowned spirobenzopyrans; Synthesis; Photoreversible; Chelation; Metal-ion

1. Introduction

There is ongoing interest in the development of reversible metal-chelating agents in which chelation can be switched on and off by exposure to light of different wavelengths [2]. Several groups have made contributions to this area [3]. A popular substrate for such studies is the 6-nitrospiro[1-benzopyran-2,2′-indole] system **1** and its analogues since these have well-documented photochemical properties [4]. Photoirradiation with UV light at 380 nm leads to the ring opened zwitterionic (merocyanine) form **2**, which can be converted back to the ring closed form either by photoirradiation with visible light or thermally. This process may be repeated many times and has formed the basis of light-induced ionic switches. The reversible chelation of specific metal-ions has been reported in several other systems by Kimura [5–8].



2. Results and discussion

Some time ago we reported the synthesis of the new substituted crowned spirocyclic systems **3b** (R = CF_3), **3c**

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Table 1

Measured UV absorbances at the ratios of crowned spiropyran (**3a**, R = —H)/metal-ions, and overall concentrations

Ratio, spiropyran/metal (**3a**)	Overall concentration (M)	No metal (535 nm)			Li^+ (510 nm)			Na^+ (540 nm)			Ca^{2+} (530 nm)			Ba^{2+} (540 nm)			Mg^{2+} (520 nm)		
		Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]
1:25 000	0.25		—		0.1	0.3	0.2	0.2	0.3	0.2	0.15	0.2	0.15	0.2	0.3	0.2	0.15	0.2	0.15
1:15 000	0.15		—		0.2	0.25	0.25	0.15	0.2	0.15	0.15	0.2	0.15	0.15	0.2	0.15	0.15	0.2	0.15
1:5000	0.05		—		0.15	0.25	0.2	0.15	0.2	0.15	0.15	0.2	0.15	0.15	0.2	0.15	0.15	0.2	0.15
1:2500	0.025		—		0.15	0.175	0.2	0.15	0.2	0.15	0.15	0.2	0.15	0.15	0.2	0.15	0.15	0.2	0.15
1:250	0.0025		—		0.15	0.15	0.25	0.15	0.2	0.15	0.15	0.2	0.15	0.15	0.2	0.15	0.15	0.2	0.15
1:50	0.0005		—		0.2	0.3	0.35	0.15	0.2	0.15	0.15	0.20	0.15	0.15	0.2	0.15	0.15	0.2	0.15
1:0	0.0	0.1	0.175	0.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

[a] Absorbance unit values obtained from UV spectra (in absorbance units) for 2×10^{-5} M solution in acetonitrile at room temperature.

[b] Absorbance unit values after irradiating with UV for 1 min — see Section 3 for details.

[c] Absorbance unit values after exposure of UV irradiated solution to visible light for 3 min — see Section 3 for details.

Table 2

Measured UV absorbances at the ratios of crowned spiropyran (**3b**, R = —CF_3)/metal-ions, and overall concentrations

Ratio, spiropyran/metal (**3b**)	Overall concentration (M)	No metal (535 nm)			Li^+ (510 nm)			Na^+ (540 nm)			Ca^{2+} (530 nm)			Ba^{2+} (540 nm)			Mg^{2+} (520 nm)		
		Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]
1:25 000	0.25		—		0.6	0.8	0.1	0.2	0.6	0.1	0.7	1.9	1.6	0.7	1.7	0.4	0.3	2.3	0.1
1:15 000	0.15		—		0.6	0.8	0.1	0.25	0.5	0.1	0.8	2.0	1.5	0.8	1.0	0.4	0.3	0.9	0.1
1:5000	0.05		—		0.5	0.8	0.1	0.2	0.45	0.1	0.8	2.0	1.2	0.6	0.8	0.5	0.4	0.8	0.1
1:2500	0.025		—		0.5	0.7	0.1	0.25	0.4	0.1	0.7	2.0	0.8	0.6	0.8	0.5	0.4	0.7	0.1
1:250	0.0025		—		0.3	0.8	0.1	0.2	0.4	0.1	0.6	1.9	0.8	0.4	0.8	0.1	0.4	0.5	0.1
1:50	0.0005		—		0.3	0.7	0.1	0.2	0.4	0.1	0.7	1.8	0.7	0.2	0.6	0.15	0.4	0.5	0.1
1:0	0.0	<0.01	0.15	<0.01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

