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Photoreversible ion-binding using spiropyran modified silica microbeads

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Abstract: In this paper, we report the covalent immobilisation of spiropyran on silica microbeads of 5 μm diameter and subsequent evaluation of the photoswitchable behaviour and light-modulated ion-binding properties of the spiropyran modified silica microbeads towards a range of different metal ions. The beads can be effectively switched using light emitting diodes between a white spiropyran form (by irradiation with a white 430–760 nm light emitting diode) and a pink merocyanine form (upon irradiation with a UV light 375 nm emitting diodes) that undergoes, under exposure to certain metal ions (such as Cu^{2+} and Zn^{2+}, final concentration of 7.7×10^{-4} M in ethanol solution), a further reversible spectral and colour change due to the formation of merocyanine-metal ion complexes. Furthermore, the accumulated ions can subsequently released from the beads on demand using light emitting diodes to reform the inactive spiro form.

Keywords: photoreversible ion binding; spiropyran; functionalised silica microbeads; adaptive material.

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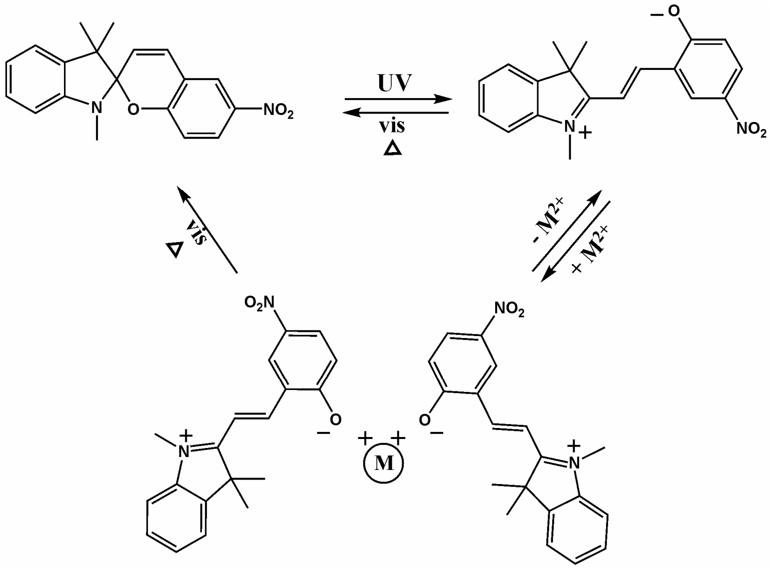
1 Introduction

Molecular photoswitches such as spiropyrans have been extensively studied for several decades because of their ability to reversibly switch between two states: a colourless, non-polar, uncharged spiro (SP) form and a highly purple coloured, planar, conjugated, zwitterionic merocyanine (MC) form with a maximum absorbance around 560 nm depending on the environment (Minkin, 2004). The MC form possesses a phenolate group that can reversibly bind metal ions (Chibisov and Görner, 1998; Görner and Chibisov, 1998) (Figure 1). Furthermore, in addition to photo-reversibility, the entire system is inherently self-indicating, as the SP, MC and MC-ion complex forms exhibit different absorbance behaviour in the visible region. Recently, the covalent immobilisation of a spiropyran modified derivative has been performed on polystyrene microbeads. It has been demonstrated that the polymeric beads can be switched using light emitting diodes (LEDs) between a white SP form and a pink MC form, which in the presence of copper ions undergoes another reversible self-indicating colour change (Scarmagnani et al., 2007). Irradiation with a UV LED (375 nm) for one minute switches the spiropyran on the bead surface to the MC form, while one minute irradiation with a white LED (430–760 nm) converts the dye back to the SP form. In the presence of Cu^{2+} ions, the MC absorbance at 560 nm decreases and a new peak appears around 445 nm. Subsequently, the metal ion can be easily expelled using a white LED converting the MC back to the SP form.

In the context of generating ‘smart’ beads using photoswitchable ligands, the immobilisation of spiropyran on silica beads has also been evaluated. In comparison to polystyrene, silica microbeads are compatible with a greater range of solvents and have different physical properties that can affect the switching equilibrium. The chemistry of the immobilisation process, similar to the one previously reported in the literature for the functionalisation of glass slides with spiropyran (Rosario et al., 2002), involves firstly the modification of the silica surface with amino functional groups and afterwards the covalent immobilisation of a modified spiropyran moiety. In this paper, we evaluate the photoswitchable behaviour and light-modulated ion-binding properties of these SP modified silica microbeads.

