

Dye-free, simultaneous multianalyte optical recognition using ionic liquid-based polymeric membrane

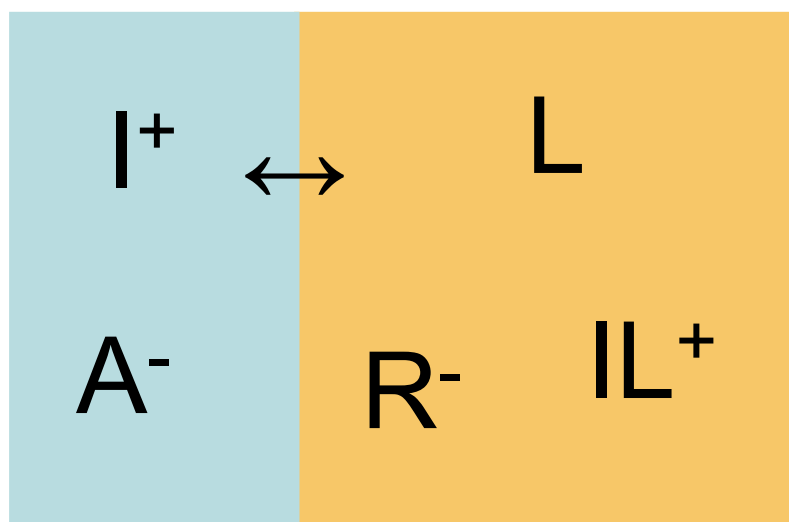
AsiaSense 2009

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Outline

- Ionophore-based chemical sensors
 - Basic principles
 - Potentiometric sensors
 - optical sensors
- Ionic liquids in chemical sensors
 - Dye-free simultaneous multianalyte recognition
 - Characterization (IR, Raman, UVVIS, response time)
- Conclusions
- Future work

Chemical sensors with potentiometric detection - Ion Selective Electrodes (ISEs)



E_{PB}



$$E_{PB} = \frac{RT}{z_I F} \ln \left(\frac{k_I \beta_{IL} [L] a_{I,aq}}{[IL^+]_{org}} \right)$$

ISEs measure activity NOT total concentration!

Potentiometric sensors

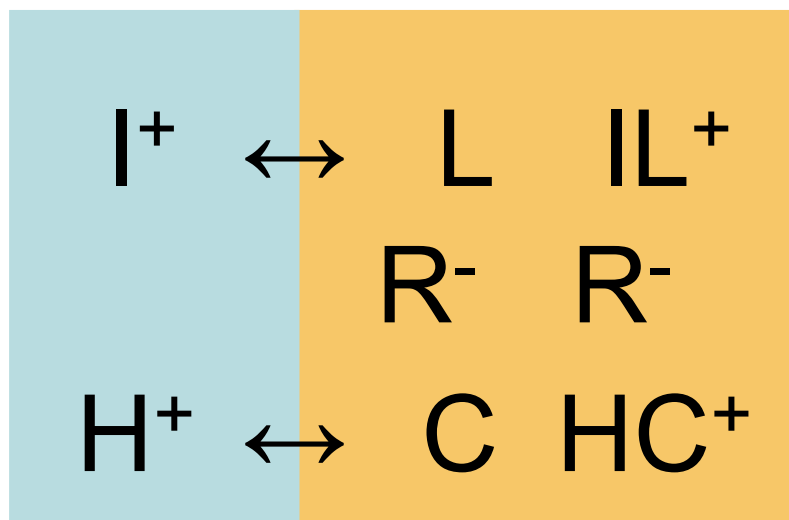
method/ion	ICPMS	AAS	ISE	EPA
Ag ⁺	0.005	1.5	0.03 ¹	50
Ca ²⁺	0.5	1.5	0.04 ²	
Cd ²⁺	0.005	0.8	0.01 ³	10
ClO ₄ ⁻			3 ⁴	1*
Cs ⁺	0.01	5	1 ⁵	
Cu ²⁺	0.005		0.01 ⁶	1300
I ⁻	1		0.25 ⁴	
K ⁺	0.5	3	0.2 ⁷	
Na ⁺	0.05	1	0.7 ⁸	
NH ₄ ⁺			0.2 ⁷	100**
Pb ²⁺	0.001	15	0.001 ⁹	50
Vitamin B1			3.3 ¹⁰	