[a] Absorbance unit values obtained from UV spectra (in absorbance units) for 2×10^{-5} M solution in acetonitrile at room temperature.

[b] Absorbance unit values after irradiating with UV for 1 min — see Section 3 for details.

[c] Absorbance unit values after exposure of UV irradiated solution to visible light for 3 min — see Section 3 for details.

($R = NO_2$) and **3a** ($R = H$), the latter also being reported by Kimura [5a], together with a qualitative description of their selective metal-ion binding capabilities [1]. Simultaneously, we reported [1] the demonstration that the use of suitably placed, electronically modifying substituents, and groups, could be used to exert a strong influence over the photoreversible selective metal-ion binding capabilities of these systems.

Further to these studies, and as indicated in our previous publication [1], we now report detailed quantitative results for these systems' ability to photoreversibly and selectively chelate a variety of ions *i.e.* Li^+, Na^+, Ca^{2+}, Ba^{2+} and Mg^{2+}. Experiments have been conducted for each of the crowned spirobenzopyrans, at seven different concentration ratios (crowned spiropyran/metal-ion) with each of the five metal-ions (above), and with a blank (no metal present) as a comparative reference for each system.

The results for the unsubstituted crowned spirobenzopyran further support our original qualitative result, and that of Kimura, and in particular, highly photoreversible states are reached in the presence of metal-ions.

The quantitative photochromic studies were principally carried out in aprotic solvents using the metal perchlorates of Li^+, Na^+, Ca^{2+}, Ba^{2+} and Mg^{2+}, measuring the position of equilibrium by UV spectroscopy. The quantitative results are given later in Tables 1–3. Freshly prepared solutions of the reagents (2×10^{-5} M) were examined after adding the metal salt and allowing equilibration in the dark for 1 h. The solutions were then exposed to first, ultraviolet light (using a focused 200-W high pressure mercury xenon light source filtered to emit light in the region 330–420 nm) for 1 min, remeasuring the UV spectrum, and then exposing the solution to visible light (high intensity 100-W tungsten spotlight for 3 min) and remeasuring the UV spectrum. The solutions were subjected to the above 'photoirradiation-cycle' three times in order to ascertain the reproducibility and photochemical robustness of the systems.

With the unsubstituted crowned spiropyran **3a**, in acetonitrile solvent, addition of Li^+ (15×, 0.15 M) caused an immediate shift to the open form (*ca.* 50%); further addition of Li^+ did not affect the equilibrium. Whilst irradiating with UV light caused a moderate increase in the amount of open form present (Table 1), irradiation with visible light only effected a small shift to the 'dark' equilibrium position, a considerable amount of the open form remaining (Fig. 1, spectra 3).

It was argued that the presence of an electron-withdrawing group *para* to the indolic nitrogen atom, at position 5′ as in **3b** and **3c**, would counteract this tendency for ring opening.

In the absence of M^+ cations, spiropyran **3c** showed virtually no photochromic behaviour (Table 3). Upon addition of M^+ ions, only a very small shift to the coloured form occurred, but photochromic behaviour was observed with the formation of the coloured merocyanine isomer together with concomitant chelation to the aza-crown. The effect of M^+ ions could be ascertained by titration, and subsequent exposure to UV light, little effect being observed until M^+ concentration exceeded 10^{-2} M.

