

Spiropyran-based reversible, light-modulated sensing with reduced photofatigue

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Abstract

Switchable materials have tremendous potential for application in sensor development that could be applied to many fields. We are focusing on emerging area of wireless sensor networks due to the potential impact of this concept in society. Spiropyran-based sensors are probably the most studied type of photoswitchable sensing devices. They suffer from many issues but photofatigue, insufficient selectivity and lack of sensitivity are probably the most important characteristics that hinder their wider application. Here, we address these issues and demonstrate that covalent attachment of modified spiropyran into a polymeric film significantly reduces photodegradation. The observed signal loss after 12th cycle of switching between the spiropyran and merocyanine forms is only about 27% compared to the loss of 57% of the initial signal in an equivalent experiment based on non-immobilized spiropyran. This has enabled us to demonstrate at least 5 reversible cycles of detection of an ion of interest (in our case H⁺) with minimal signal loss. Furthermore, we demonstrate that the sensitivity can be increased by incorporation of additional binding groups in the parent spiropyran molecule. Using molecular modeling to calculate the relevant bond lengths as a measure of interaction between MC and H⁺, the calculated increase of H-bond strength is approximately an order of magnitude for a derivative containing a methoxy group incorporated in the *o*-position of the parent spiropyran in comparison to the equivalent unsubstituted phenol. This theoretical result was found to correspond very well with experimental observation. As a result, we have increased the sensitivity to H⁺ by approximately one order of magnitude.

Introduction

Recently, the area of wireless sensor networks (WSN) has emerged as a topic of considerable importance, under which it is envisaged that in the near to medium term, many millions of sensors will feed data into a ubiquitous communications infrastructure, providing information on personal health indicators, the status of the environment, the quality of our food, or the presence of a threat or hazard.¹ However, despite the obvious importance of information that can be provided by chemo/bio-sensors, there is still very limited activity in the literature that convincingly demonstrates the application of these devices in a WSN.² A major inhibiting factor to the widespread deployment of chemical sensors/biosensors within WSNs is the need to perform regular calibration, due to changes occurring at the active sensing surface of the device.³ Calibration involves integrating liquid control features which, with current technologies, results in a much more complex and expensive device than would be desirable for WSN deployments. A conceptually intuitive solution to this problem could be provided by the use of 'adaptive materials' that can switch between a passive form that is relatively unaffected by exposure to the real world, and an active, sensing form that can be occasionally invoked when a measurement is required, after which the surface is switched back to the passive form.⁴

A way to demonstrate aspects of this concept may be found through materials that are known to undergo light induced switching between two or more isomers, only one of which undergoes complexation with the target species.^{5,6} One of the oldest and possibly the most studied group of photochromic chelating agents is the family of spiropyrans. Upon irradiation with UV light, spiropyran switches from an uncharged, passive, colourless spiropyran (SP) isomer to a zwitterionic, highly coloured, merocyanine (MC) isomer that possesses an electron-rich

phenolate oxygen atom capable of serving as a binding site for certain metal ions.^{7, 8} Conversely, irradiation with visible (green) light causes the ejection of bound metal ions from the MC-complex and regeneration of the passive SP form.⁹ This very interesting behaviour stimulated us to investigate whether SP could be used to make systems that exhibited photo-reversible ion-binding behaviour hence becoming the serious candidates for design of self-regenerated, “calibrationless” sensors.

Ion binding behaviour of transition¹⁰⁻¹² and alkali metal ions¹³ by the SP/MC system is relatively well-studied; however a number of challenges must be addressed before a fully functioning devices can be produced for real-life applications.¹⁴ For example, the equilibrium between SP and MC is not only driven by light but also by the temperature and the polarity of the environment. The latter does not allow simple integration of SP in non-polar polymer matrixes as it is done in typical optical sensors¹⁵ since the polar MC may easily leach out of the membrane. Covalent attachment of SP to the surface,¹⁶ polymer backbone¹⁷ or to beads¹⁸ is therefore seen as general solution for such type of issues. Furthermore, phenolate group in MC is a sole binding center and with its not overly strong binding of metal ions, it does not express exceptional sensitivity and selectivity. The major limitation for using SP in reversible sensing system as regarded by many researchers is the photodegradation of SP.¹⁴ In addition to issues arising from the chemical nature of SP, size, cost, simplicity of construction and usage of power are all issues that should not be overlooked while thinking of developing and deploying a large number of sensor in a WSN. In our work we are systematically addressing all of the aforementioned issues. For example, we have earlier developed a system based on light emitting diodes (LEDs) as both light emitters and detectors.¹⁹ This allowed us not only to develop very simple, low cost, low

power sensing platform²⁰ but it somewhat surprisingly resulted in reducing the photodegradation of SP.¹⁴

In this work, we demonstrate the reversible, light-modulated sensing that is a step in the direction of achieving sensing with reduced need for calibration. We also describe our effort to strengthen the binding of metal ion by introducing secondary binding centre within the molecule of SP while employing molecular modelling as a powerful tool for predicting the effect of introducing new groups within a molecule. Finally, we address the photodegradation and demonstrate that it is possible to significantly reduce the degree of photodegradation of SP through covalent attachment to a polymer surface.

Experimental

Materials and instruments: 6-Nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] 98% (spiropyran), ethylene diamine 99% (redistilled), 1,8 diamino octane 99%, methacrylic acid 99% (redistilled), omega,omega-dimethoxy-omega-phenylacetophenone (DMPA), NaOH, boric acid, citric acid and potassium dihydrogenphosphate (KH₂PO₄) were purchased from Aldrich. Polymethyl methacrylate (PMMA) was purchased from Goodfellow. 1-ethyl-3-(3-dimethylamino propyl) carbodiimide hydrochloride (EDC) was purchased from Fluka Scientific. Aqueous solutions were made with deionized Nanopure water (18 MΩ•cm). The UV irradiation source BONDwand UV-365nm was obtained from Electrolite Corporation. The white light source was obtained from Chiu Technical Corporation. Spectra were recorded on a UV-Vis-NIR Perkin-Elmer Lambda 900 spectrometer. The thickness of ~130 μm of the SP-polymer film was measured using a PARISS imaging spectrometer coupled to a Nikon eclipse E800 microscope.