* suggested

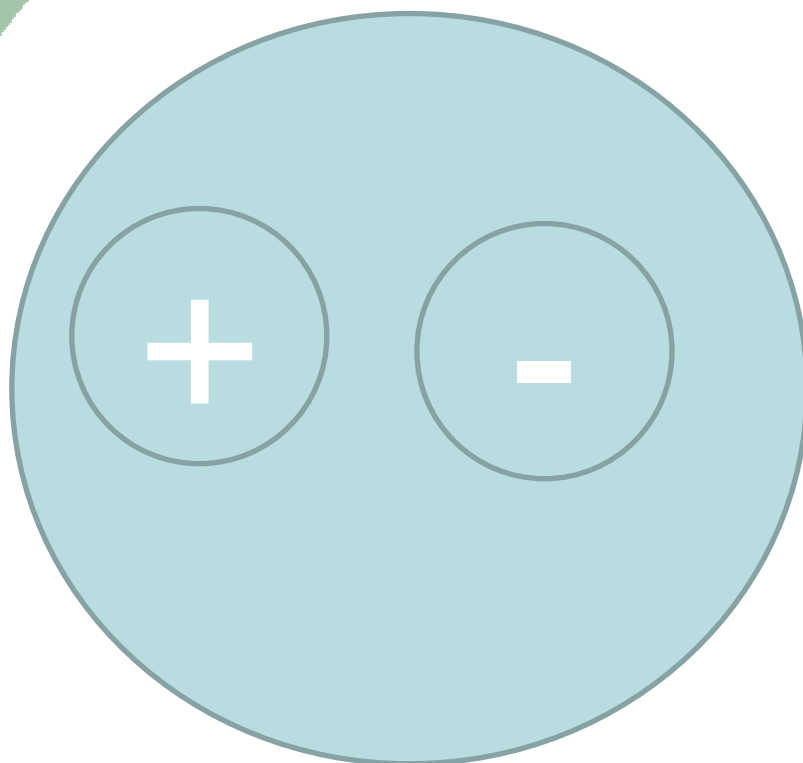
** (depending on pH and T)


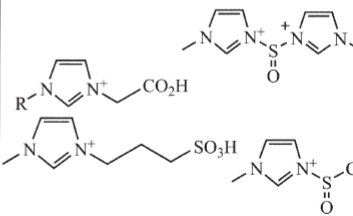
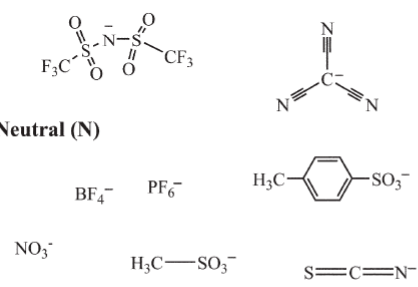
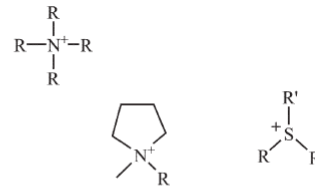
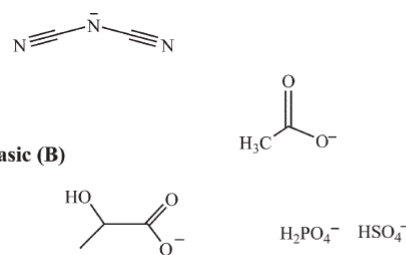
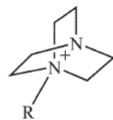
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2. Radu A., Peper S., Bakker E., Diamond; *Electroanalysis*, **2006**, 18, 1379-1388
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Chemical sensors with optical detection - optodes



Ionic liquids



Anion	Cation
H_2PO_4^- HSO_4^- amphoteric	 protonated cations
Acidic (A)	
	
	
Basic (B)	