The trifluoromethyl derivative **3b** exhibited photochromic properties, similar to, but less pronounced to those of **3c**. In the absence of cations it showed a partial tendency to open

Table 3
Measured UV absorbances at the ratios of crowned spiropyran (**3c**, $R = NO_2$)/metal-ions, and overall concentrations

Ratio spiropyran/metal (**3c**)	Overall concentration (M)	No metal (535 nm)			Li^+ (510 nm)			Na^+ (540 nm)			Ca^{2+} (530 nm)			Ba^{2+} (540 nm)			Mg^{2+} (520 nm)		
		Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]	Dark[a]	UV[b]	Vis[c]
1:25 000	0.25		–		0.05	0.2	0.05	<0.1	<0.2	<0.1	0.3	0.45	0.2	0.2	0.35	0.15	0.2	0.4	0.15
1:15 000	0.15		–		0.05	0.2	0.05	0.1	0.2	0.1	0.1	0.4	<0.1	0.15	0.35	0.1	0.2	0.3	0.25
1:5000	0.05		–		0.05	0.2	0.05	0.1	0.2	0.1	0.1	0.3	<0.1	0.1	0.35	0.1	0.15	0.2	0.15
1:2500	0.025		–		0.05	0.2	0.05	0.1	0.2	0.1	0.1	0.2	0.15	0.1	0.2	0.1	0.15	0.2	0.1
1:250	0.0025		–		0.05	0.15	0.05	0.1	0.2	0.1	0.1	0.2	0.15	0.1	0.2	0.1	0.1	0.2	0.1
1:50	0.0005		–		0.05	0.1	0.05	0.1	0.15	0.1	0.1	0.2	0.15	0.1	0.2	0.15	0.1	0.2	0.1
1:0	0.0	0.05	0.1	<0.01	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

[a] Absorbance unit values obtained from UV spectra (in absorbance units) for 2×10^{-5} M solution in acetonitrile at room temperature.

[b] Absorbance unit values after irradiating with UV for 1 min – see Section 3 for details.

[c] Absorbance unit values after exposure of UV irradiated solution to visible light for 3 min – see Section 3 for details.

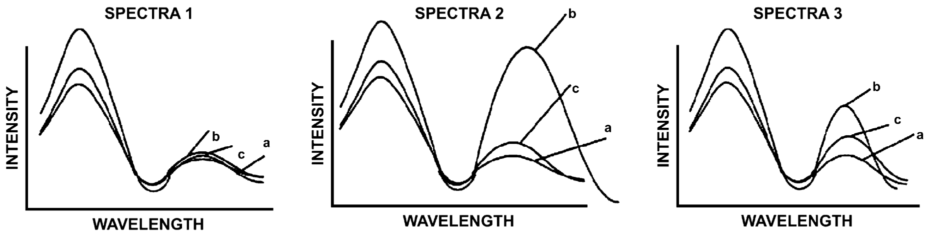


Fig. 1. Effect of varying [M^+] on the photochromic behaviour of **3a**–**c**. All curves after irradiating with light of $\lambda_{max} < 400$ nm; on irradiating at 580 nm colour is lost as reversion to closed form occurred. The photochromic cycle could be repeated. Conc 2×10^{-5} M, molar ratios of $M^+ClO_4^-$ for curve a 50:1; b 250:1; c 25 000:1; d 5000:1; e 15 000:1; f 25 000:1 (maximal effect). In acetonitrile solutions (where $M^+ = Li^+$, Na^+, Ca^{2+}, Ba^{2+} and Mg^{2+}).

(see Table 2) but either thermally, or in the presence of light reversed to give the closed spirocyclic form. Addition of Li^+ caused a larger shift to the open form than that observed with **3c** (Table 3) although the equilibrium could be shifted in either direction by exposure to UV or visible light.