Synthesis: Two derivatives of SP have been synthesized according to the procedure outlined below²¹.

1-(3-Carbomethoxypropyl)-3,3-dimethyl-6-nitrospiro[2H-1]-benzopyran-2,2-indoline. The solution of 5-nitrosalicylaldehyde (0.7g, 2 mmol) in ethanol (10 ml) was added drop wise to a solution of 1-(3-carbomethoxypropyl)-3,3-dimethyl-2-methyleneindolinium bromide (0.34g, 2 mmol) in ethanol (10 ml) over 30 minutes. The reaction mixture was refluxed over one day. The resulting yellow precipitate was filtered off and washed using cold ethanol. The yellow product was recrystallised from ethanol two times to obtain yellow crystals 0.7g, yield -83 %.

1-(3-Carbomethoxypropyl)-3,3-dimethyl-8-methoxy-6-nitrospiro[2H-1]-benzopyran-2,2-indoline. The solution of 3-methoxy-5-nitrosalicylaldehyde (0.5g, 1.45 mmol) in ethanol (10 ml) was added drop wise to a solution of 1-(3-carbomethoxypropyl)-3,3-dimethyl-2-methyleneindolinium bromide (0.28g, 1.45 mmol) in ethanol (10 ml) over 30 minutes. The reaction mixture was refluxed over one day. The resulting brown solution was cooled down and the product was precipitated out by adding ethyl acetate. The yellow precipitate was filtered and washed with cold ethanol. The crude product was purified by column chromatography, silica/ethyl acetate, to obtain pure crystal ester-spiropyran 0.3g, yield-46 %.

Figure 1 depicts the two compounds used in this work and their transformation from neutral and passive “spiro” form (SP) to zwitterionic and active merocyanine form (MC).

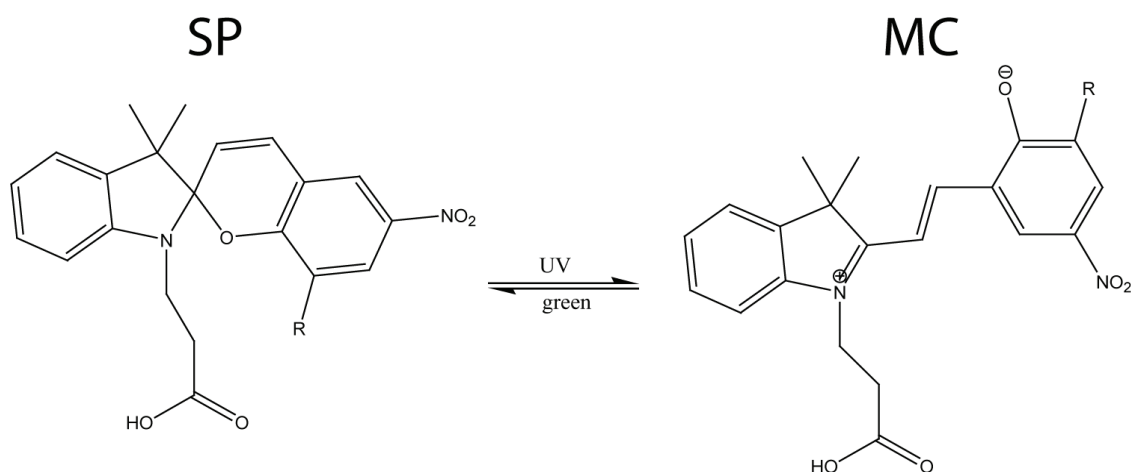


Figure 1. Light modulated transformation from passive spiropyran form (SP) to active merocyanine form (MC). Two derivatives were used in this work – SP1 (R=H) and SP2 (R=OMe). Note that they are labeled as MC1 and MC2 while in the equivalent merocyanine form.

Experiments: 1,8-diaminooctane was covalently attached to the PMMA surface as a linker group of the requisite length for the carboxylated spiropyran derivative as described elsewhere.¹⁶

Universal buffer (30 mM of boric acid, citric acid and KH_2PO_4) in water was prepared and stored in the dark. Prior to each measurement, a small piece of the film of approximately 1x 0.5 cm was cut out, immersed in deionized water if required, exposed to visible light for 1 minute and the spectrum of the closed form (SP) was recorded. The reference spectrum of the opened form (MC) was obtained after the same film was exposed to UV light for 1 minute. When required, the active film (MC) was exposed to buffer solution with appropriate pH adjusted using NaOH and new spectra were recorded.

Discussion

Reversible ion detection. Doping of traditional, hydrophobic plasticized polymeric membranes by SP intuitively seems as the simplest solution for its utilization in chemical sensors. Unfortunately, the MC form is significantly more polar than SP²² which makes it prone to leaching out of the membrane. Over the years, covalent attachment of sensing components

emerged as an attractive solution for the problem of their insufficient retention.²³ We have earlier demonstrated that modified SP can be attached to activated polymethylmethacrylic (PMMA)-based surface binding sites with full preservation of the ability of SP to switch between the active and passive form and detection of Co^{2+} while in active form.¹⁶ In light of our attempts for simplification of sensing platform, it is important to note that the switching can be achieved using simple LEDs.²⁴ In order to use SP in the vision of simple, self-regenerated sensors, it is critical to demonstrate the reversibility of switching between the active and passive form as well as the complete regeneration of sensing film and return to the original, pre-sensing state.

The typical absorbance spectrum of the film used in this work is given in Figure 2A. Dotted line depicts the spectrum of SP-modified PMMA film irradiated with green light. In this case, spiropyran is present in its SP form and the film appears transparent.

