



Reversible photo-responsive hydrogels based on spiropyran

Larisa Florea

Dublin City University

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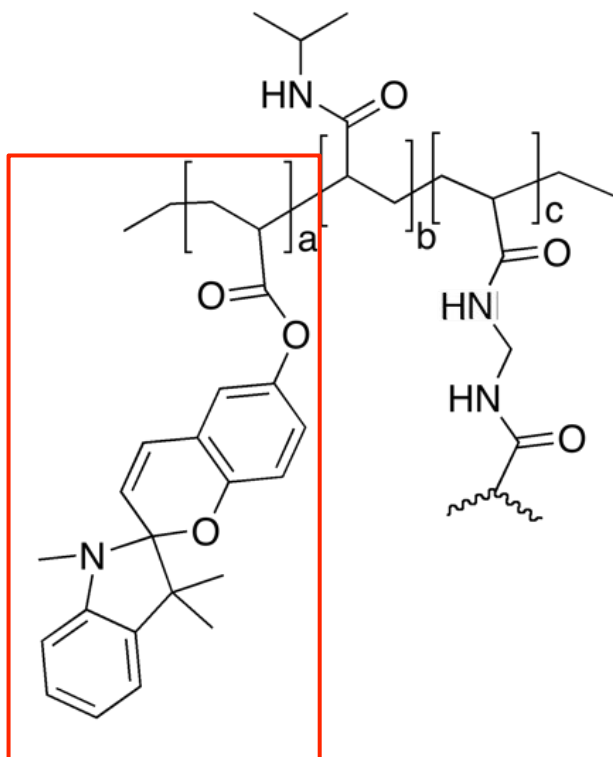


Background

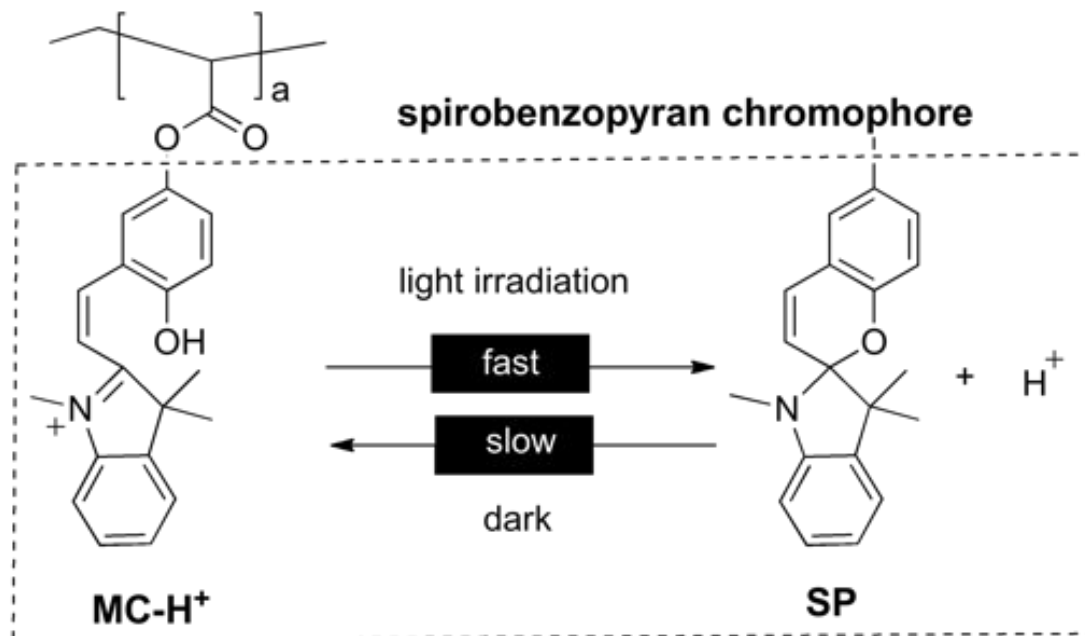
Self-protonating photo-responsive hydrogels

- Hydrogel fabrication
- Characterization
- Optimisation of hydrogel composition
- Photo-actuation properties
- Photo-induced shrinking and reswelling behaviour
- Porous hydrogels for improved reswelling kinetics

