

## EXPERIMENTAL SUPPLEMENTARY INFORMATION

### Sensor Technologies Based on a Cellulose Supported Platform

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**Materials.** The ligand, 1-(2-pyridylazo)-2-naphthol (PAN), was obtained from Lancaster (Windham, NH). All other chemicals (unless otherwise noted) were obtained from Aldrich (Milwaukee, WI). Solvents were of reagent grade, and used without further purification. Aqueous solutions were prepared in deionized water that was polished to 18.3 MΩ cm with a Barnstead deionization system (Dubuque, IA). A series of Hg(II) stock solutions were prepared by weighing out an appropriate amount of Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O and dissolving it in 0.01 M HNO<sub>3</sub>. NaOAc/HOAc buffered solutions were prepared using reported methods.<sup>1</sup> The pH of all buffers and solutions were verified using a 220 Corning pH meter obtained from Corning Incorporated Science Products Division (Corning, NY). The ruthenium based dye N621, *cis*-dithiocyanatobis-2,2'-(bipyridine-4,4'-(COOH)<sub>2</sub>-4,4'-tridecyl-2,2'-bipyridineruthenium(II) ([Ru(dcbpyH)-(tdbpy)(NCS)<sub>2</sub>]), was obtained from the Grätzel research group at EPFL in Lausanne, Switzerland, where it was synthesized.

**Preparation of Ionic Liquid.** The ionic liquid (IL) 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim]Cl) was synthesized using previously described methods.<sup>2</sup> To ensure purity (i.e., complete reaction) the IL was analyzed using a Bruker NMR (<sup>1</sup>H at 360 MHz). The <sup>1</sup>H NMR spectrum of [C<sub>4</sub>mim]Cl contained peaks corresponding to the cation, and indicated no residual reactants. The dry IL was a white crystalline solid at room temperature.

**Cellulose Dissolution.** All studies were carried out using microcrystalline cellulose (MCC) as purchased, with no pretreatment. To a vial was added 16.00 g of [C<sub>4</sub>mim]Cl, then heated by microwave irradiation (Samsung domestic microwave, Model MU4290W, 700 W ) with 2-3 s pulses for 1 min to reduce the viscosity of the IL. MCC was weighed out (1.60 g) as 10% (w/w) with respect to the IL and added to the vial with vigorous stirring. The MCC-IL mixture was irradiated again with 2-3 s microwave pulses for 1-2 min to dissolve the cellulose, with vigorous stirring between each pulse. The mixture was then centrifuged (2000 g, 2 min), and the liquid cellulose solution decanted off in order to remove any non-dissolved cellulose.

**Sensor Preparation.** PAN in cellulose composites were prepared by first dissolving the cellulose in the IL as described above. The cellulose solution was allowed to cool slightly (~70 °C), whereupon 0.08 g of PAN were weighed out as 5% (w/w) with respect to the cellulose concentration in the cellulose/IL solution. The resultant solution was then stirred vigorously to ensure a homogenous distribution of PAN throughout the cellulose/IL solution.

The PAN/cellulose/IL solution was poured in a thick line (1.5 cm x 6 cm) from the vial onto a clean glass plate and was cast into a thin film using coating rods obtained from R&D Specialties (Webster, NY). The solution was pulled by hand across the plate in one direction with the coating rod using even pressure, yielding films of even thickness. After casting, the films were washed with copious amounts of deionized water in order to remove the water soluble [C<sub>4</sub>mim]Cl. The film was free from visible particles, orange in color, and opaque. After washing of the film was complete, strips (1.5 cm x 3 cm) were cut from the cast sheet, and stored in deionized water to prevent them from drying.