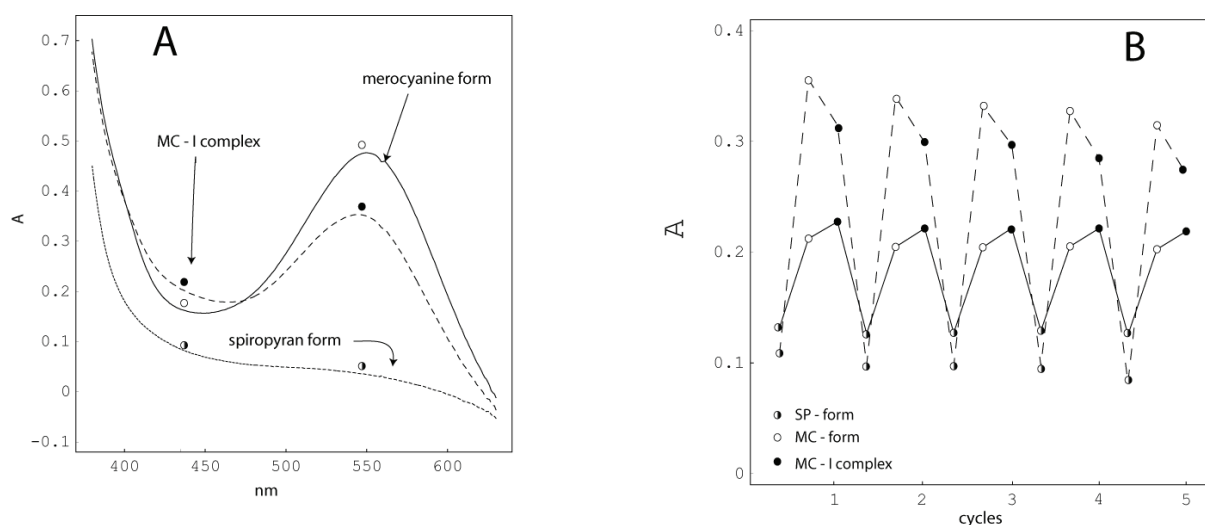


Figure 2. A) spectra of three possible forms of SP – passive spiropyran (dotted line), active merocyanine (full line) and complex of MC with ion of interest indicated as MC-I complex (dashed line). B) Absorbancies measured at 431 nm (full line) and at 560 nm (dashed line) for cyclical transformation between the SP, MC and MC-I (with H^+ used as ion of interest). Absorbancies measured for SP, MC and MC-H^+ are depicted with semi-filled, open and full circles as indicated in A.

When the film is irradiated with UV light, SP converts to the MC form and the film develops a purple colour, with a strong absorbance band appearing in the visible region centred around 560 nm (full line). When the film in the MC form is exposed to an aqueous universal buffer solution (pH=3.5) binding of the proton by the phenolate anion of the MC leads to the formation of a MC-H⁺ complex, and the colour changes to yellow, due to the emergence of a new absorbance band centred around 430 nm, and a simultaneous decrease in the absorbance at 560 nm (dashed line). Hence inter-conversion between the three states (SP, MC, MC-H⁺) can be detected by simultaneously monitoring the absorbance at approximately 430 nm and 560 nm. Note that H⁺ is not bound by the SP form and Figure 2B therefore depicts the reversible, light-controlled detection of H⁺. The film was first irradiated with white light in order to start from the passive, non-sensing SP-film and the spectral values were obtained at 431nm and 560nm (semi-filled circles). Next, the film is then irradiated with UV light using the BONDwand UV-365 nm source placed 3 cm from the film for 1 minute and the UV-VIS spectrum obtained. The new spectral values at both wavelengths are depicted with open circles. The film was then exposed to acidic buffer solution to form the MC-H⁺ complex. The spectrum of the MC-H⁺ complex was obtained after immersing the film in the buffer solution and leaving for 10 minutes in the dark. The resulting spectral values at 431nm and 560nm are depicted with full circles. Finally, the film was transferred to deionised water and exposed to white light using a 40 W bulb from a distance of 3 cm. The bound H⁺ ions appear to be expelled and MC reverts back to the passive SP form. Once again, the spectral values were recorded and are depicted with semifilled circles. Data obtained at 431nm are connected with full lines, while data obtained at 560nm are connected with dashed line. Examination of the results shows a clear pattern emerging. In the SP form, the initial absorbance at 560 nm is relatively small as expected. Upon conversion to MC due to

exposure to UV light, this absorbance rises rapidly, but subsequently decreases as the MC-H⁺ complex forms in the presence of H⁺ ions. Exposure of the MC-H⁺ complex to white light leads to the break-up of the complex and reversion of the film to the SP form (return to baseline). The evidence at 560 nm is confirmed by the pattern observed for the same events at 431 nm. Initially, the film is in the SP form and the absorbance at 431 nm is low. Conversion to the MC form gives rise to a smaller increase in absorbance at 431 nm compared to 560 nm, followed by *an increase* in absorbance upon exposure to H⁺ ions due to the formation of the MC-H⁺ complex. These patterns of behaviour are entirely consistent with the responses predicted by the spectra of each form (SP, MC, MC-H⁺) as seen in Figure 2A. This cycle is repeated five times, demonstrating that the entire process (SP to MC to MC-H⁺ to SP) is repeatable. It is important to note that although there appears to be slight drift, an imaginary line drawn through the semi-filled circles associated with the response measured at 431 nm (Figure 2B) has almost unity slope (slope = -0.00532 a.u./cycle). This indicates reasonably stable response and an effective return to the baseline after each cycle, so the pattern is clearly reproducible. The resulting film can be photoswitched to the strongly coloured MC form which can bind H⁺ ions. Exposing the MC-H⁺ complex to white light causes expulsion of the H⁺ ions and reversion to the SP form. This implies that it should be possible to maintain the surface in the passive SP-form, and activate to the H⁺ binding MC form using UV light when required, confirm the presence of the H⁺ ion using colour/UV-Vis measurements, expel it and subsequently revert to the passive form, again under photonic control.

The implications of these results are substantial. For example, this material could be used for optical sensing of H⁺ and other heavy metals,^{10, 12, 14} as well as amino acids and proteins^{25, 26} using photonic control to select when and where ion-binding is activated and deactivated. This

has obvious potential for the realisation of light modulated separation systems, or photonically controlled ion-filters.

Careful analysis of Figure 2B reveals very little photodegradation of MC form since there is very little loss of the signal monitored at 560 nm during the transformation from SP to MC (see signals between semi-filled and open circles associated with dashed line in Figure 2B). The average difference in absorbance measured from transformation of SP to MC in 5 cycles is 0.237 ± 0.007 a.u. with virtually no loss in the signal between the 1st and the 5th cycle.