Conclusions



- Spiropyran – Photochromic behaviour**

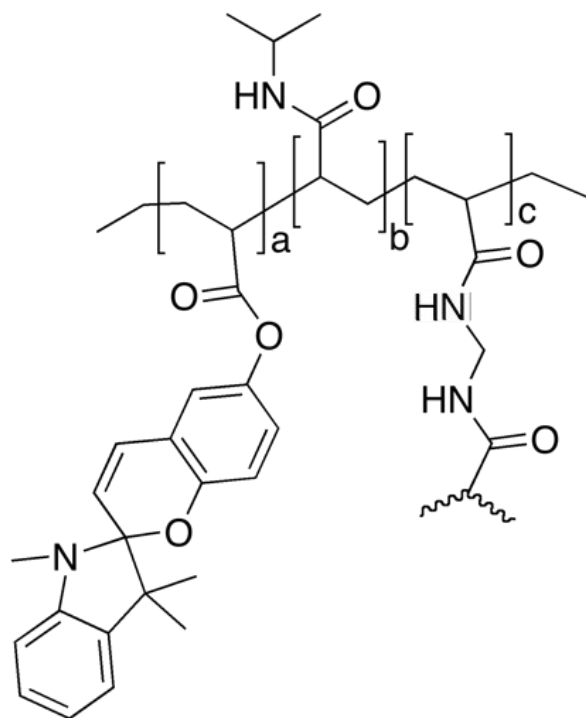


Spiropyran **a = 1**

NIPAAm **b = 100**

MBAA **c = 2**

[1] Sugiura et al., Sens. Act. A, 140 (2007) 176–184



- Size: 120-170 μm [1]
- Shrinking: to 68% of initial size after 120 s
- Maximum shrinking: to 52 % of initial size [1]
- Necessary time for reswelling: > one hour

Drawbacks

- Gels are soaked in 0.5 mM HCl overnight
- Operating only in acidic environment
- Suitable for single-use only