LEDs were chosen as light sources for controlling the photochromic equilibrium on the surface of the microbeads. We have previously demonstrated that using LEDs instead of more powerful light sources substantially reduces the well-known photodegradation processes (Radu et al., 2007) that occur when the switching equilibrium between the SP and the MC form is performed repeatedly over time (Baillet et al., 1993, 1994; Matsushima et al., 2001; Li et al., 2004; Demadrille et al., 2004). Despite the fact that the power of LEDs is much lower than the more commonly employed arc lamp light sources (1 mW/cm^2 compared to 50–100 W), the switching efficiency is relatively unaffected and repeated switching can be successfully performed (Radu et al., 2007; Stitzel et al., 2006; Byrne et al., 2006).

Figure 1 Scheme of the spiropyran switching between the closed and uncharged SP form (by white light irradiation) and the open charged MC form (by UV irradiation)



Notes: In the presence of certain metal ions, especially transition metals such as Cu^{2+} and Co^{2+} (Radu et al., 2007; Byrne et al., 2006), the MC forms a complex where two phenolate groups bind the metal ion. Then upon irradiation with white light, the SP form is reestablished and the metal ion is expelled.

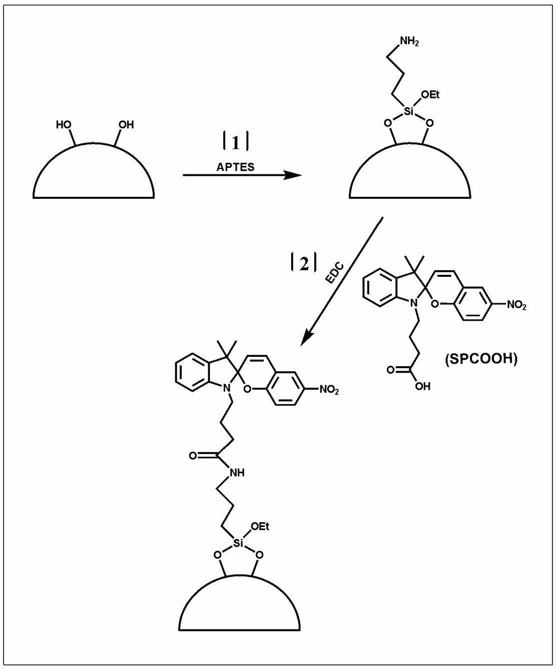
2 Materials and methods

2.1 Materials

Silica microbeads 5 ± 0.35 μm diameter (5 % solid contents), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC hydrochloride), (3-Aminopropyl) triethoxysilane (APTES), calcium nitrate hydrate, copper (II) nitrate trihydrate, calcium chloride hexahydrate, mercury (II) chloride, zinc chloride, cadmium nitrate tetrahydrate, cobalt (II) nitrate hexahydrate were purchased from Sigma Aldrich (Ireland). Ammonia solution 25% was purchased from Sharlau Chemie (Spain) and 1’-(3-carboxypropyl)-3’, 3’-dimethyl-6-nitrospiro(2H-1)benzopyran-2, 2’-(2H)-indole (SPCOOH) was synthesised as described elsewhere (Rosario et al., 2002) (Figure 2).

UV (375 nm) and white (430–760 nm) LEDs were purchased from Roithner Laser Technik, Austria. Absorbance spectra were recorded using a well plate spectrometer (Medical Supply Co., Ireland). Sample spinning was carried out using a Rotofix 32 centrifuge (Global Medical Instrumentation, Inc., USA.). Homogeneous suspensions of microbeads were generated using a Bransonic Ultrasonic Cleaner 5510 from Branson Ultrasonics Corporation, USA.

Figure 2 Reaction scheme on the silica microbead surface



Note: The first step [1] involves the amination coating of the silica surface and followed by [2] the formation of an amide group using EDC catalysis between the amine group on the bead surface and the carboxylic group on the SPCOOH derivative.