Photodegradation. The results presented in Figure 2B are somewhat surprising as the photodegradation of MC is a well known problem that limits application of SP in reversible, self-regenerated sensing devices. It is generally accepted that interaction of MC form with singlet and triplet oxygen leads to photodecomposition of MC.²⁷ Therefore, by putting together a pair of the films containing the photochromic compound within an air-tight environment, Matsushima et al. were able to significantly reduce the photodegradation of fulgimides.²⁸ Interestingly, this approach did not provide any improvement in photo-fatigue of spiropyrans. On the other hand, they noticed that when the concentration of SP in the film was reduced, the degree of photodegradation also reduced, implying that aggregation of MC also has important role in the photodegradation process. A similar conclusion was drawn by Arai et al. and Tork et al. while studying photodegradation of MC in solution²⁹ and polymer matrixes,³⁰ respectively. The work of these research groups indicates that reducing the degree of motion of MC reduces the possibility of interaction between MC molecules and has beneficial effects on reducing the photo-fatigue. Therefore, since covalent attachment drastically limits the movement of MC it should result in films showing improved photo-fatigue. To further study this hypothesis we have prepared a film containing non-modified SP which is not covalently attached to the surface and

compared its responses at 560 nm upon series of switching between SP and MC with the film containing covalently attached SP. The loading of SP in both films was approximately 1% w/w. Figure 3 depicts the comparison of the signals obtained for the two films measured at 560 nm.

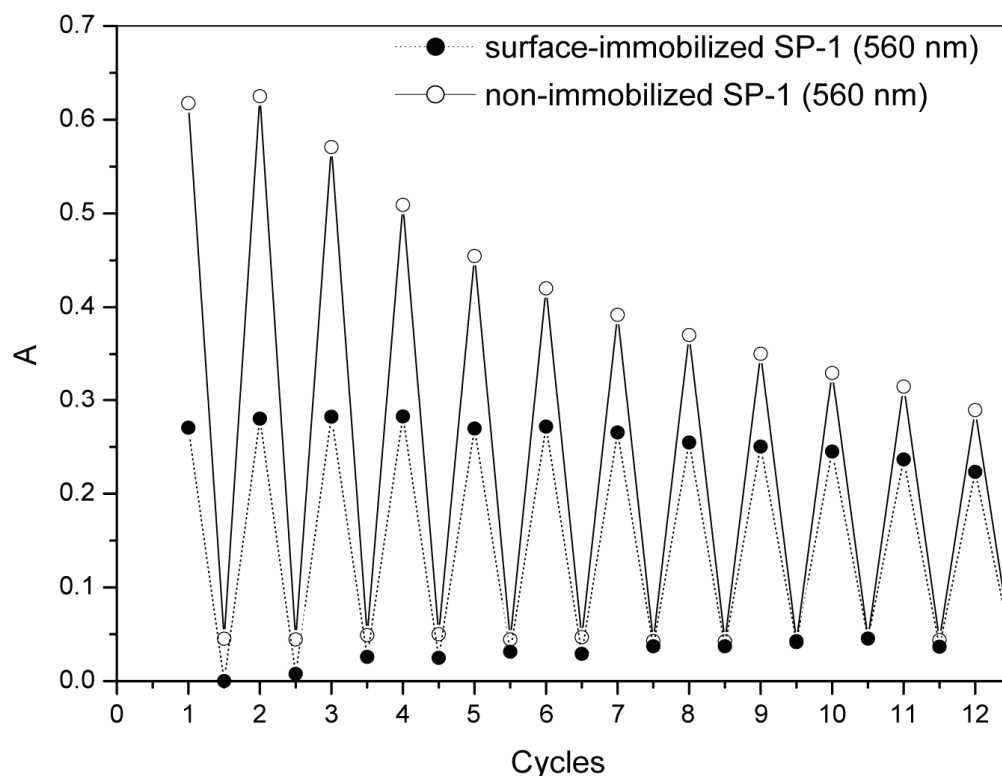


Figure 3. Absorbance measured at 560 nm for cyclical switching between SP and MC when for surface immobilized (full circles) and non-immobilized (open circles) SP-1.

As expected, the loss of signal in the case of non-attached SP is dramatic. The difference in absorbance between SP and MC forms after 12 cycles is only 43% that of the 2nd cycle. In contrast, in the case of covalently immobilized SP, the signal is significantly more stable with the 12th cycle 73% of the 2nd cycle. Therefore, the immobilization of SP has clearly improved the stability of the signal and reduced its photodegradation. This is a very promising result for stabilisation of this material for photoswitchable sensing applications, although more work is

required on further stabilization if the number of effective switching cycles is to be increased to hundreds, or thousands.

Sensing range. The phenolate ion in MC is not regarded as an exceptionally strong binding centre. However, several research groups have developed ligands based on placement of additional binding groups typically at the ortho position relative to the MC phenolate ion.^{11, 31-33} In this work, we have adopted a similar approach and synthesized a methoxy derivative as shown in Figure 1. It is expected that addition of this additional electron withdrawing group should increase the charge density on the phenolate ion and also create another oxygen binding centre for multivalent ions.³⁴ In order to further examine this hypothesis, we employed molecular modelling to calculate the relevant bond lengths as a measure of the degree of interaction between MC and H⁺. Standard density functional theory (DFT) calculations were carried out using GAUSSIAN 03.³⁵ The derivatives MC1, MC2 and their corresponding protonated forms were optimised at B3LYP/6-31G(d) level of theory. It is important to note that these calculations represent descriptions of gas phase molecules only, and do not include solvent interactions. However, the ability of gas phase calculations to estimate bond lengths and bond energies in substituted phenol and merocyanine isomers with acceptable accuracy has been demonstrated previously.^{36, 37} The optimized geometries of MC1, MC2, MC1-H⁺ and MC2-H⁺ generated using this approach, including relevant bond lengths, are shown in Figure 4.