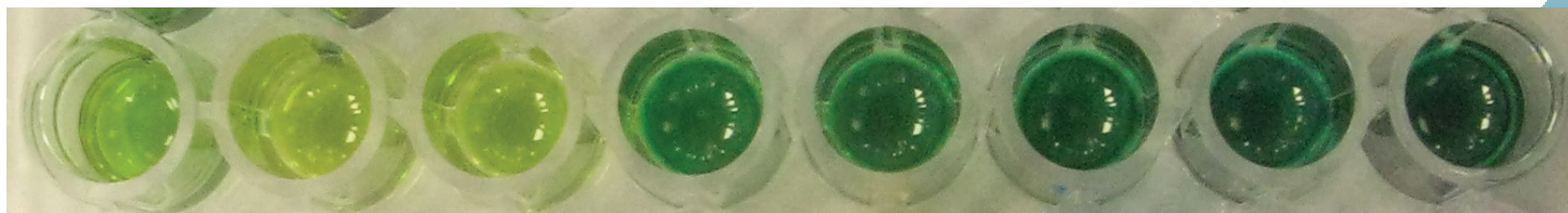
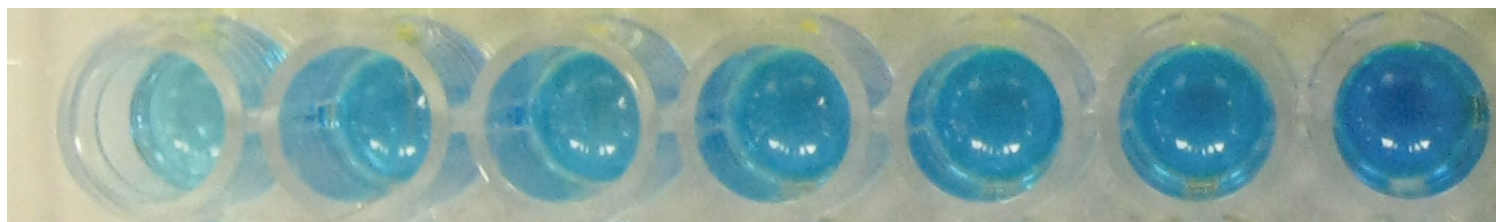
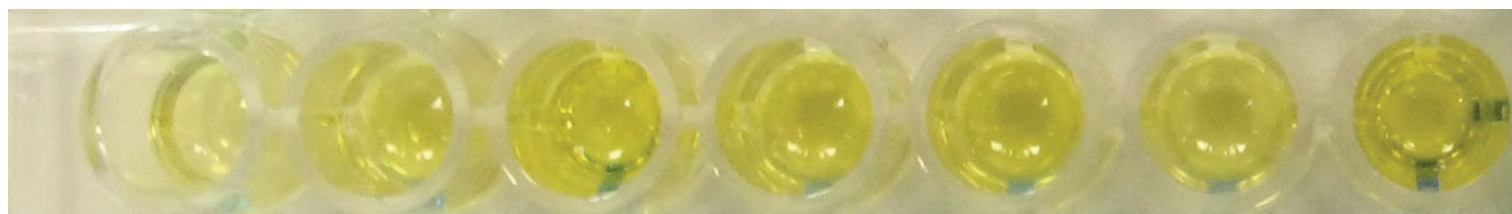
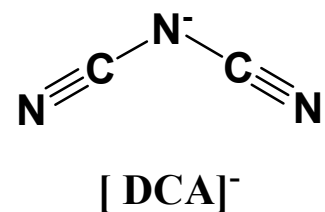
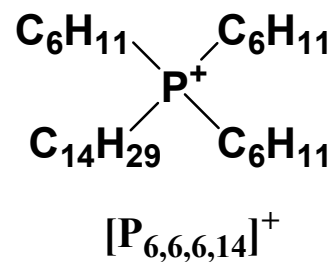
Ionic Liquids

- Almost negligible vapour pressure
- Non-flammable
- Good solubility for inorganic and organic compounds
 - Solvents
 - Matrixes
 - Sample preparation
 - Separation
- Sensors
 - Use of ILs is starting to emerge
 - Plasticizers (ionophore-based sensors)
 - Matrixes (QCM - change in viscosity due to solubilization)

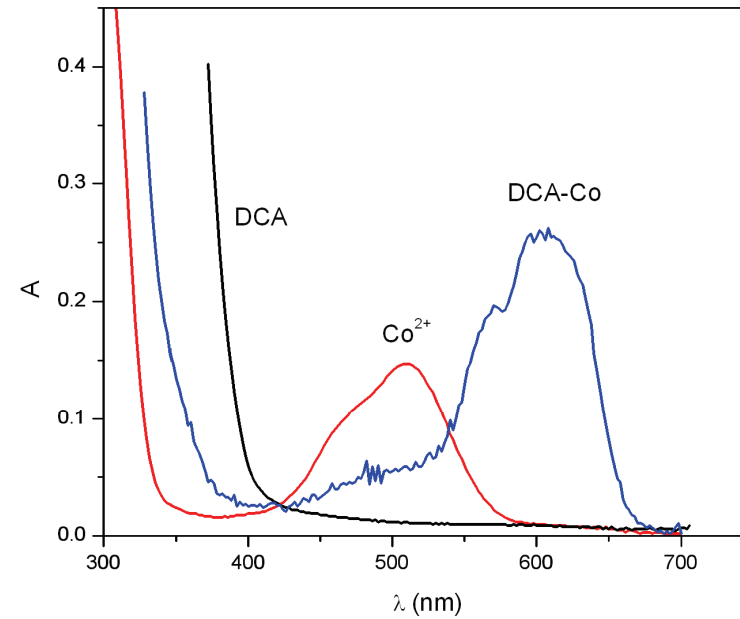
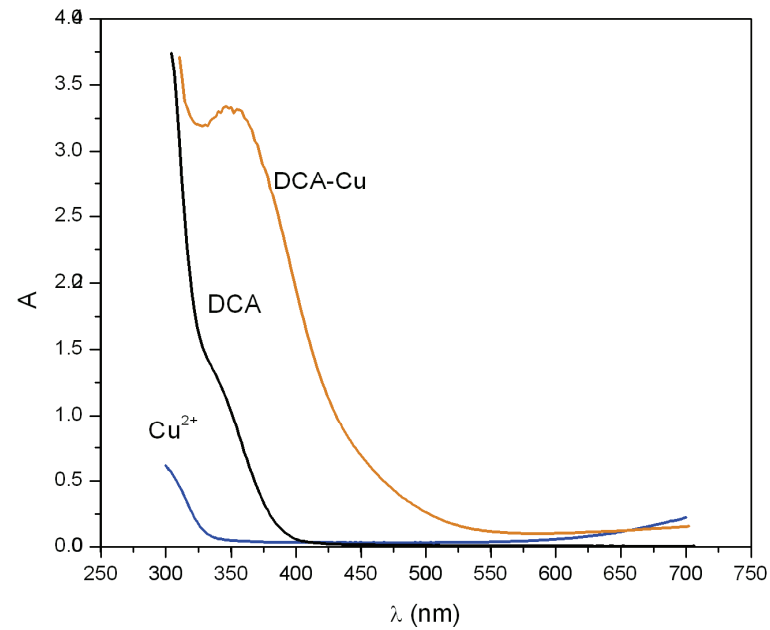
ILs as ligands?