2.2 Amino groups coating of the silica microbead surface

A sample of a suspension of silica microbeads (0.1 g in 2 ml of water) was diluted with 22.5 ml ethanol, 2.5 ml of ammonia solution, 25% and 2 ml of APTES were added and the mixture stirred under reflux for 48 hours (Figure 2). The microbead suspension was then cooled, separated from the reaction mixture by centrifugation, suspended in 4 ml of ethanol and washed six times with fresh ethanol. The washing procedure consists of a four-step process:

1. centrifugation of the suspension for three minutes at 4000 rpm
2. removal of the supernatant, addition of 4 ml of fresh solvent
3. sonication of the suspension for five minutes
4. subsequent further centrifugation.

2.3 Covalent immobilisation of spiropyran on the surface of amino groups functionalised silica microbeads

3 ml of a 15 mg ml^{-1} solution of SPCOOH in ethanol was added to 2 ml of an 11 mg ml^{-1} solution of EDC in ethanol. The reaction mixture was stirred for half an hour at room temperature in the dark. A 1 ml suspension of 0.1 g of the amino functionalised

microbeads in ethanol was added to the spiropyran/EDC solution and the reaction mixture stirred for 72 hours at room temperature in the dark (Figure 2). Finally, the spiropyran functionalised microbeads were profusely washed ten times with ethanol following the above procedure and stored at 4ºC in the dark.

2.4 Physical absorption of spiropyran on the surface of silica microbeads

In order to compare the characteristics of covalently functionalised beads, a sample of silica beads with physically adsorbed SPCOOH was prepared.

An aliquot of a suspension of the previously amino functionalised silica microbeads (0.025 g in 3 ml of ethanol) was added to 1 ml of a 15 mg ml^{-1} ethanolic solution of SPCOOH and the mixture stirred for 72 hours in the dark at room temperature. The beads were then washed ten times with fresh ethanol using the above reported procedure and stored at 4ºC in the dark.

2.5 Sample preparation for UV-vis spectroscopic analysis

The optical properties of the spiropyran functionalised microbeads were evaluated using a plate well spectrometer. 1.2 ml of a 0.0125 g suspension of the microbeads in ethanol was placed in each plate well and left for one hour in the dark to enable settlement of the microbeads. After this period, the microbeads formed a compact homogeneous layer, which was suitable for obtaining UV-vis absorption spectra because of the semitransparent nature of the silica microspheres.

2.6 Switching properties of the spiropyran immobilised on silica microbead surface

The optical properties of the functionalised silica microbeads have been evaluated for the two different immobilisation strategies for a period of one to five minutes (increasing by one minute) using this procedure:

1. The microbeads were irradiated for ten minutes with a white LED to make sure that the spiropyran was predominantly in the SP form.
2. The microbeads were irradiated with the UV LED for five minutes, with spectra obtained after each minute (i.e., after one, two, three, four and five minutes irradiation). At this stage, the beads were predominantly in the MC form.
3. The microbeads were then irradiated with the white LED for five minutes, with spectra obtained after each minute (i.e., after one, two, three, four and five minutes irradiation). This caused the MC to switch back to the SP form.

2.7 Evaluation of the SP immobilisation strategies

The influence of immobilisation strategy on switching efficiency was evaluated for the two different spiropyran functionalised microbead samples [covalently immobilised (–SP(CI)) and physically absorbed (–SP(PA)) spiropyran] switching the microbeads between the SP and MC forms ten times using UV and white LEDs using the following procedure:

1 The microbeads were irradiated for four minutes with a white (430–760 nm) LED.

2 The spectrum was immediately captured.

3 The microbeads were then irradiated with a UV (375 nm) LED for two minutes.

4 The spectrum was again captured.

5 This process was then repeated.

2.8 Evaluation of metal ion interactions with SP-coated microbeads

Spiropyran coated microbeads suspended in ethanol were exposed to different metal ion ethanolic solutions in order to evaluate the extent of complex formation at the bead surface. The metal ions used were: Ca^{2+} [from $Ca(NO_3)_2$] and $CaCl_2$ to test any possible effects deriving from the anion, Cu^{2+} [from $Cu(NO_3)_2$], Hg^{2+} [from $Hg(NO_3)_2$], Cd^{2+} [from $Cd(NO_3)_2$], Co^{2+} [from $Co(NO_3)_2$] and Zn^{2+} [from $ZnCl_2$]. Each experiment was carried out using the following procedure:

1 On each well, a sample of 0.0125g of microbeads in 1.2 ml of ethanol was exposed to a white LED (430–760 nm) for four minutes to ensure the SP form was predominant.