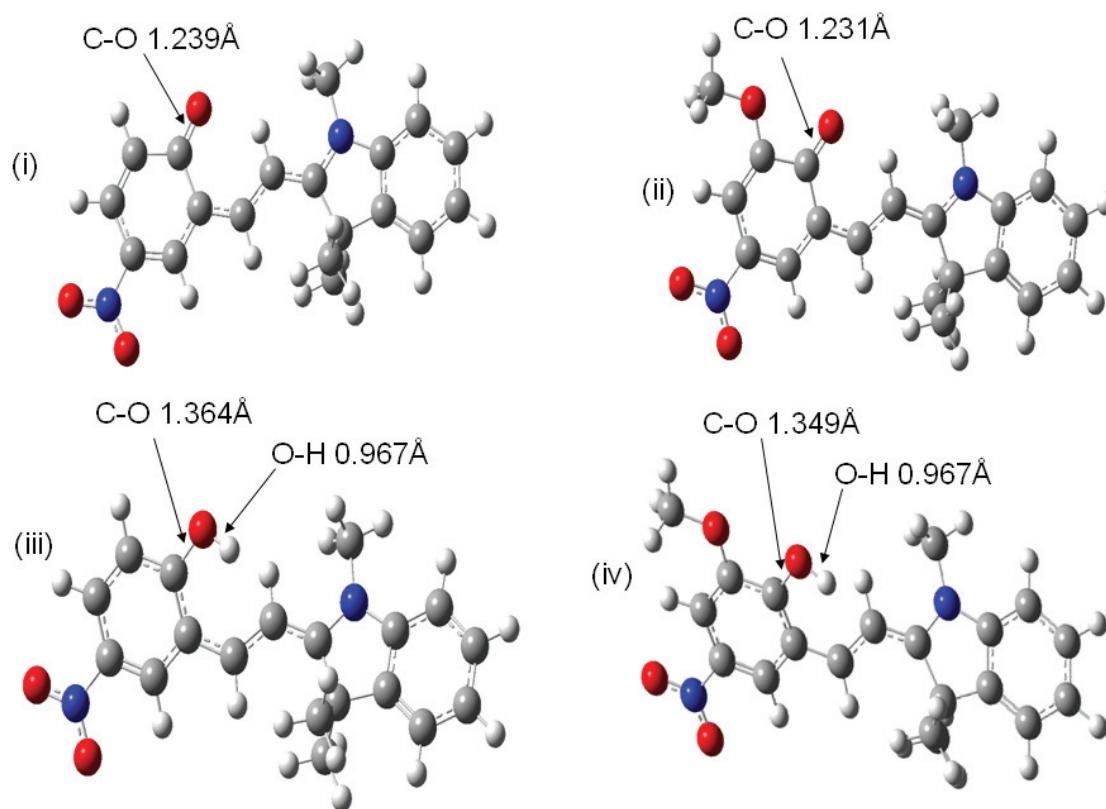


Figure 4. Optimized structures of (i) MC1 (ii) MC2, (iii) MC1-H⁺, (iv) MC2-H⁺ at B3LYP/6-31G(d).

From the geometry optimized structures in Figure 4 we can estimate the relevant bond lengths. The bond length of C-O in (i) is 1.239 Å, and this reduces to 1.231 Å in (ii) due to the *o*-methoxy substitution. Recently it has been shown by DFT modeling of nitrophenol systems that the C-O bond length is a reliable measure of the intermolecular H-bond strength in an associated C-O-H system; the stronger the H-bond, the shorter the associated C-O bond length.³⁸ It is also noted from previous work that *o*-methoxy substitution of phenols leads to a lengthening of the

equivalent O-H bond and shortening of the C-O bond.³⁷ This substituent effect on bond lengths is attributed to an intramolecular interaction between the hydroxyl (O-H) and methoxy (O-CH₃) groups. It can be clearly seen that we observe this substituent effect from the results observed for compounds (iii) and (iv) in Figure 4. Compound (iii) shows bond lengths of C-O (1.364Å) and O-H (0.967Å). In contrast, compound (iv), which includes the *o*-methoxy substituent, has a significantly shorter C-O bond length of 1.349Å compared to that of the unsubstituted compound. These calculations support the hypothesis that the addition of methoxy group in the *o*-position increases H-bond strength significantly in comparison to unsubstituted phenol implying the increase in SP2-H⁺ binding constant.

Encouraged by these findings, we prepared films made incorporating the two derivatives (SP1 and SP2) and studied their H⁺ binding behaviour. A small piece of the film was cut, exposed to UV light for 1 min thereby transforming SP1 and SP2 into MC1 and MC2, respectively, and then immersed in universal buffer of known pH. The results are shown in Figure 5.