- PVC-IL is the most simple chemical sensor (no leaching of the components)
- Combinations are endless (both cation- and anion-based combinations serving as ligands)
- Self-indicating
- Allows printing of thin yet sensitive films
- Simultaneous multianalyte analysis

ILs as ligands



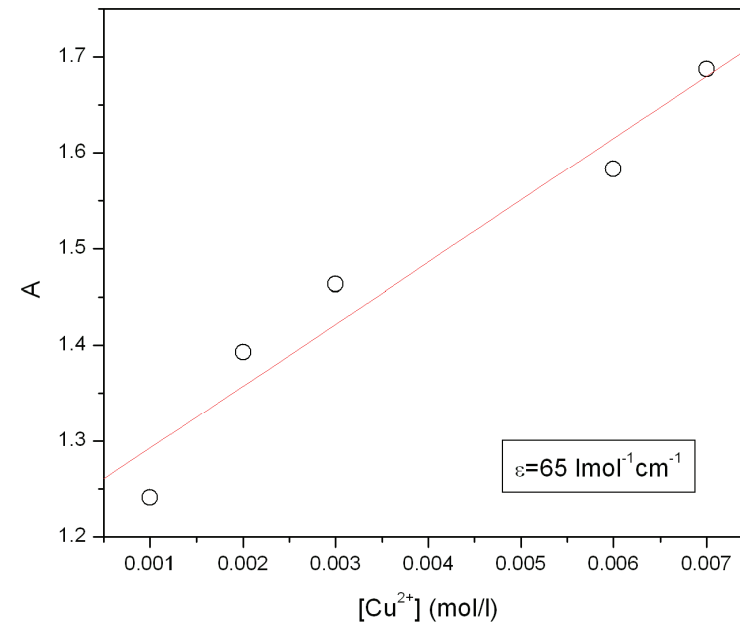
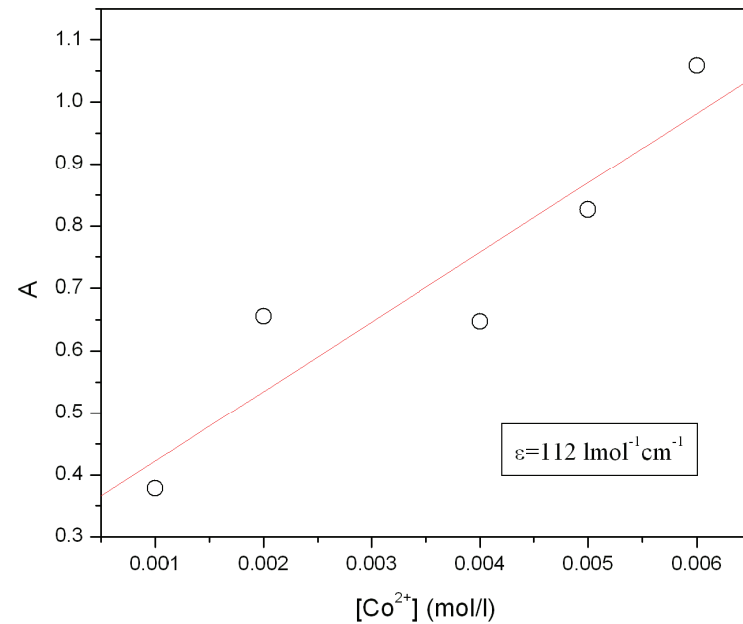
DCA + ions