2 The spectrum of the colourless SP form was obtained.

3 The microbeads were exposed to a UV (375 nm) LED for two minutes to promote SP conversion to the MC form.

4 The spectrum of the coloured MC form was obtained.

5 0.1 ml of 10^{-2} M of metal ion ethanolic solution (final concentration 7.7×10^{-4} M) was added.

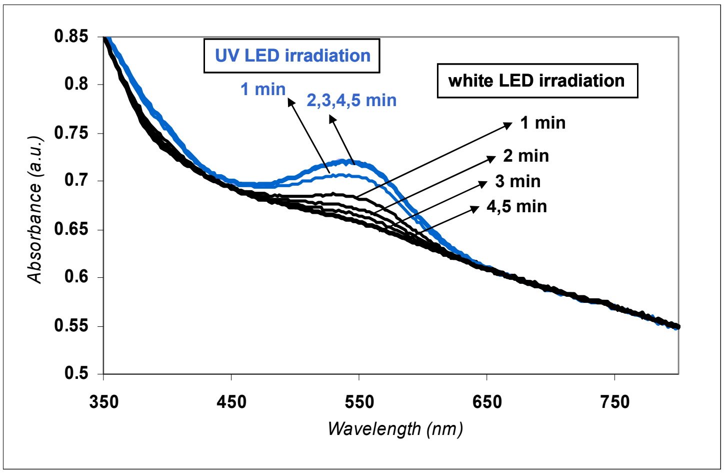
6 The resulting spectrum was taken immediately after.

3 Results and discussion

3.1 Optical properties of spiropyran coated microbeads

It was previously demonstrated that polystyrene microbeads with spiropyran covalently bound using similar immobilisation strategies could be successfully switched between the pink MC form and the colourless SP form, using a UV LED 375 nm (for the SP → MC conversion), and a white LED 430–760 nm (for the MC → SP conversion) (Scarmagnani et al., 2007). In order to evaluate the switching efficiency of the silica –SP(CI) microbeads sample, these LEDs were chosen as light sources for the irradiation and the samples were exposed to increasing irradiation to estimate the optimum exposure time for efficient switching (Figure 3). The results show that the conversion from the SP to the MC form is essentially complete after two minutes irradiation, as further irradiation does not cause any appreciable increase in the absorbance value at 558 nm. For the reverse MC → SP switching, complete conversion was achieved after four minutes irradiation with the white LED, by which time the characteristic 558 nm MC peak had disappeared.

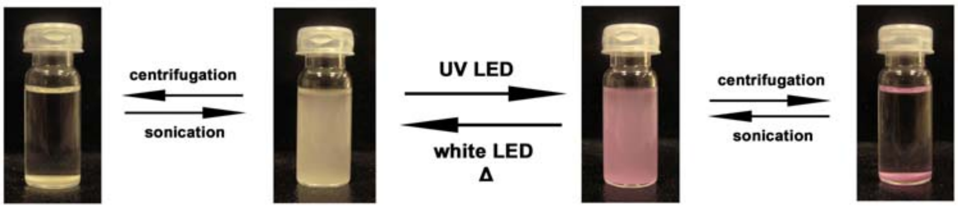
Figure 3 UV-vis spectra of a –SP(CI) microbead sample (see online version for colours)



Notes: Irradiated first with UV LED for five minutes (blue lines), with spectra obtained after each minute (i.e., after one, two, three, four and five minutes irradiation) and then with white LED for five minutes (black lines) with spectra obtained after each minute (i.e., after one, two, three, four and five minutes irradiation). Two minutes UV LED irradiation is enough to reach the maximum absorbance value for the MC form at 558 nm, while four minutes white LED exposure is required to convert the MC back to the SP form.