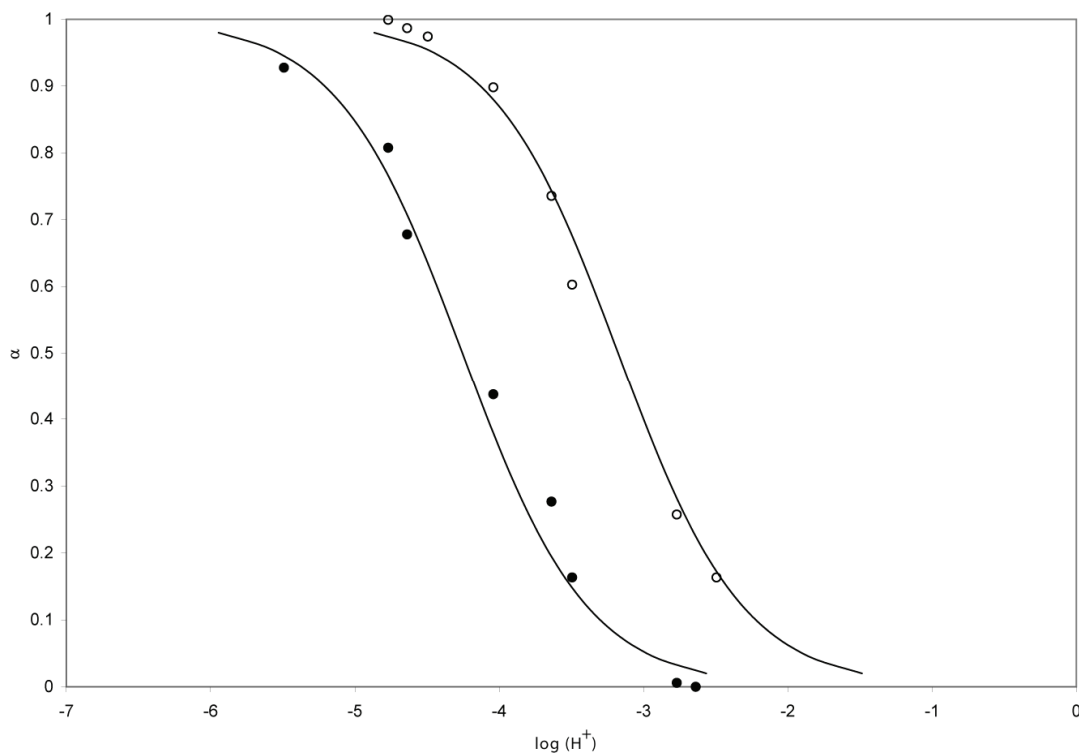


Figure 5. Responses obtained for MC1 (open circles) and MC2 (full circles) measured at 431 nm.

The line drawn through the experimental data points (marked as circles) was obtained by treating the equilibrium between the ligands and H^+ ion ($nL + mM^{n+} \rightarrow M_mL_n$ where L denotes ligand and M stands for ion of interest of charge n).

The corresponding association constant (K) is given by;

$$K = \frac{[M_mL_n]}{[M^{n+}]^m [L]^n} \quad (1)$$

where $[M_mL_n]$, $[M^{n+}]$ and $[L]$ are the concentration of respective species, and the parameter α is the ratio between the free ligand concentration $[L]$ and the initial ligand concentration $[L_{tot}]$.

Upon derivation as described elsewhere^{39,40} we obtained the following:

$$[H^+] = \frac{1-\alpha}{K\alpha} \quad (2)$$

By fitting the curve to the experimental points, the value for the complex formation constant was estimated as $\log K=3.2$ and $\log K=4.3$. The increase of approximately one order of magnitude in the observed complex formation constant is in excellent agreement with the molecular modeling calculations, as discussed above. Two important conclusions arise from these results.

- (1) The addition of carefully selected binding group can indeed increase the binding strength of the phenolate ion, and;
- (2) Molecular modeling calculations are an excellent prediction tool in selecting the appropriate binding group. It should be noted that the experimental data were obtained by measuring the absorbance at 431 nm, where the most intensive absorption by the MC-H⁺ complex occurs.

Next, we have prepared films to characterise each of the three steps in the preparation of SP-modified polymer. Namely,

Film A: consists of PMAA sheet modified by PMMA (PMAA-PMMA) film,

Film B: has an amine-terminated polymer surface (PMAA-PMMA-NH₂), and;

Film C: is the final product, which has SP is attached to the polymer backbone (PMAA-PMMA-NH₂-SP).

In order to demonstrate that the response obtained at 431 nm originate from the formation of the MC-H⁺ complex, Figure 6A compares the responses of film C upon irradiation with UV light and exposure to the pH buffer of pH=3.5 (dashed line) and to deionized water (full line). The responses presented in this figure are calculated as the spectral difference after a given time from

the start of experiment. Therefore, the resulting absorbances observed at 431 nm are in the positive region of y-axes (full circles) due to the formation of the MC-H⁺ complex, while the equivalent values obtained at 560 nm lie in the negative region (empty circles) due to a decrease in the absorbance at 560 nm, as the MC is converted to MC-H⁺. The clear increase in absorbance at 431nm in the case of film exposed to H⁺ indicates that an external source of H⁺ is indeed leading to a new complex. The observed response time (time to reach 95% of the signal) was 40 min which is a reasonable and comparable to response times of common optodes.¹⁵ On the other hand, the absence of a positive change in absorbance at 431 nm when the film is exposed to deionized water indicates that there is no conversion of MC to the MC-H⁺ complex. The decrease of absorbance at 560 nm that occurs in this experiment arises from thermal decolouration of the film (i.e. reversion of MC to SP). Figure 6B shows the responses at 431 nm of films A and B (circles and diamonds respectively) and film C upon exposure to white light (triangles) and to UV light (squares). As expected, due to the lack of active components (spiropyran) films A and B show negligible response compared to film C when exposed to UV light. A slight upward drift is observed in the case of film C exposed to pH=3.5 upon irradiation with visible light. This is not a surprising observation as it is known that the SP and MC forms are in a state of thermal equilibrium, and it is therefore possible that the SP form spontaneously converts to the MC, and, in the presence of acid, the MC-H⁺ complex is obtained.³⁴ Although this finding implies that these systems may not necessarily be completely passive before the irradiation with UV light, a relatively simple adjustment in the programming of irradiation sequence may be a satisfactory solution. For example, irradiation of the film with green light at regular intervals should bring the thermally activated MC back to SP form and keep the system in passive mode.

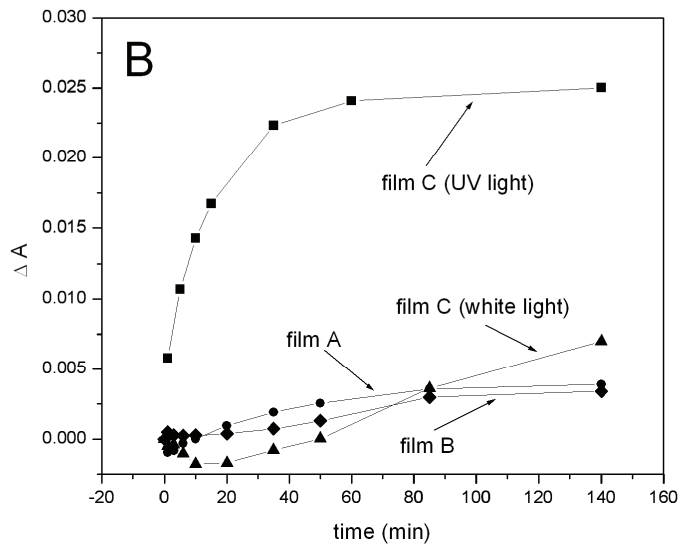
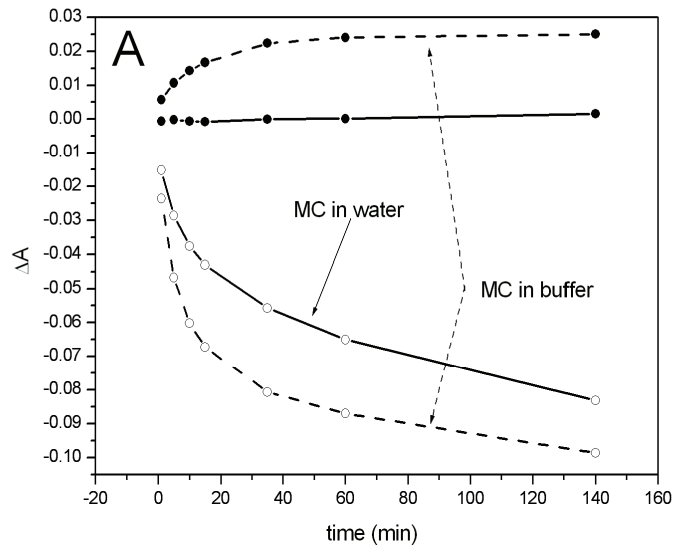