No interferences

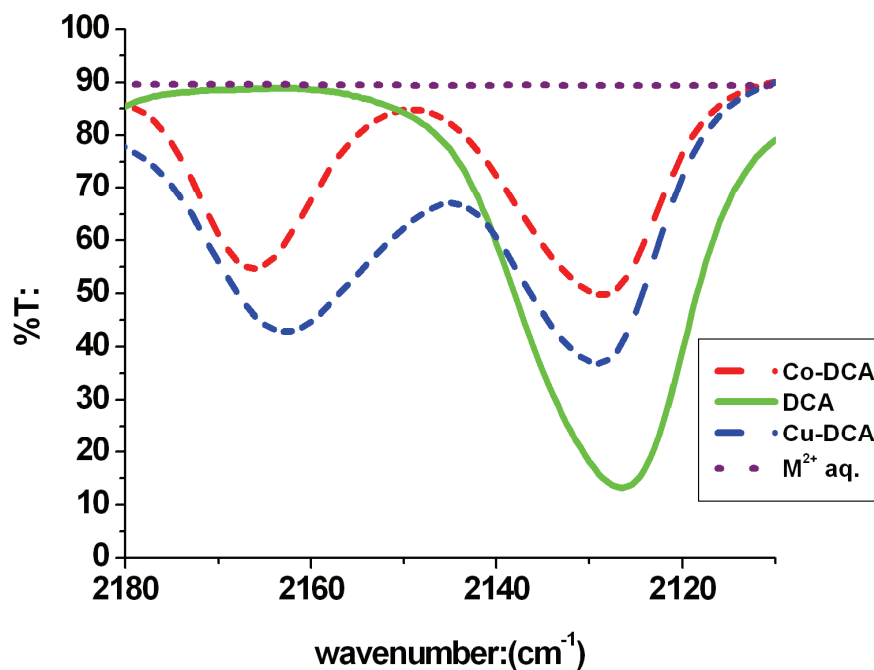
Ni²⁺, H⁺, Na⁺, K⁺

Individual calibration

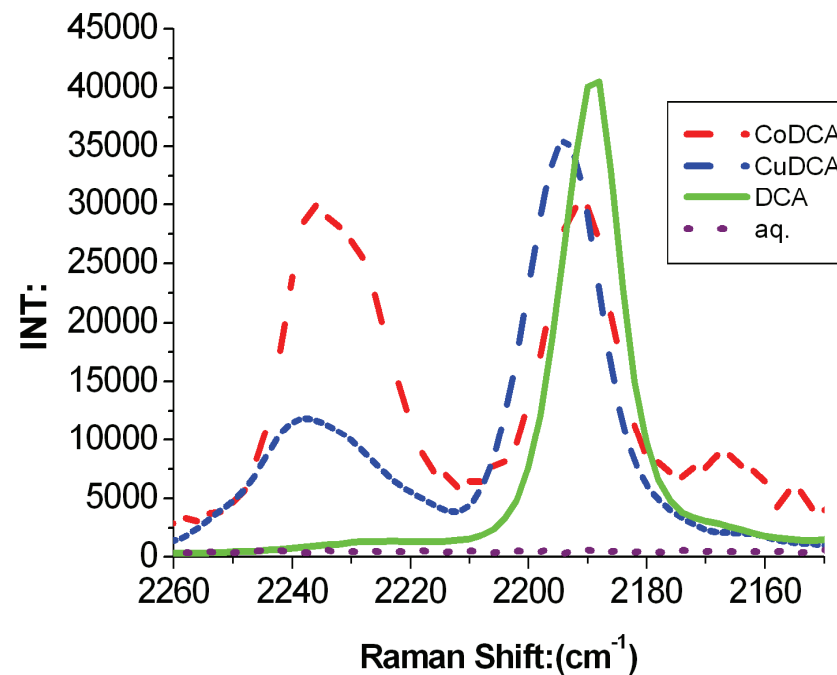