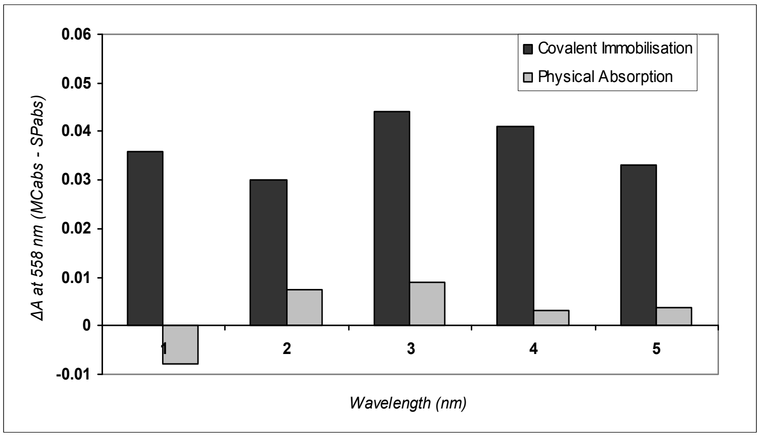
In conclusion, the efficient SP → MC switching was complete after two minutes UV LED irradiation, and after four minutes for the MC → SP conversion using white LED illumination (Figure 4). This was further applied to compare the switching efficiencies of the microbead samples modified using the two different immobilisation strategies: –SP(CI) and –SP(PA). The switching cycle SP ↔ MC (performed by irradiating the samples alternatively for two minutes with UV LED, followed by four minutes with a white LED) on both samples was repeated five times and the differences in absorbance values at 558 nm ($MC_{absorbance} - SP_{absorbance}$) plotted (Figure 5).

Figure 4 Silica –SP(CI) microbead sample (0.025 g in 1.3 ml ethanol) in a glass vial is switched between the colourless SP form and the purple MC form (see online version for colours)



Note: The centrifugation process demonstrates that the colour change is happening on the microbead surface and not in the solution medium.

Figure 5 Differences in aborbance values at 558 nm ($MC_{absorbance} - SP_{absorbance}$) extracted from five switching cycles (two minutes UV LED and four minutes white LED) on a silica –SP(CI) microbead sample compared to silica –SP(PA) microbeads sample



Notes: Both samples contain 0.0125 g microbeads in 1.2 ml ethanol suspension. A much larger absorbance difference is evident in the case of the microbeads with covalently bound SP indicating that the SP molecules have enough conformational freedom to switch between the SP and MC forms efficiently.

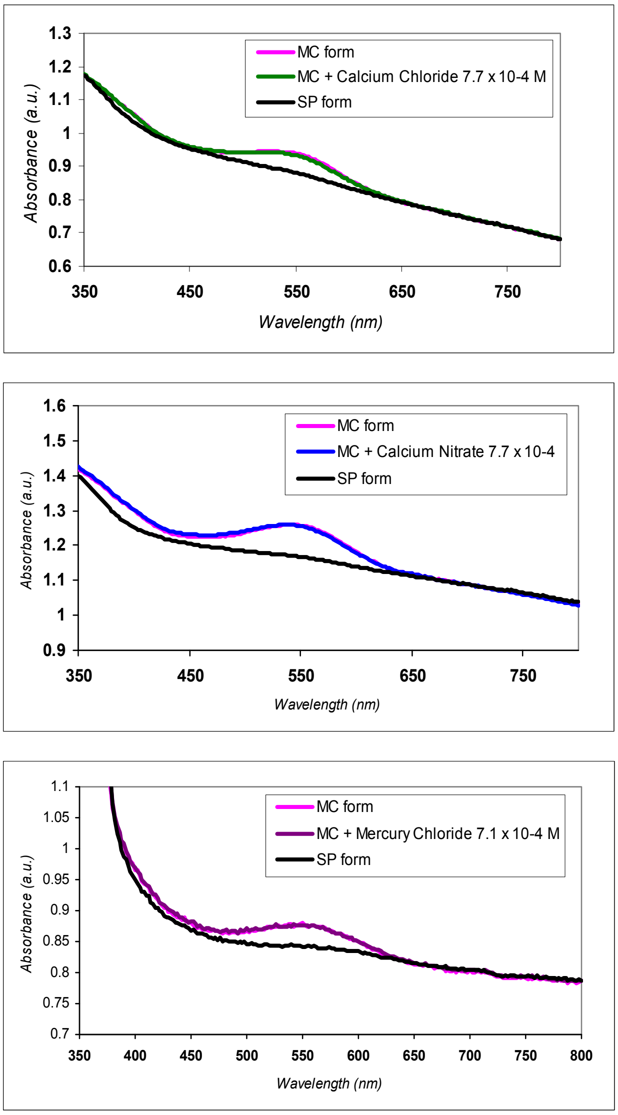
The graph clearly shows the effectiveness of the covalent immobilisation over the physical absorption. There is almost no significant difference between the absorbance value at 558 nm of the SP and the MC forms for the –SP(PA) sample, while there is obvious switching between the SP and MC forms in the case of the –SP(CI) sample, demonstrating that the covalent immobilisation allows effective switching. As previously reported, the presence of a tether spacer group increases the degree of conformational flexibility allowing an efficient spiropyran switching (Byrne et al., 2006). In this case, the tether is obviously sufficiently long to allow the molecular rearrangement accompanying SP/MC switching to happen in a free manner. Therefore, the silica –SP(CI) microbead samples were used for further investigation of its photoreversible ion-binding properties.