Spiropyran **a = 1**

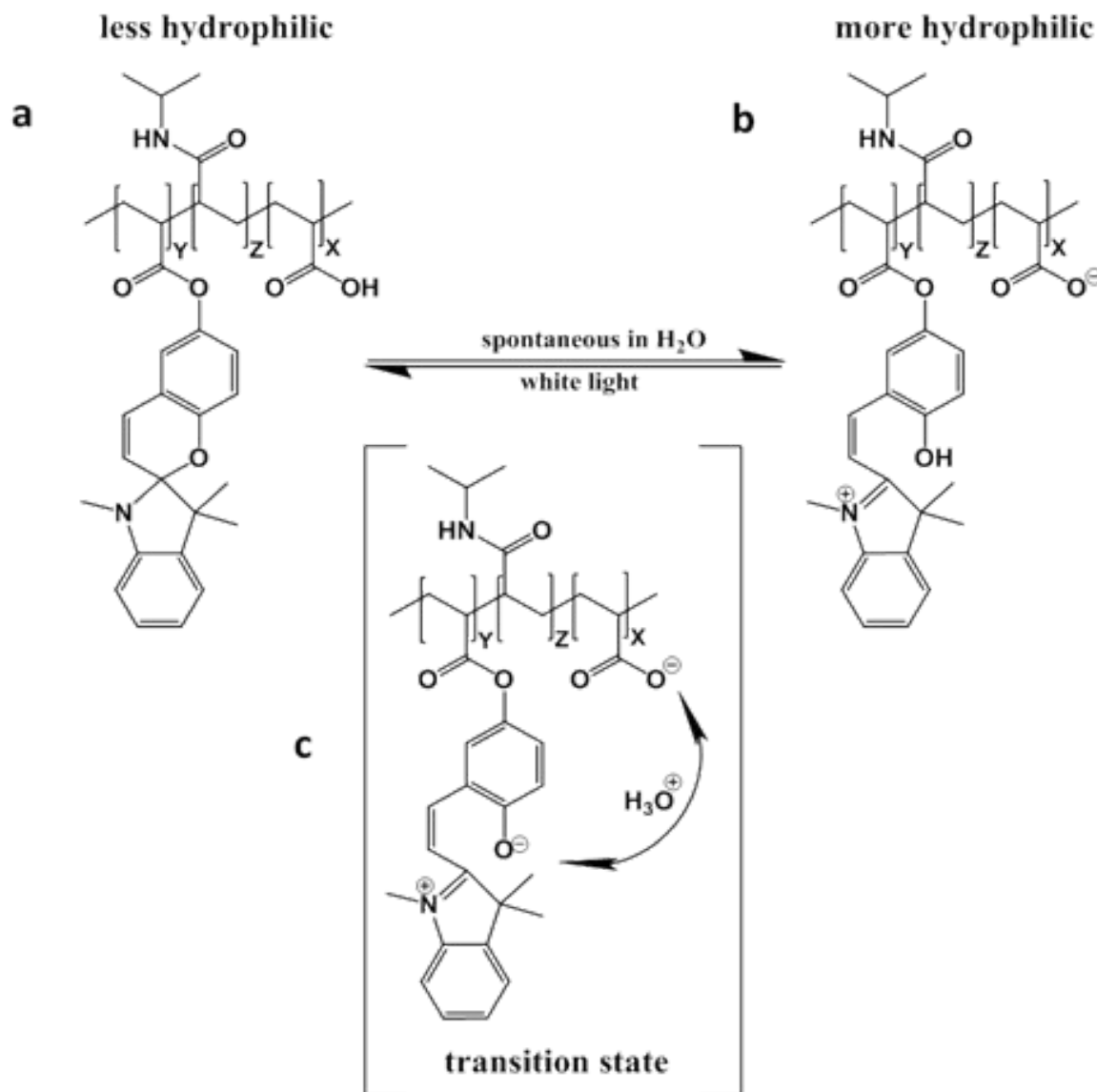
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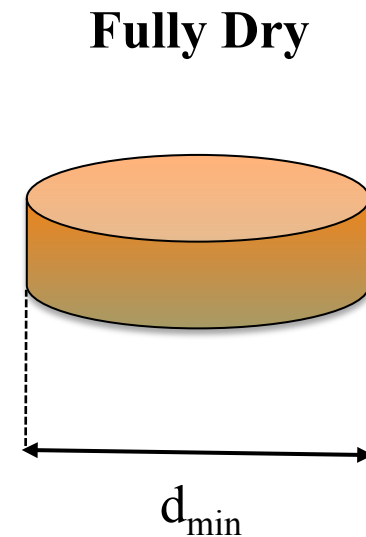
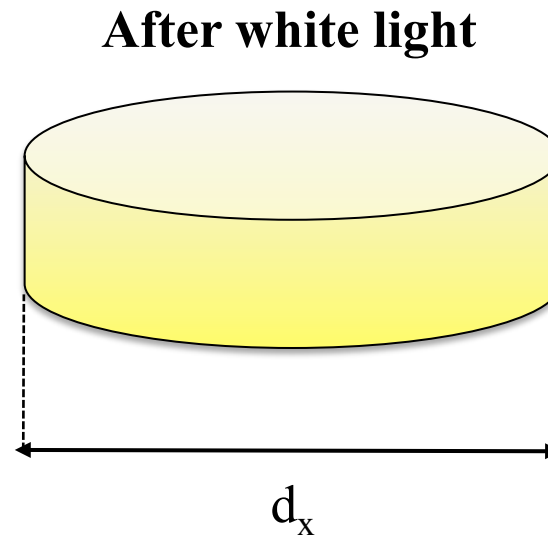
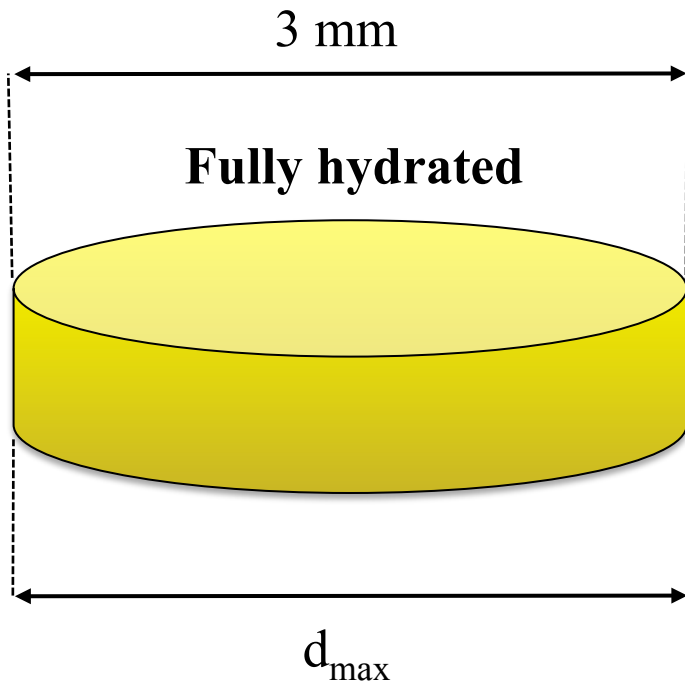