Some important trends and observations were noted using the cations Li^+, Na^+, Ca^{2+}, Ba^{2+} and Mg^{2+}. For the systems **3a**–**c** relatively smaller perturbations in the equilibrium position were observed using the monovalent cations Li^+ and Na^+ (Fig. 1, spectra 3). However, large changes in the equilibrium positions of **3b** were induced by divalent cations such as Ba^{2+}, Ca^{2+} and Mg^{2+} (Fig. 1, spectra 2). In particular, these divalent cations converted the compounds **3a**–**c** into photochemically reversible systems; whose effects were studied further in order to develop cleaner, or more clearly defined, 'on–off' switchable ion-chelating systems, as against the more partial effects previously described (see Fig. 1, spectra 3).

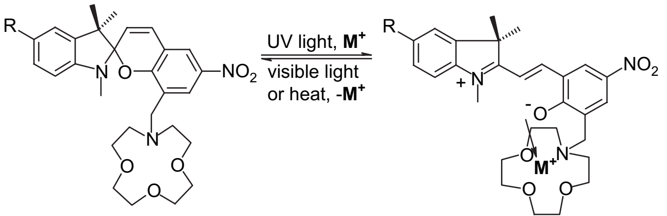
The spectral cycle (the UV/vis behaviour) for the crowned spiro system **3b** is given in spectra 1–3, in the absence and presence of metal.

- Spectra 1: no metal; little formation of the open form present.
- Spectra 2: typical results for Ba^{2+} (similar results with Ca^{2+}, Mg^{2+}); photoreversibility observed.
- Spectra 3: typical results for Li^+ (similar results with Na^+); photoreversibility observed.

Lastly, the system **3b** was examined in an aqueous acetonitrile mixture (1:1) in order to ascertain its behaviour in a water-based medium. Results showed that it was still possible to obtain about 40% of the merocyanine that formed in purely organic solvents, as might be predicted, and, importantly the system retained its photoreversible capability. This is an important result and potentially opens up the use of these compounds in aqueous-based media, and thus as possible cellular metal-ion probes.

In summary, the results obtained for compound **3a** support the excellent work of Kimura et al. However, compounds **3b** and **3c** demonstrate greater photochromic effects (due to the 5-*para* electron-withdrawing substituents in the indolic-ring), with the biasing of the spiropyran ↔ merocyanine equilibrium, in the presence of metal-ions, towards the spiropyran (closed form), allowing metal-ions to compensate this effect. The above changes can only be explained by interaction with M^+ ions.

These systems therefore present a further step towards a true 'on–off' switchable photoreversible ion-chelating system.



3a R= H
3b R= CF_3
3c R= NO_2

4a R= H
4b R= CF_3
4c R= NO_2

The overall effect, with various ratios of metal-ion/crowned spirobenzopyran concentration, is shown in the UV spectrum depicted in Fig. 2. A clear trend of increasing λ_{max} with metal-ion concentration, after photoirradiation, can be seen with a ratio of 25 000:1 producing maximal effect, as expected.

2.1. Relative competitive selective metal-ion extractions of the trifluoromethyl-substituted crowned benzospiropyran

A series of experiments were conducted in which equimolar concentrations (2×10^{-5} M) of a mixture of two different

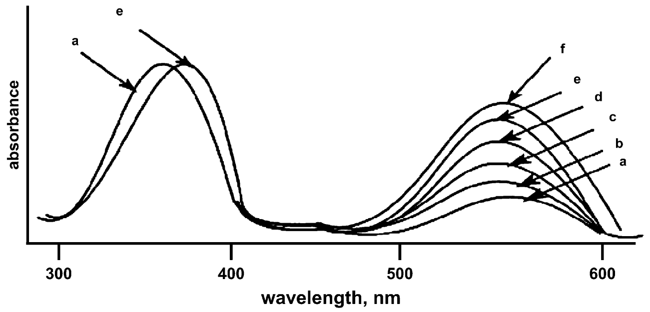


Fig. 2. Effect of varying [M^+] on the photochromic behaviour of **3b**. All curves after irradiating with light of $\lambda_{max} < 400$ nm (on irradiating at 580 nm colour is lost as reversion to closed form occurred). The photochromic cycle could be repeated several times. Conc 2×10^{-5} M, molar ratios of $M^+ClO_4^-$ for curve a, 50:1; b, 250:1; c, 25 000:1; d, 5000:1; e, 15 000:1; f, 25 000:1 (maximal effect). In acetonitrile solutions (where $M^+ = Ba^{2+}$).