3.2 Photoreversible ion-binding properties

The reversible binding properties of spiropyran towards a range of different metal has been widely reported in the literature (Chibisov and Görner, 1998; Görner and Chibisov, 1998; Wojtyk et al., 2001) and even though the phenolate of the MC form binding site is not particularly selective, the nitro spiropyran derivative used in these studies is particularly sensitive to certain transition metals such as Co^{2+}, where the Job's plot has shown a 1 (Co^{2+}): 2 (MC ligand) stiochiometry (Byrne et al., 2006), Cu^{2+}, whose chelating properties towards spiropyran has been demonstrated both in solution (Zhou et al., 1995) and on a polymeric surface (Radu et al., 2007) and Zn^{2+} where again a 2:1 ligand:metal molar ratio has been shown in solution studies (Collins et al., 1999) and complex formation was demonstrated with surface immobilised MC (Wen et al., 2006).

In contrast, alkaline earth ions such as Ca^{2+} and Mg^{2+} only exhibit binding behaviour with MC when the two MC are pre-arranged in a bis-benzospiropyranindoline bidentate ligand (Filley et al., 1998).

Figure 6 Absorbance spectra of silica –SP(CI) microbeads (0.0125 g in 1.2 ml ethanol suspension) switched from the SP to the MC form (see online version for colours)



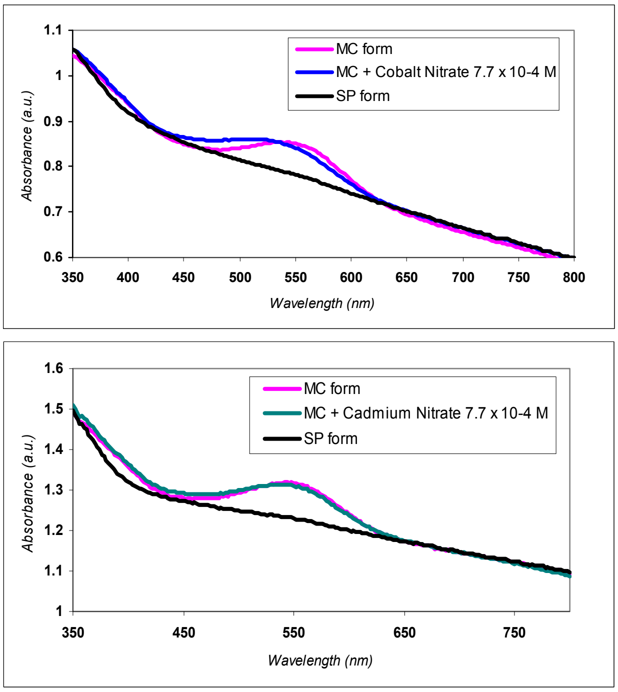
Note: No spectral changes are observed upon addition of Hg^{2+} and Ca^{2+} (final concentration 7.7 × 10^{-4} M in ethanol).

On the basis of literature investigations and previous solution studies, Cu^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} and Ca^{2+} ions were tested in order to investigate the ion complexation properties of the –SP(CI) microbead sample. To test for anion effects, both the chloride and nitrate salts of Ca^{2+} (a metal ion that does not cause any appreciable change in the MC spectrum), were prepared in ethanol (final concentration 7.7 × 10^{-4} M) and placed in contact with microbeads in the MC form. In both cases, no significant spectral changes were observed and the 558 nm peak of the MC remained unaffected in the presence of

Ca^{2+} (Figure 6). This demonstrates that Ca^{2+} ions have no interaction with the MC form on the beads surface and that the anion has no independent effect.