N621 was synthesized in the Grätzel laboratory as previously described.<sup>3</sup> Because the dye is not readily soluble in [C<sub>4</sub>mim]Cl, the procedure for its encapsulation in cellulose is slightly different than for the PAN-based films. Cellulose dissolution in the IL was carried out identically as in the previous PAN sensor, however, the amount of N621 was calculated and weighed as 1% (w/w) with respect to the mass of cellulose used in the cellulose/IL solution (0.016 g N621). Dichloromethane was added dropwise to the dye and stirred vigorously to fully dissolve the dye. A small portion (1.60 g) of [C<sub>4</sub>mim]Cl was then added to the CH<sub>2</sub>Cl<sub>2</sub>/N621 solution and stirred vigorously to ensure incorporation of the dissolved dye into the IL, and then gently heated with a heat gun to evaporate the dichloromethane, leaving a solution of dissolved N621 in [C<sub>4</sub>mim]Cl. This solution was then combined with the remaining [C<sub>4</sub>mim]Cl and the previously weighed cellulose. The combined solution was vigorously stirred and irradiated with 2-3 s microwave pulses for 1-2 min with stirring between each pulse. This yielded a translucent, red-orange viscous solution. The N621/cellulose/IL solution was poured in a thick line (1.5 cm x 6 cm) onto a clean glass plate and was cast, washed, and cut into thin sensor films as in the PAN/cellulose sensors.

**Hg(II) Solution Preparation.** A stock solution of 1000 ppm of Hg(II) solution from Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O was prepared by dissolving an appropriate amount of metal salt in 0.01 M HNO<sub>3</sub>. Standards of lower concentration were prepared by dilution from this 1000 ppm stock solution with the acetate buffer. To study pH effects on sensor performance, buffered solutions of 50 ppm aqueous Hg(II) were prepared at pH values of 3.4, 4.0, 4.5, 5.0, 5.5, 5.9, 6.5, and 7.2. Acetate buffers were prepared with sodium acetate (NaOAc) and acetic acid (HOAc) and diluted with deionized water as follows: 0.50 mL 2M NaOAc and 9.50 mL 2M HOAc diluted to 100 mL (pH 3.4); 1.85 mL 2M NaOAc and 8.15 mL 2M HOAc diluted to 100 mL (pH 4.00); 4.15 mL 2M NaOAc and 5.85 mL 2M HOAc diluted to 100 mL (pH 4.5); 6.95 mL 2M NaOAc and 3.05 mL 2M HOAc diluted to 100 mL (pH 5.0); 8.75 mL 2M NaOAc and 1.25 mL 2M HOAc diluted to 100 mL (pH 5.5), and 9.50 mL 2M NaOAc and 0.50 mL 2M HOAc diluted to 100 mL (pH 5.9). Phosphate buffers were prepared with NaOH and KH<sub>2</sub>PO<sub>4</sub> and diluted with deionized water as follows: 13.9 mL 0.1M NaOH and 50 mL 0.1M KH<sub>2</sub>PO<sub>4</sub> diluted to 100 mL (pH 6.5); and 46.1 mL 0.1M NaOH and 50 mL 0.1M KH<sub>2</sub>PO<sub>4</sub> diluted to 100 mL (pH 7.2).

**Preparation of Cu(II), Zn(II), and Zn(II)/Hg(II) Solutions.** A series of aqueous buffered solutions of Cu(II) (as CuCl<sub>2</sub>) and Zn(II) (as ZnSO<sub>4</sub>), and also of Zn(II)/Hg(II) (as ZnSO<sub>4</sub>/Hg(NO<sub>3</sub>)<sub>2</sub>) were prepared. A similar NaOAc/HOAc buffer was used, but at pH 5.9 rather than pH 5.5. This buffer was prepared by mixing 47.5 mL 2M NaOAc with 2.5 mL 2M HOAc and diluting to 500 mL with deionized water. Cu(II) standard solutions were prepared by dissolving appropriate amount of CuCl<sub>2</sub> in buffer: 5.29 mg in 100 mL of buffer (25 ppm); 10.58 mg in 100 mL of buffer (50 ppm); and 21.16 mg in 100 mL of buffer (100 ppm). Likewise, the Zn(II) standard solutions were prepared by dissolving ZnSO<sub>4</sub> in the buffer solution: 6.09 mg in

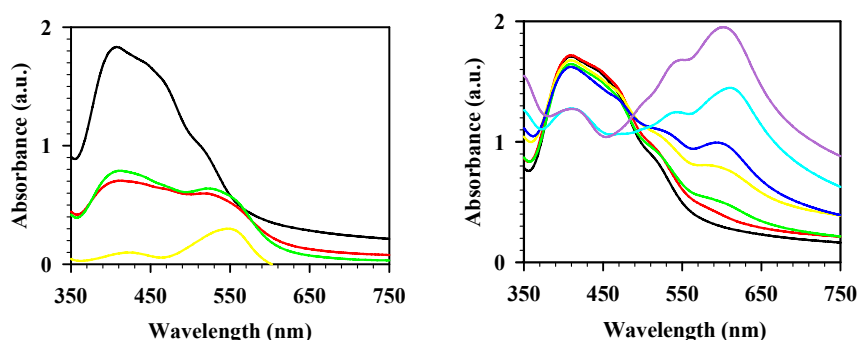
100 mL of buffer (25 ppm); 12.19 mg in 100 mL of buffer (50 ppm); and 24.39 mg in 100 mL of buffer (100 ppm).