metal-ions were simultaneously mixed with the crowned benzospiropyran **3b** (conc 2×10^{-5} M), photoirradiated and the resultant UV absorbance spectra recorded. (Note: the 5-trifuoromethyl substituted crowned spirobenzopyran was chosen as it was previously found to produce the largest spectral changes in UV λ_{max} values.) A quantitative determination of the relative chelation of the metal-ions was then made by measurement of the λ_{max} absorption peaks. Further competition experiments were conducted according to the 'matrix' given in Table 4.

From Table 5 it can be deduced that the relative priority order for the competitive selective chelation of metal-ions by the trifluoromethyl-substituted crowned benzospiropyran **3b** is as follows:

$$Mg^{2+} > Ca^{2+} > Li^{+} > Ba^{2+} > Na^{+}$$

Although it is possible to ascertain this relative priority order of selective chelation, the biasing of the equilibrium in these systems is probably multifactorial and likely to involve a complex set of interactions that are influenced by the following parameters: (1) the type and nature of the substituent at the 5-position, (2) the crown, (3) the size of the metal-ion, (4) the charge density of the metal-ion, (5) the distribution of charge throughout the zwitterionic structure (in particular that on the phenoxide-ion), (6) solvent interactions and (7) the conformation of the overall system in solution. Thus, a detailed explanation of why, under competitive ion-chelation, the priority order we have ascertained is such, is outside the scope of this paper. (Note: detailed theoretical studies of the electronic and stereochemical parameters may help to clarify this difficult and challenging problem.)

Table 4
Metal-ion selectivity experiments

Metal-ion	Mg^{2+}	Ba^{2+}	Na^{+}	Li^{+}	Ca^{2+}
Mg^{2+}	X	MgBa	MgNa	MgLi	MgCa
Ba^{2+}	X	X	BaNa	BaLi	BaCa
Na^{+}	X	X	X	NaLi	NaCa
Li^{+}	X	X	X	X	LiCa
Ca^{2+}	X	X	X	X	X

2.2. *Demonstration of metal-ion transportation in the trifluoromethyl-substituted crowned system **3b** using quantitative UV studies*

ICP-MS is a reliable, widely used and accurate routine industrial technique for the quantification of metal species. This was thus applied to quantify metal-ion concentrations in the aqueous layers of the following test system, and thus as a demonstration that photo-controlled metal-ion transport is taking place. As mentioned earlier, the most pronounced photoreversible metal-ion chelating effects occurred with the trifluoro-substituted system **3b**, and thus this was chosen as the compound for this study. The transport system, as depicted below, was devised to test whether this system could be used to photoreversibly transport metal-ions across a barrier (two immiscible layers of water and 1,2-dichloroethane).