Structural characterization

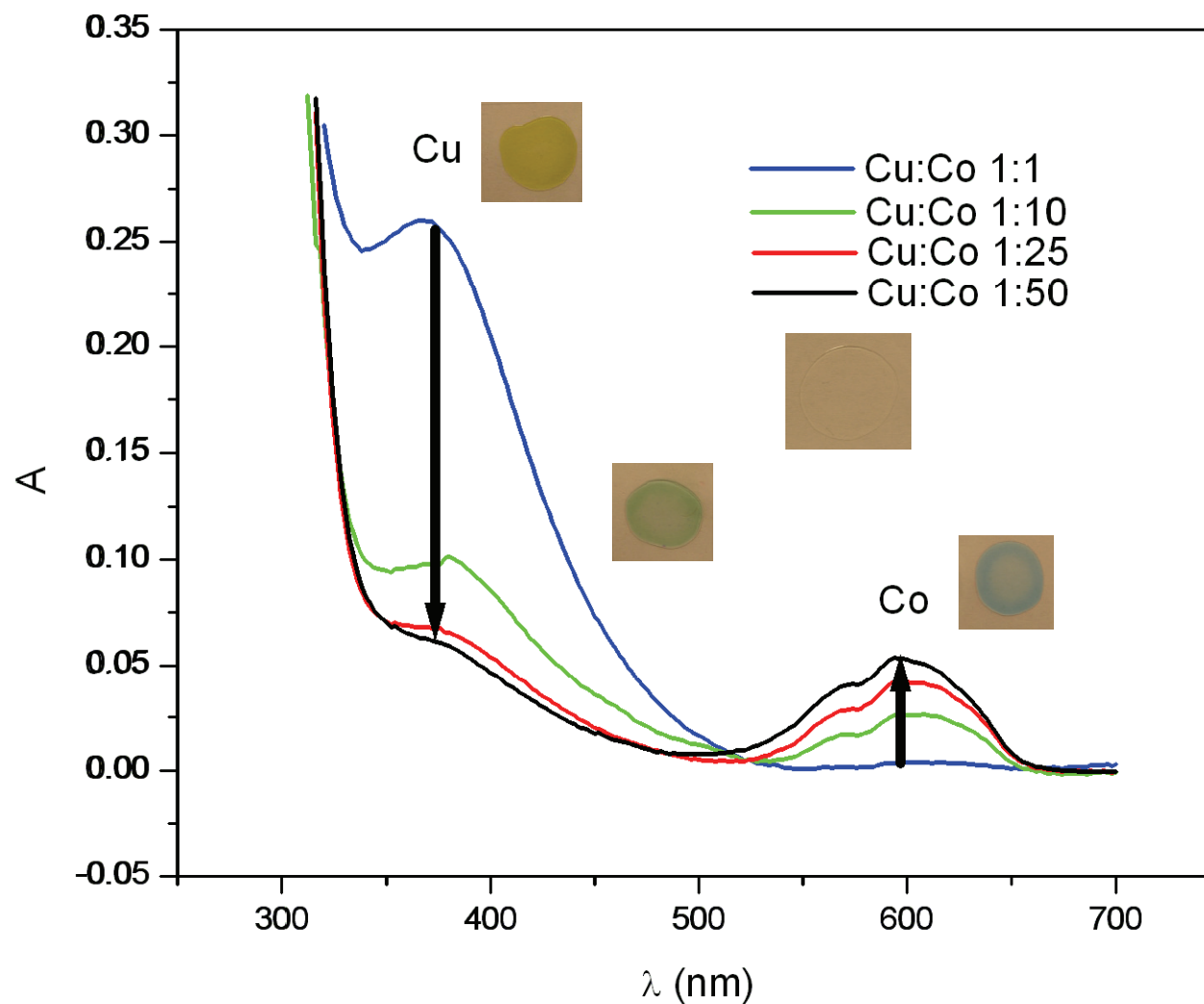
IR



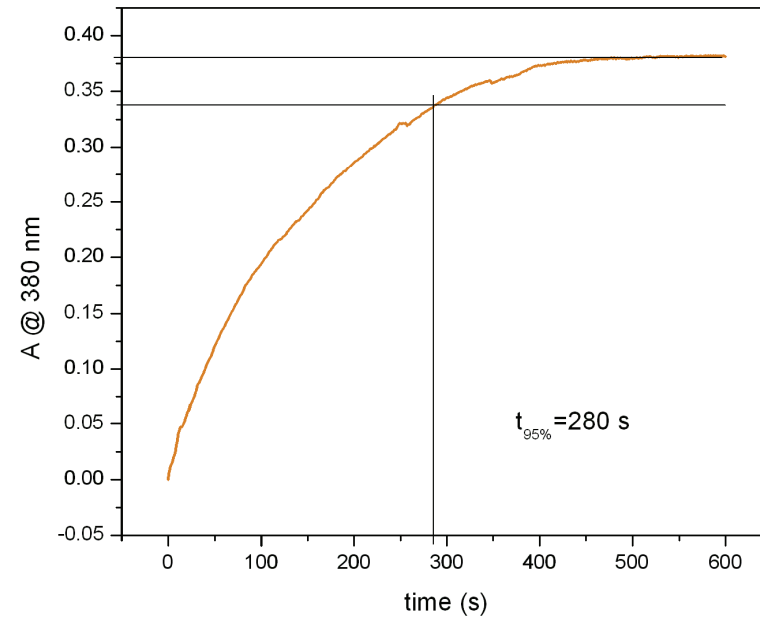
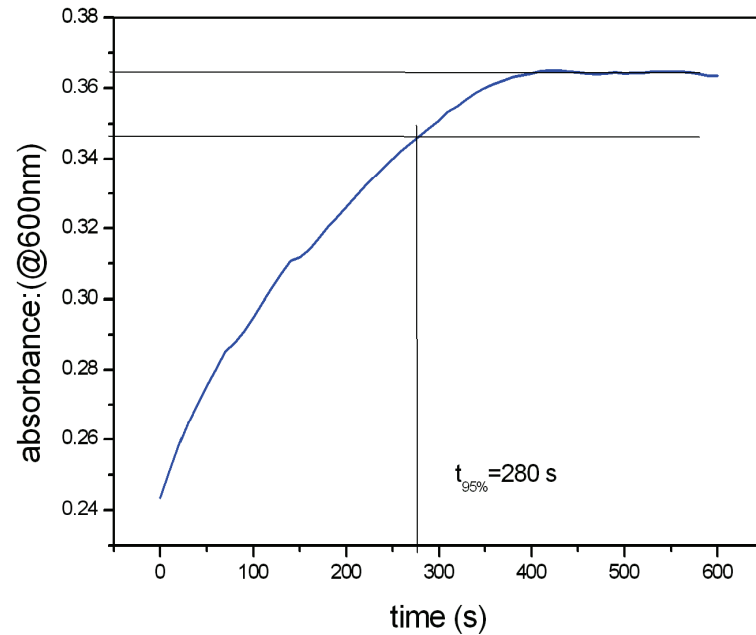
Raman