Subsequently, the effect of ethanolic solutions of Cu^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} at the same concentration in ethanol were tested. As with Ca^{2+}, no spectral changes were observed with Hg^{2+} ions (Figure 6), whereas blue shifts at the MC maximum absorbance wavelength occurred in the presence of Cd^{2+} and Co^{2+} ions, from 558 nm to 540 nm and to 550 nm respectively (Figure 7).

Figure 7 Absorbance spectra of silica –SP(CI) microbeads (0.0125 g in 1.2 ml ethanol suspension) switched from the SP to the MC form and after the addition of Co^{2+} and Cd^{2+} (see online version for colours)

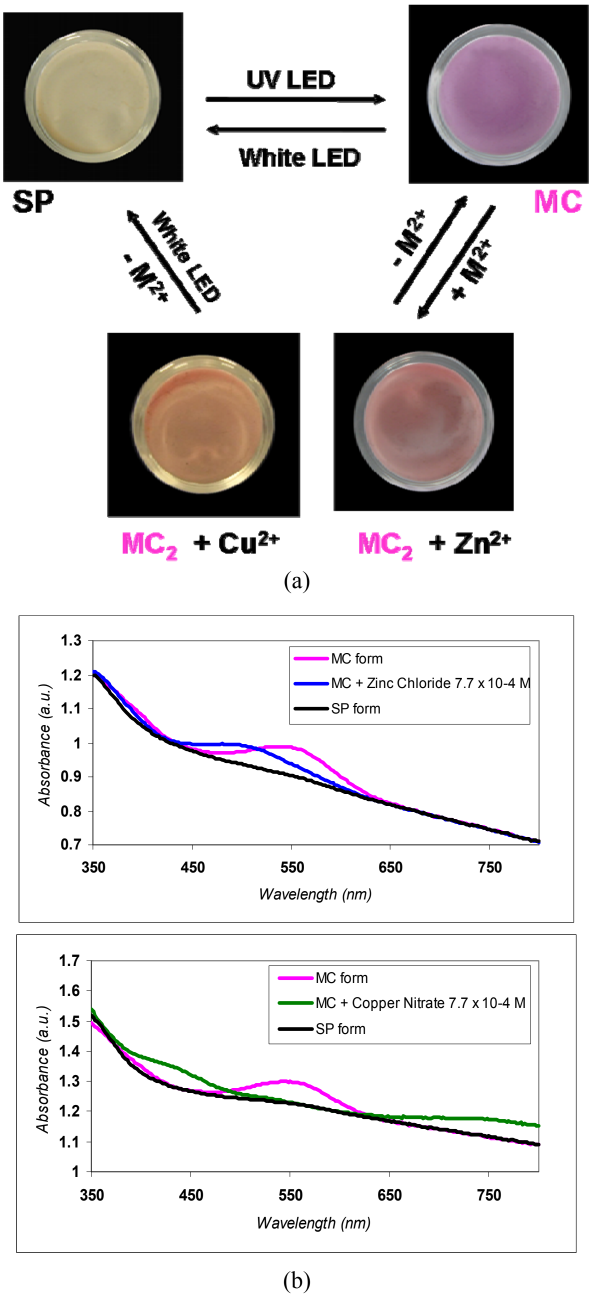


Note: Small blue spectral sifts of the 558 nm MC peak were recorded, to 550 nm (Cd^{2+}) and to 540 nm (Co^{2+}).

However, much larger effects were observed in the case Zn^{2+} and Cu^{2+} ions (Figure 8). In the presence of Zn^{2+}, a clear visual colour change from purple (MC) to light pink (MC_2-Zn^{2+}) can be observed. This is caused by a decrease in the MC absorbance band at 558 nm and the emergence of a new absorbance band centred around 525 nm arising from the MC-metal ion complex.

Similarly, addition of Cu^{2+} ions at the same concentration to MC-microbead sample resulted in a colour shift from purple to orange (MC_2-Cu^{2+} complex) occurred, which arose from the disappearance of the 558 nm MC peak and the simultaneous appearance of two new absorbance bands at 440 nm and 750 nm.