Self-protonating hydrogels





- Photo-polymerised in circular PDMS moulds



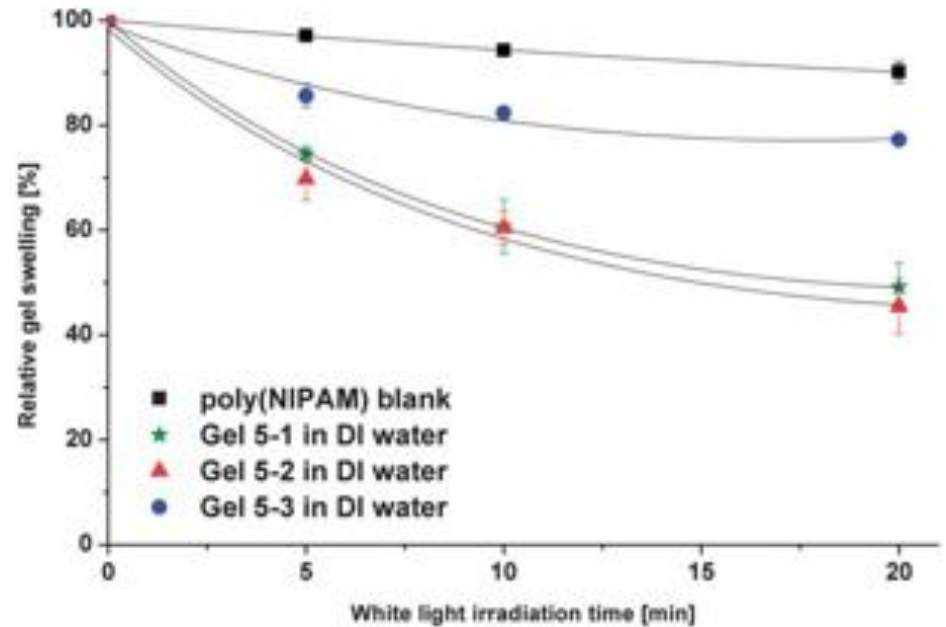
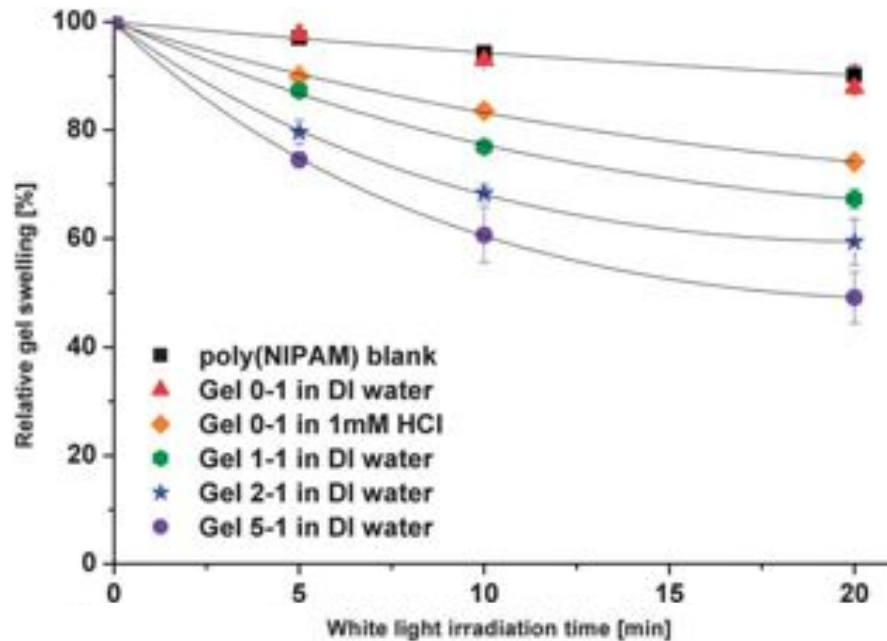
$$D\% = \left[1 - \left[\frac{(d_{\max} - d_x)}{(d_{\max} - d_{\min})} \right] \right] \times 100\%$$