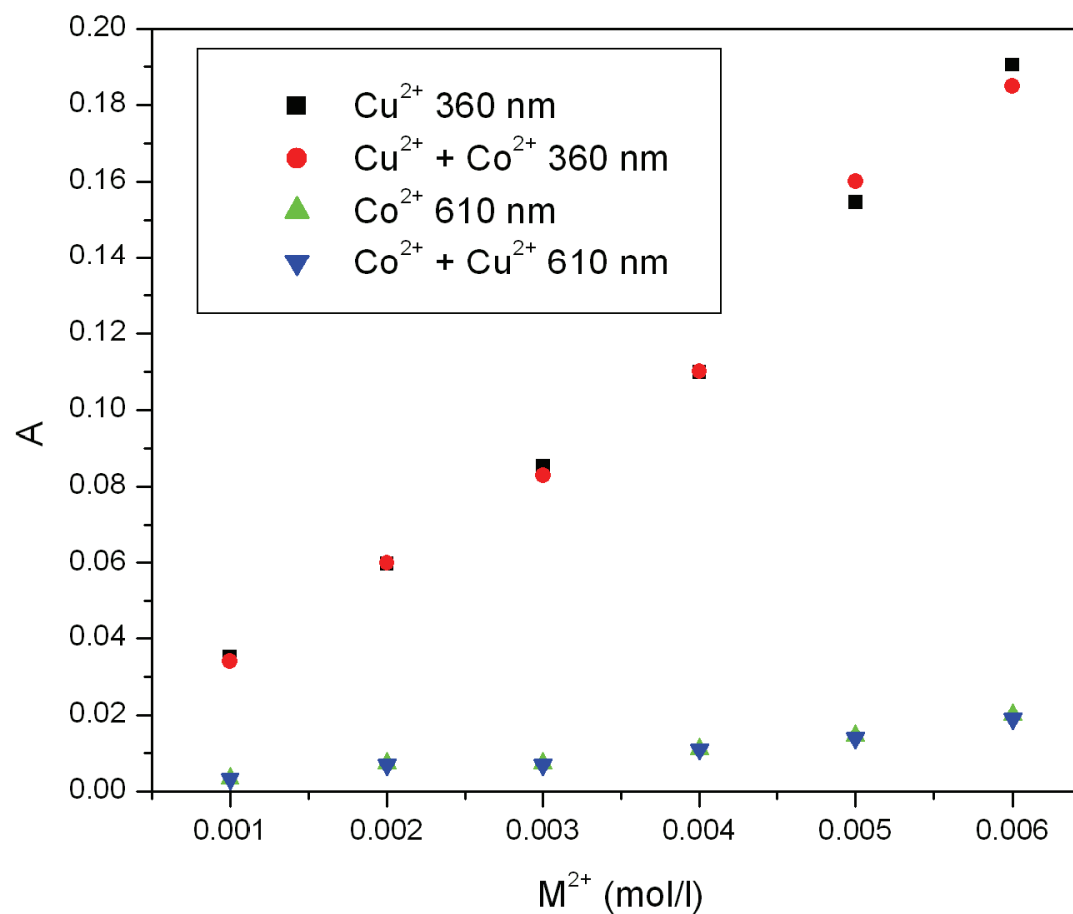
Simultaneous multianalyte recognition



Response time



Simultaneous multianalyte recognition



Conclusions

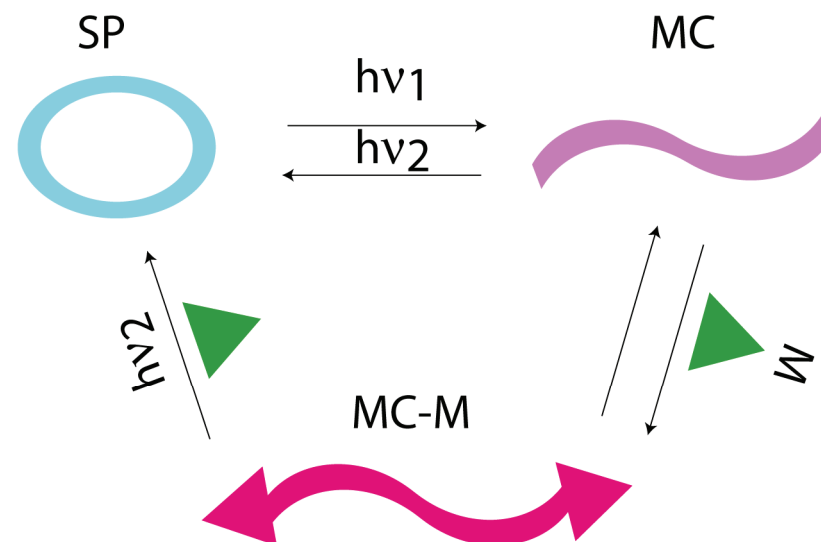
- Anions in IL can behave as ligands - utilization in chemical sensors
- Fast response time
- DCA simultaneously binds Cu^{2+} and Co^{2+} with development of distinct colours - simultaneous, multianalyte recognition
- Synthesis of IL of interest fairly easy - can an ionophore be an anion?