Figure 6. A) Responses of film C upon exposure to UV light and buffer solution of pH=3.5 (dashed line) and deionized water (full line) measured at 431nm (full circles) and 560 nm (open circles). B) Responses of film A (circles), film B (diamonds), film C after exposure to white light (triangles) and UV light (squares) measured at 431 nm.

Conclusions

While there is still a long way to go until simple, “calibrationless” sensors are ready to come to market, this work shows that materials that utilize photoswitchable compounds have great potential. Surface immobilization of SP appears to reduce its photodegradation behaviour significantly. Furthermore, we were able to demonstrate reversible, photo-reversible binding and detection of H^+ ions with very efficient reversal to the base line. Moreover, these materials can be used for photo-controlled uptake and release of guest species. Because they are self-indicating, simple ratiometric measurements using, for example, LEDs centred around 560 nm and 430 nm can be used for reporting on their status. In addition, due to the efficient light-induced regeneration and reversal to the base line, these systems may require minimal, if any calibration which could significantly simplify the manner in which chemical sensing measurements are made.

However, realisation of effective sensors based on these principles will require substantial further improvement in sensitivity, selectivity and ruggedness. Clearly, substitution of appropriate groups at particular locations can considerably improve binding behaviour, but optimisation of this remains a tricky task – too weak and there is limited selectivity, too strong and the binding is irreversible! Theoretical calculations can assist in the molecular design process through prediction of guest binding behaviour, and thereby improve the efficiency of the synthesis/characterisation cycle, which is the limiting stage of the entire materials development process.

Acknowledgment

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Literature

- (1) Diamond, D.; Internet-scale sensing, *Anal. Chem.*, 2004, **76**, 278A-286A.
- (2) Diamond, D.; Coyle, S.; Scarmagnani, S.; Hayes, J.; Wireless sensor networks and chemo-/biosensing, *Chem. Rev.*, 2008, **108**, 652-679.
- (3) Diamond, D.; Lau, K. T.; Brady, S.; Cleary, J.; Integration of analytical measurements and wireless communications - Current issues and future strategies, *Talanta*, 2008, **75**, 606-612.
- (4) Byrne, R.; Diamond, D.; Chemo/bio-sensor networks, *Nat. Mater.*, 2006, **5**, 421-424.
- (5) Wang, Z.; Cook, M. J.; Nygrd, A.-M.; Russell, D. A.; Metal-Ion Chelation and Sensing Using a Self-Assembled Molecular Photoswitch, *Langmuir*, 2003, **19**, 3779-3784.
- (6) Willner, I.; Rubin, S.; Wonner, J.; Effenberger, F.; Baeuerle, P.; Photoswitchable binding of substrates to proteins: photoregulated binding of α -D-mannopyranose to concanavalin A modified by a thiophenfulgide dye, *J. Am. Chem. Soc.*, 1992, **114**, 3150-3151.
- (7) Phillips, J. P.; Mueller, A.; Przystal, F.; Photochromic chelating agents, *J. Am. Chem. Soc.*, 1965, **87**, 4020.
- (8) Taylor, L. D.; Nicholson, J.; Davis, R. B.; Photochromic chelating agents, *Tetrahedron Lett.*, 1967, 1585-1588.
- (9) Winkler, J. D.; Bowen, C. M.; Michelet, V.; Photodynamic Fluorescent Metal Ion Sensors with Parts per Billion Sensitivity, *J. Am. Chem. Soc.*, 1998, **120**, 3237-3242.
- (10) Shao, N.; Zhang, Y.; Cheung, S.; Yang, R.; Chan, W.; Mo, T.; Li, K.; Liu, F.; Copper Ion-Selective Fluorescent Sensor Based on the Inner Filter Effect Using a Spiropyran Derivative, *Anal. Chem.*, 2005, **77**, 7294-7303.
- (11) Stauffer, M. T.; Weber, S. G.; Optical Control of Divalent Metal Ion Binding to a Photochromic Catechol: Photoreversal of Tightly Bound Zn^{2+} , *Anal. Chem.*, 1999, **71**, 1146-1151.
- (12) Suzuki, T.; Kawata, Y.; Kahata, S.; Kato, T.; Photo-reversible Pb^{2+} -complexation of insoluble poly(spiropyran methacrylate-co-perfluorohydroxy methacrylate) in polar solvents, *Chem. Comm.*, 2003, 2004-2005.
- (13) Inouye, M.; Ueno, M.; Kitao, T.; Tsuchiya, K.; Alkali metal recognition induced isomerization of spiropyran, *J. Am. Chem. Soc.*, 1990, **112**, 8977-8979.
- (14) Radu, A.; Scarmagnani, S.; Byrne, R.; Slater, C.; Lau, K. T.; Diamond, D.; Photonic modulation of surface properties: a novel concept in chemical sensing, *J. Phys. D: Appl. Phys.*, 2007, **40**, 7238-7244.
- (15) Bakker, E.; Buehlmann, P.; Pretsch, E.; Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics, *Chem. Rev.*, 1997, **97**, 3083-3132.
- (16) Byrne, R. J.; Stitzel, S. E.; Diamond, D.; Photo-regenerable surface with potential for optical sensing, *J. Mater. Chem.*, 2006, **16**, 1332-1337.
- (17) McCoy, C. P.; Donnelly, L.; Jones, D. S.; Gorman, S. P.; Synthesis and characterisation of polymerisable photochromic spiropyran: towards photomechanical biomaterials, *Tetrahedron Lett.*, 2007, **48**, 657-661.
- (18) Bell, N. S.; Piech, M.; Photophysical effects between spirobenzopyran-methyl methacrylate-functionalized colloidal particles, *Langmuir*, 2006, **22**, 1420-1427.