Figure 8 (a) Visual colour changes observed with –SP(CI) microbeads (0.025 g in 1.3 ml ethanol) at the bottom of a sample vial that accompany switching from the colourless SP form to the pink MC form, and after addition of Cu^{2+} and Zn^{2+} to the MC form (b) absorbance spectra of –SP(CI) microbeads (0.0125 g in 1.2 ml ethanol suspension) underlying these colour changes (see online version for colours)

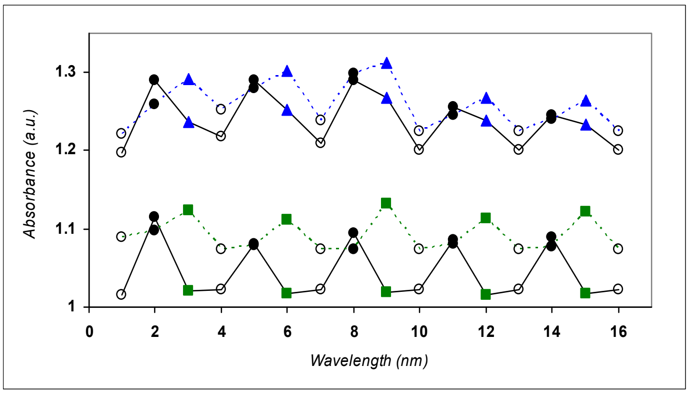


Note: Upon addition of Cu^{2+} ions, the 558 nm MC peak disappears, and new absorbance bands appears at 440 nm and 750 nm; addition of Zn^{2+} leads to reduction in the MC 558 nm absorbance and appearance of a new band around 525nm.

In both cases, after the formation of the MC-metal ion complex, replacement of the metal ion solution with clean ethanol, followed by irradiation of the microbeads for four minutes with a white LED lead to expulsion of the bound Cu^{2+} ions and complete reformation of the SP form on the beads. Following this, irradiation of the microbeads for two minutes with the UV-LED converted the SP back to the MC form, ready for another metal ion uptake and release cycle.

The binding and releasing cycles between the SP ↔ MC ↔ MC-metal complex have been successfully repeated five times using the same microbead sample for both Cu^{2+} and Zn^{2+} ions, demonstrating that the spiropyran coated silica microbeads represent a reversible ion binding and detecting system, whose properties can be externally modulated by light (Figure 9).

Figure 9 Aborbance values of –SP(CI) microbeads (0.0125 g of microbeads in 1.2 ml ethanol suspension) plotted after performing of five switching cycles from the SP form (empty circle), MC form (full circle) and from here to the MC-Cu^{2+} complex (green square) and MC-Zn^{2+} complex (blue triangle) (see online version for colours)



Note: The absorbance values have been monitored at 558 nm (continuous line), 490 nm (blue dotted line) and at 440 nm (green dotted line), where the maximum spectral differences between the MC and the MC-ion complex forms appear.

This behaviour has important implications for light-controlled ion uptake and release. For example, preconcentration of metal ions from solution can be effected on beads within cheomatography, flow-injection analysis or lab-on-a-chip platform, using light to control where and when binding/release occurs. For example, beads can be used to pick up ions at one location within a flow system, transport the ‘cargo’ to a second location, where they are released, again using light to control where and when these events occur.

4 Conclusions

In conclusion, SP-functionalised silica microbeads are inherently self-indicating entities capable of switching between non ion-binding (inactive) spiropyran and ion-binding (active) forms, with switching between these states, and indeed the uptake and release of the bound ions controlled entirely using light of an appropriate wavelength. The microbeads surface can be modulated between a sensing colourless inactive form and an active state is highly coloured and undergoes further reversible colour changes in the presence of Cu^{2+} and Zn^{2+} ions, with smaller spectral changes occurring in the presence of Cd^{2+} and Co^{2+}, while it is insensitive to $Ca^{2+}$and Hg^{2+}.

Therefore, these beads could form the basis of a system capable of selectively binding certain metal ions from mixtures, but only when switched to the 'active' state using UV-light. The acquired ions can subsequently be released when the beads are illuminated using white light. Clearly, this behaviour could have many interesting applications in selective preconcentration on certain ions, transport of bound ions to remote locations, and controlled release of bound ions, using light as the external controlling stimulus. The same underlying mechanisms may also be applicable to selective uptake and release of other species, such as amino acids or more complex guests (Byrne and Diamond, 2006).

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