Acknowledgments

- Andrew Kavanagh
- Dr. Robert Byrne
- Prof. Dermot Diamond



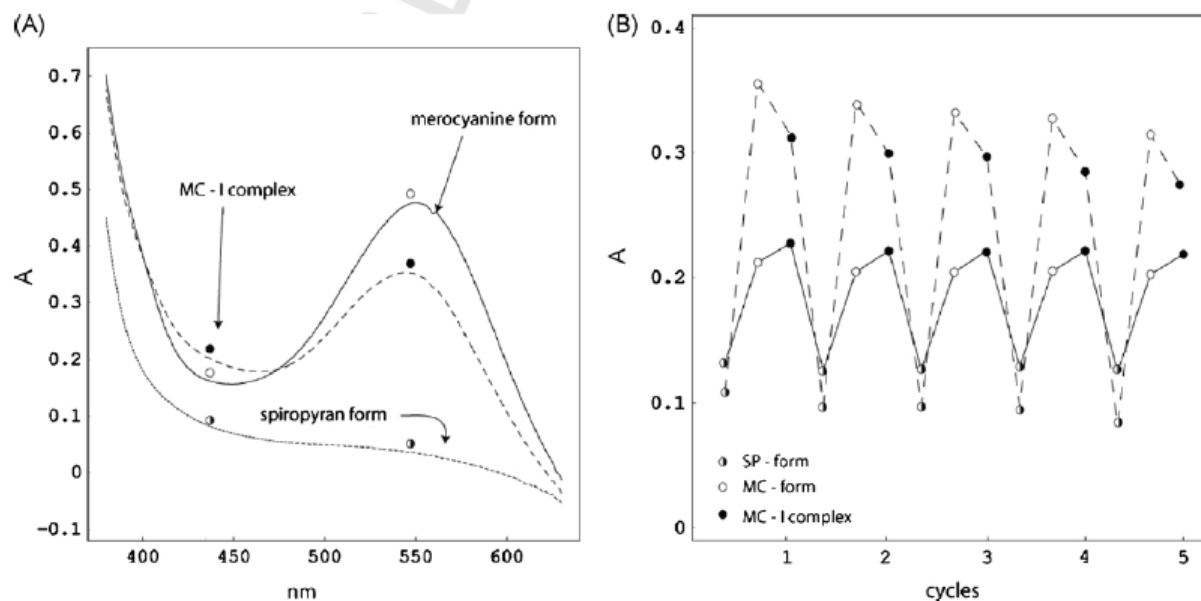
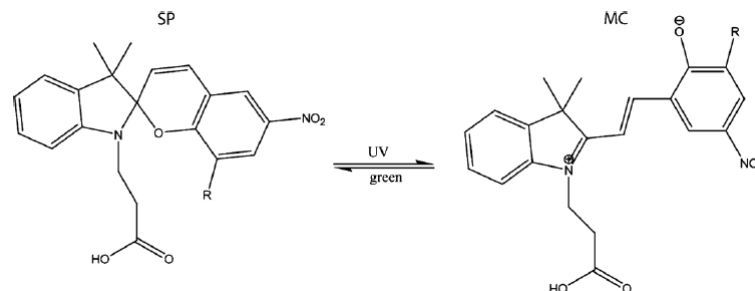
Optical sensors with “smart” ligands



Radu et al. “Photonic Modulation of Surface Properties: A Novel Concept In Chemical Sensing”; *J.Phys. D: Appl. Phys.* 40, **2007**, 7238-7244

This work is supported by Science Foundation Ireland under grant 07/CE/I1147

Optical sensors with “smart” ligands



Radu et al. “Spiropyran-based reversible, light-modulated sensing with reduced photofatigue”; *J.Photochem. Photobiol. A: Chem*, **2009**, In press

$$a_I = (zK_{\text{exch}}^{IL_n})^{-1} \left(\frac{\alpha}{1-\alpha} a_H \right)^z \times \frac{R_T^- - (1-\alpha)C_T}{\{L_T - (R_T^- - (1-\alpha)C_T) \frac{1-\alpha}{\alpha}\}}$$