Additionally, buffered (pH 5.9) Zn(II)/Hg(II) solutions were prepared from ZnSO<sub>4</sub> and Hg(NO<sub>3</sub>)<sub>2</sub>: 2.5 mL 1000 ppm Hg(NO<sub>3</sub>)<sub>2</sub> stock solution and 6.09 mg ZnSO<sub>4</sub> were diluted to 100 mL with buffer (25 ppm Hg(II)/25 ppm Zn(II)); 2.5 mL 1000 ppm Hg(NO<sub>3</sub>)<sub>2</sub> stock solution and 12.19 mg ZnSO<sub>4</sub> diluted to 100 mL with buffer(25 ppm Hg(II)/50 ppm Zn(II)); 2.5 mL 1000 ppm Hg(NO<sub>3</sub>)<sub>2</sub> stock solution and 24.39 mg ZnSO<sub>4</sub> diluted to 100 mL with buffer (25 ppm Hg(II)/100 ppm Zn(II)); 5.0 mL 1000 ppm Hg(NO<sub>3</sub>)<sub>2</sub> stock solution and 6.09 mg ZnSO<sub>4</sub> diluted to 100 mL with buffer (50 ppm Hg(II)/25 ppm Zn(II)); and 10 mL 1000 ppm Hg(NO<sub>3</sub>)<sub>2</sub> stock solution and 6.09 mg ZnSO<sub>4</sub> diluted to 100 mL with buffer (100 ppm Hg(II)/25 ppm Zn(II)).

**Testing PAN Sensors.** The PAN/cellulose films (except for a blank) were exposed to buffered Hg(II) 50 ppm solutions at pH 3.4, 4.0, 4.5, 5.0, 5.5, 5.9, 6.5 and 7.2 for 10 min after which they were removed and their UV-visible absorbance spectra (Varian Optical Cary 3C UV-visible spectrophotometer; Mulgrave, Australia) recorded for the reacted and unreacted films. Spectra were collected by mounting the films on glass microscope slides after the baseline absorbance of the microscope slide was subtracted. The wet films adhered easily to the glass slides. It was determined that the lowest optimum pH was 5.5, and all subsequent studies were carried out in buffered solutions of pH 5.5.

A series of Hg(II) solutions of concentrations 5, 10, 25, 50, 75, and 100 ppm were prepared by dilution from the 1000 ppm stock solution with the pH 5.5 acetate buffer. PAN films were allowed to soak in the solution for 10 min, after which their UV-visible absorbance spectra were measured as described above. Complex formation was achieved within 1-10 min, depending on the concentration of Hg(II) in the aqueous solution. For higher concentrations of Hg(II), a visual color change was observed almost immediately. At lower concentrations of Hg(II), a visual color change could be observed after approximately 5 min contact time.

**Selectivity and Competition Studies.** The PAN sensors were tested for their selectivity for Hg(II) by exposure to aqueous buffered solutions of Cu(II) and Zn(II), and also of buffered Zn(II)/Hg(II) mixtures. PAN films were allowed to soak in the Cu(II) standard solutions of concentration 25, 50, and 100 ppm for 10 min and their UV-visible spectra was measured following the same procedure described as before. The absorbance spectra for the Cu(II)-reacted films (Figure 1) show that the PAN complexes with Cu(II). A peak is seen growing in near 540 nm with an increase in Cu(II) concentration, while the peak near 400 nm for uncomplexed PAN decreases.