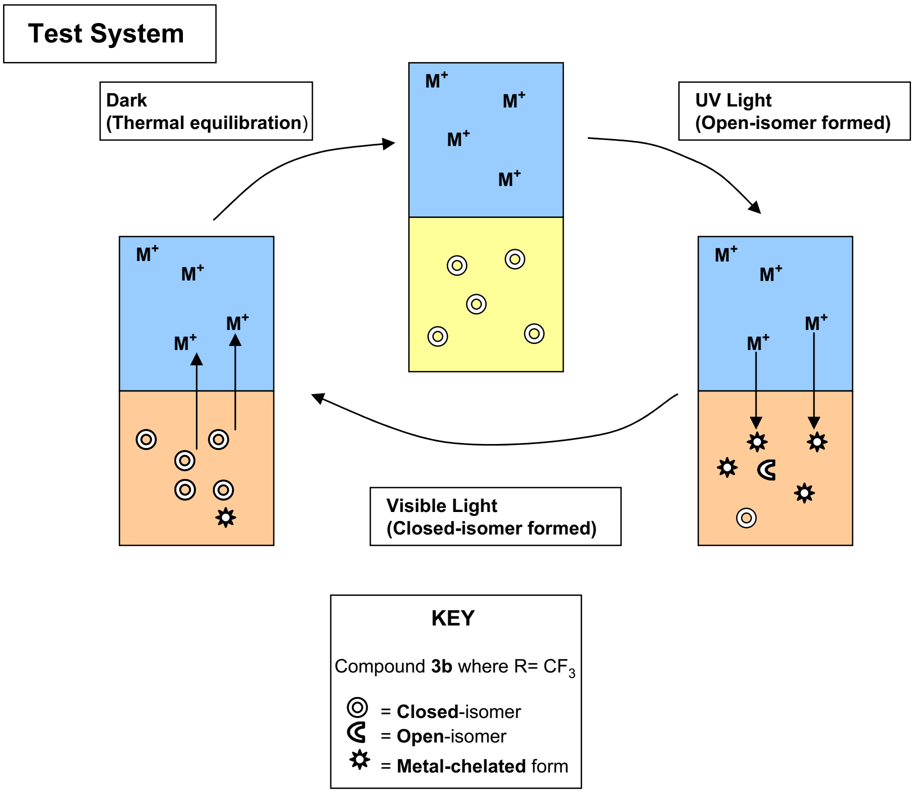


Table 5
Summary of results for the metal-ion selectivity experiments

Metal-ion	λ_{max} (open form complexed to M^+ ions) nm	λ_{max} (open form complexed to a mix of M^+ ions) nm	Size of the cation (Å)	General observations for the spiropyran **3b**
Ba^{2+}	540	540	1.43	Large cation, however, only wins when in competition with Na^+, λ_{max} for Ba^{2+} observed
Mg^{2+}	500	490–500	0.78	Ring opens immensely, strongest binding together with Ca^{2+}. Binding effects can still be seen with ratios as low as 1:1 of crowned spiropyran to metal. λ_{max} for Mg^{2+} is observed at all times
Na^+	540	530–540	0.98	Loses when in competition with Ba^{2+}
Li^+	520	515	0.78	Wins when in competition with Ba^{2+} and Na^+
Ca^{2+}	510	505	1.06	Ring opens immensely, along with Mg^{2+}
Control	540	540	–	Photochromic, however, not to the extent of the crowned spirobenzopyrans with added metals

The bottom layer consisted of the crowned spiropyran (2×10^{-4} M) in 1,2-dichloroethane and the top layer metal perchlorate (2×10^{-4} M) in water (1:1 ratio). The position of equilibrium was measured by UV spectroscopy for compound **3b**: (a) before adding the metal salt (control); (b) after adding the metal salt in the dark; (c) on exposure of the solution to UV light, allowing remeasurement of the UV spectrum; finally (d) on exposure to visible light, and remeasuring the spectrum.

The experiments were repeated consecutively four times with 3 mL of the aqueous layers collected, for each of the metals ($M^+ = Ca^{2+}$, Ba^{2+} and Mg^{2+}). Additionally, the experiments were performed at the lower concentration of 2×10^{-5} M (see below). The metal-ion concentrations were quantified, in the aqueous layers, using ICP analysis, with the measurements (parts per million) observed for each system given in Table 7.