- (19) Lau, K. T.; Baldwin, S.; Shepherd, R. L.; Dietz, P. H.; Yezunis, W. S.; Diamond, D.; Novel fused-LEDs devices as optical sensors for colorimetric analysis, *Talanta*, 2004, **63**, 167-173.
- (20) Lau, K.-T.; McHugh, E.; Baldwin, S.; Diamond, D.; Paired emitter-detector light emitting diodes for the measurement of lead(II) and cadmium(II), *Anal. Chim. Acta*, 2006, **569**, 221-226.
- (21) Garcia, A. A.; Cherian, S.; Park, J.; Gust, D.; Jahnke, F.; Rosario, R.; Photon-Controlled Phase Partitioning of Spiropyrans, *J. Phys. Chem. A*, 2000, **104**, 6103-6107.
- (22) Bletz, M.; Pfeifer-Fukumura, U.; Kolb, U.; Baumann, W.; Ground- and First-Excited-Singlet-State Electric Dipole Moments of Some Photochromic Spirobenzopyrans in Their Spiropyran and Merocyanine Form, *J. Phys. Chem.*, 2002, **106**, 2232-2236.
- (23) Bakker, E.; Qin, Y.; Electrochemical sensors, *Anal. Chem.*, 2006, **78**, 3965-3983.
- (24) Stitzel, S.; Byrne, R.; Diamond, D.; LED switching of spiropyran-doped polymer films, *J. Mater. Sci.*, 2006, **41**, 5841-5844.
- (25) Ipe, B. I.; Mahima, S.; Thomas, K. G.; Light-Induced Modulation of Self-Assembly on Spiropyran-Capped Gold Nanoparticles: A Potential System for the Controlled Release of Amino Acid Derivatives, *J. Am. Chem. Soc.*, 2003, **125**, 7174-7175.
- (26) Tomizaki, K. Y.; Mihara, H.; A novel fluorescence sensing system using a photochromism-based assay (P-CHROBA) technique for the detection of target proteins, *J. Mater. Chem.*, 2005, **15**, 2732-2740.
- (27) Demadrille, R.; Rabourdin, A.; Campredon, M.; Giusti, G.; Spectroscopic characterization and photodegradation studies of photochromic spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyrans], *J. Photochem. Photobiol., A*, 2004, **168**, 143-152.
- (28) Matsushima, R.; Nishiyama, M.; Doi, M.; Improvements in the fatigue resistances of photochromic compounds, *J. Photochem. Photobiol., A*, 2001, **139**, 63-69.
- (29) Arai, K.; Shitara, Y.; Ohyama, T.; Preparation of photochromic spiropyran linked to methyl cellulose and photoregulation of their properties, *J. Mater. Chem.*, 1996, **6**, 11-14.
- (30) Tork, A.; Boudreault, F.; Roberge, M.; Ritcey, A. M.; Lessard, R. A.; Galstian, T. V.; Photochromic behavior of spiropyran in polymer matrices, *Appl. Opt.*, 2001, **40**, 1180-1186.
- (31) Atabekyan, L. S.; Chibisov, A. K.; Complex formation of spiropyran with metal cations in solution: A study by laser flash photolysis, *J. Photochem.*, 1986, **34**, 323-331.
- (32) Grofcsik, A.; Baranyai, P.; Bitter, I.; Grun, A.; Koszegi, E.; Kubinyi, M.; Pal, K.; Vidoczy, T.; Photochromism of a spiropyran derivative of 1,3-calix[4]crown-5, *J. Mol. Struct.*, 2002, **614**, 69-73.
- (33) Zhou, J.; Zhao, F.; Li, Y.; Zhang, F.; Song, X.; Novel chelation of photochromic spironaphthoxazines to divalent metal ions, *J. Photochem. Photobiol., A*, 1995, **92**, 193-199.
- (34) Zhou, J.-W.; Li, Y.-T.; Song, X.-Q.; Investigation of the chelation of a photochromic spiropyran with Cu(II), *J. Photochem. Photobiol., A*, 1995, **87**, 37-42.
- (35) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.;

- Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian Inc: Wallingford CT, 2004.
- (36) Byrne, R.; Fraser, K. J.; Izgorodina, E.; MacFarlane, D. R.; Forsyth, M.; Diamond, D.; Photo- and solvatochromic properties of nitrobenzospiropyran in ionic liquids containing the [NTf₂]⁽⁻⁾ anion, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5919-5924.
- (37) Zhang, L.; Peslherbe, G. H.; Muchall, H. M.; Ultraviolet absorption spectra of substituted phenols: A computational study, *Photochem. Photobiol.*, 2006, **82**, 324-331.
- (38) Krygowski, T. M.; Szatyłowicz, H.; Zachara, J. E.; How H-Bonding Affects Aromaticity of the Ring in Variously Substituted Phenol Complexes with Bases. 4. Molecular Geometry as a Source of Chemical Information, *J. Chem. Inf. Comput. Sci.*, 2004, **44**, 2077-2082.
- (39) Radu, A.; Scarmagnani, S.; Byrne, R.; Slater, C.; Alhashimy, N.; Diamond, D.; Photoswitchable surfaces: A new approach to chemical sensing, *Remote Sensing for Environmental Monitoring, Gis Applications, and Geology VII*, 2007, **6749**, Z7491-Z7491.
- (40) Yang, R.; Li, K. a.; Wang, K.; Zhao, F.; Li, N.; Liu, F.; Porphyrin assembly on β-cyclodextrin for selective sensing and detection of a zinc ion based on the dual emission fluorescence ratio, *Anal. Chem.*, 2003, **75**, 612-621.