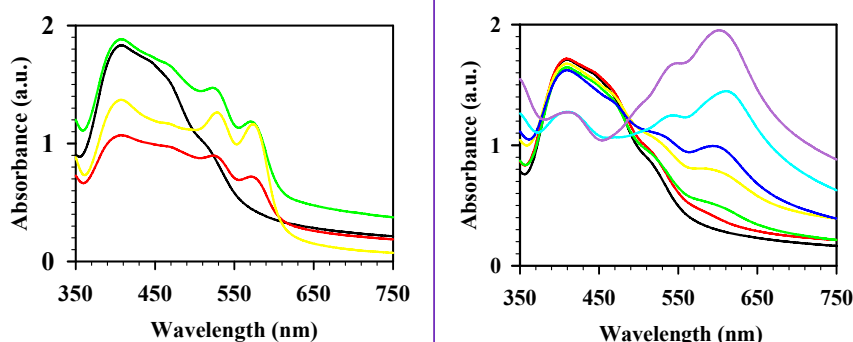


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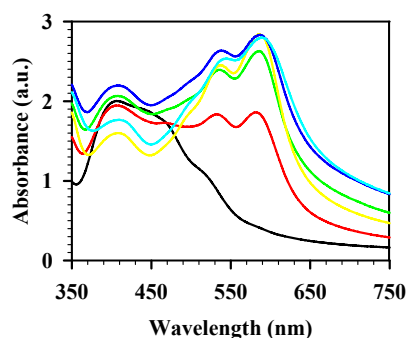
**Figure 1.** Left: Absorbance spectra of buffered Cu(II) solutions: (black blank PAN film; red 25 ppm; green 50 ppm; yellow 100 ppm). Right: Absorbance spectra after contact with solutions of varying concentrations of Hg(II) (black blank; red 5 ppm; green 10 ppm; yellow 25 ppm; blue 50 ppm; cyan 75 ppm; purple 100 ppm).

The PAN sensors were allowed to soak in Zn(II) solutions of concentration 25, 50, and 100 ppm for 10 min and their UV-visible spectra was measured following the same procedure described earlier. The absorbance spectra for the Zn(II) solutions (Figure 2) show that the PAN does complex with the Zn(II): two peaks grow in around 520 nm and 565 nm with an increase in Zn(II) concentration, while the peak near 400 nm for uncomplexed PAN decreases.



**Figure 2.** Left: Absorbance spectra of buffered Zn(II) solutions (black blank PAN film; red 25 ppm; green 50 ppm; yellow 100 ppm). Right: Absorbance spectra after contact with solutions of varying concentrations of Hg(II) (black blank; red 5 ppm; green 10 ppm; yellow 25 ppm; blue 50 ppm; cyan 75 ppm; purple 100 ppm).

To investigate competition for complexation with PAN between Hg(II) and Zn(II), the PAN films were exposed to buffered Hg(II)/Zn(II) solutions, and their UV-visible absorbance spectra measured (Figure 3). The spectra show that the PAN does not selectively complex with one metal over the other; it appears as if the spectra for the two metals were added together. The 'double peak' seen for Zn(II) appears, but as Hg(II) concentration increases, the peak near 600 nm grows larger and dominates the spectra.



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**Figure 3.** Absorbance spectra of solutions of varying concentrations of Hg(II) and Zn(II) (black blank PAN film; red 25 ppm Hg/25 ppm Zn; green 25 ppm Hg/50 ppm Zn; yellow 25 ppm Hg/100 ppm Zn; blue 50 ppm Hg/25 ppm Zn; cyan 100 ppm Hg/25 ppm Zn).

**Testing N621 Sensors.** Initial tests of N621-based sensors show that the Hg(II) complexed dye is not affected by its encapsulation within the cellulose matrix. N621 sensors were prepared as described above and N621 sensitized TiO<sub>2</sub> sensors were prepared by the Grätzel group as previously described.<sup>3</sup> In each set of sensors, one cellulose sensor was exposed to a 50 ppm aqueous solution of Hg(II) for 10 min, and one sensor was left unreacted. As can be seen from Figure 6 (left) in the main manuscript, the color change for both sets is identical. This shows that, at least visually, the encapsulation of N621 in cellulose does not interfere in its complexation with Hg(II).

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<sup>1</sup> D. D. Perrin, B. Dempsey, *Buffers for pH and Metal Ion Control*; John Wiley & Son: New York, 1974; p 134.

<sup>2</sup> J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, *Chem. Comm.*, 1998, **16**, 1765.

<sup>3</sup> M. K. Nazeeruddin, D. Di Censo, R. Humphrey-Baker, M. Grätzel, *Adv. Funct. Mater.*, 2006, **16**, 189.