A decrease in the aqueous layer metal-ion concentration is observed between the dark equilibrium state before and after photoirradiating it with UV light (migration of metal-ions into the organic layer), as indicated in Table 6. An increase in the water layer metal-ion concentration was measured on exposure to visible light as the reverse-migration of the metal-ions back into the water layer occurred. Graph 1 shows that of the three metal-ions Ba^{2+} resided mostly in the water layer, photoirradiation with UV light, causing a reduction in concentration as they migrated towards the organic layer: it was possible to reverse this process by photoirradiation with visible light, causing a migration of metal-ions back into the water layer. The most efficient 'on–off' photoreversible transportation effects were for Ba^{2+} (clearly depicted in Graph 2), it being possible to almost completely reversibly cycle between the 'dark' and 'visible' metal-ion concentration levels. This photoreversible equilibrium biasing was almost as good with Ca^{2+} with some effect, although not as pronounced, still evident with Mg^{2+}.

Table 6
Metal concentrations in parts per million (ppm) in the water layer (starting with a 2×10^{-4} M solution)

	Mg^{2+}	Ba^{2+}	Ca^{2+}
Control	5.694	14.812	8.774
Dark	2.81	14.972	7.57
Irradiated (UV)	0.697	10.799	3.654
Visible light	2.377	13.879	4.78

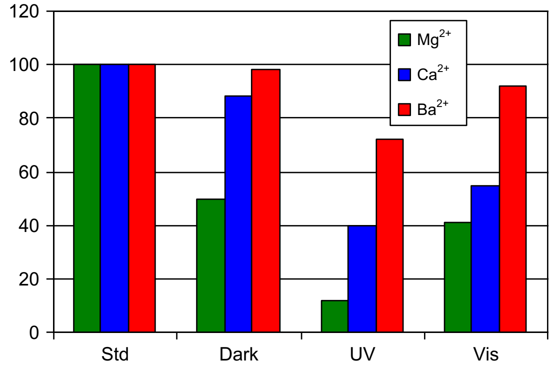
Under UV irradiation the most highly extracted metal-ion was Mg^{2+} with a good deal of photo-induced reversible transport being evident – Graph 2).

It was additionally possible to demonstrate this reversible transportation process for Ca^{2+} ions (Graph 2).

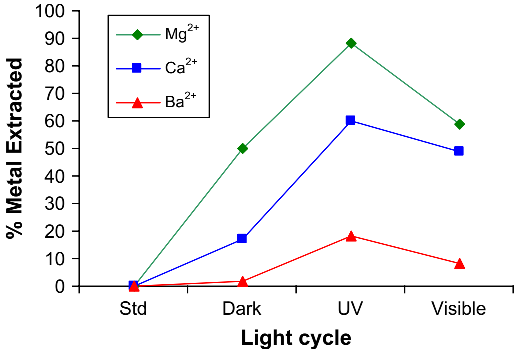
In summary, we have demonstrated that the system **3b** is capable of reversibly transporting the metal-ions Ba^{2+}, Mg^{2+} and Ca^{2+} across a barrier, formed between two immisible layers, using photochromic control (Graphs 1 and 2). This useful result opens up the potential for these systems to be used for the transport of metal-ions across a membrane.

The experiments, as described above, were repeated at the lower concentrations of 2×10^{-5} M, the results obtained being shown in Table 7, and depicted in Graphs 3 and 4.

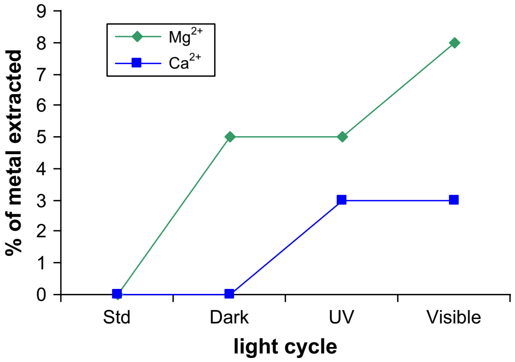
In summary, at the lower concentration of 2×10^{-5} M, the maximal percentage of metal-ions extracted was for magnesium (this might have been predicted, by extrapolation, from the previous experiments at higher concentration), however, it was less than 10% and the effect did not appear to be photoreversible. Perhaps this is not surprising since at lower concentrations the photochromic process is probably attenuated, to a far higher degree, within the overall 'gross' effects: possibly due to water molecule quenching, carried into the organic layer on partial hydration of the metal-ions.



Graph 1. Compound **3b**, percentage metal-ions left in the aqueous layer.



Graph 2. Compound **3b**, percentage metal-ions extracted from the aqueous layer.

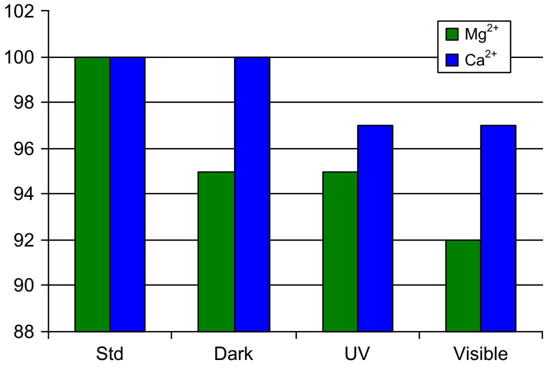


Graph 4. Compound **3b**, percentage metal-ions extracted from the aqueous layer (starting with a 2×10^{-5} M solution).

3. Experimental

3.1. Photoirradiation studies

The photochromic properties of these compounds were explored by making-up solutions (2×10^{-5} mol dm^{-3} unless otherwise stated), in the dark, in freshly dried and redistilled solvents (generally tetrahydrofuran or acetonitrile). Perchlorate salts were dried over P_2O_5 for several days before use. Solutions were placed in a stoppered 1-cm cuvette at room temperature (20–25 °C) and allowed to equilibrate for 1 h before measurement of their UV/vis absorption curves (dark curves). The solutions were then irradiated for 1 min with UV light of $\lambda = 365$ nm generated from a steady power source. The UV light source was a 200-W mercury/xenon lamp, focussed in a LOT-Oriel air-cooled lamp housing, with solution filters to eliminate light of <320 nm and >400 nm (this allows photoirradiation with a λ_{max} of around 380 nm, the absorption wavelength of the spirobenzopyrans, and additionally avoids photoirradition of the formed merocyanine, which has a λ_{max} of around 550 nm). The UV absorption spectra were measured (UV curve) and then the cuvette was exposed to a visible light source for 3 min using a 100-W tungsten spotlight, and the UV absorption spectrum remeasured. The solutions were recycled a second time to ensure reproducible results were obtained.



Graph 3. Compound **3b**, percentage metal-ions left in aqueous layer (starting with a 2×10^{-5} M solution).

Table 7
Metal concentrations in parts per million (ppm) in the water layer (starting with a 2×10^{-5} M solution)

	Mg^{2+}	Ca^{2+}
Control	0.620	0.825
Dark	0.589	0.870
Irradiated (UV)	0.589	0.849
Visible light	0.57	0.855

^{1}H NMR studies were carried out with a JEOL FX2000 spectrometer using deuteriochloroform or dimethyl sulfoxide-d_6 as the solvent with tetramethylsilane as the internal reference. Elemental analyses were carried out in-house by Medac analytical services.

UV spectroscopy was carried out using Perkin–Elmer Lambda 5 and Lambda 9 spectrometers; both instruments are double beamed with thermostatically controlled cell blocks. The Lambda 9 is also fitted with an RS 232 port, which allows remote control by PC. All UV measurements were taken at 25 °C using 3-cm^3 quartz cells with a 1-cm path length and are referenced against air.

Preparation of the starting indolenines was as described previously [9].

The crowned indolenine **3a** was prepared by the method of Kimura et al. [5b] and the other 5-substituted crowned indolenines **3b** and **3c** prepared using a slightly modified procedure, and with a different solvent mixture from that previously erroneously reported [1] – the solvent used for the reaction mixture was in the case of the 5-trifluoro derivative ethanol (9 mL) and DMF (1 mL), and in the case of the 5-nitro derivative ethanol (8 mL) and DMF (1 mL).

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