Optimization of hydrogel composition



- Photo-induced shrinking

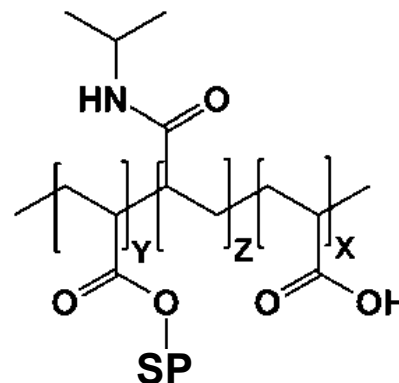




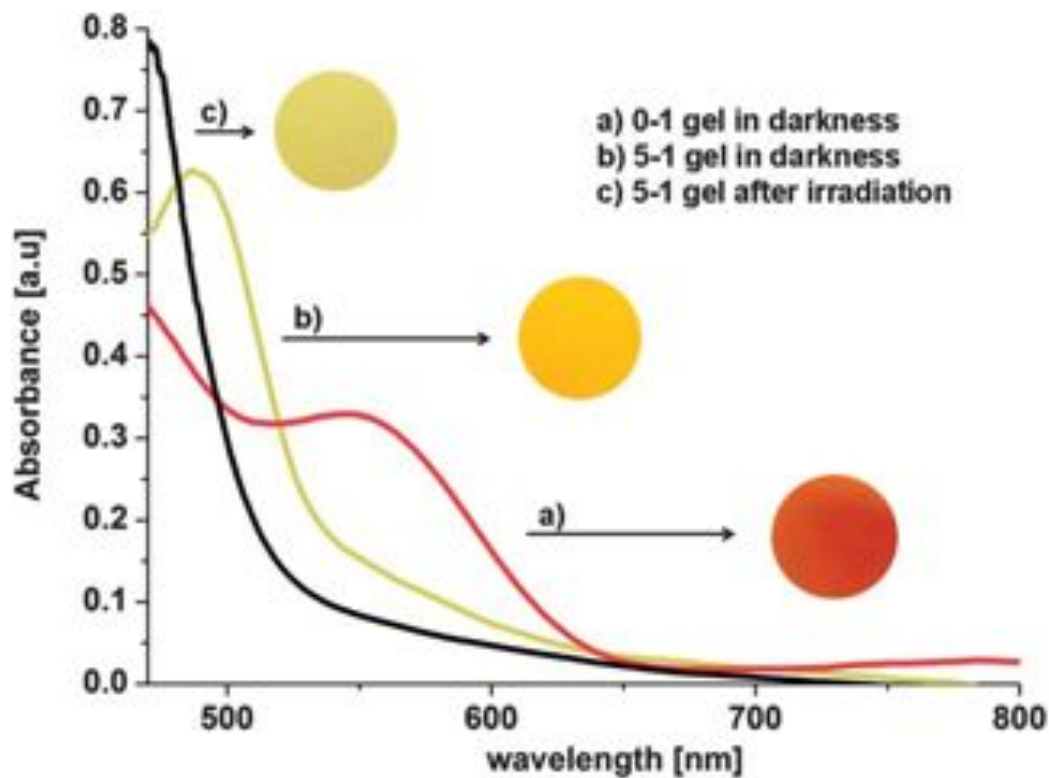
Shrinking/Reswelling Behaviour

sample	20 [min] (Vis. light)	std dev	60 [min] (in darkness)	std dev
poly(NIPAM) blank	87.85 %	1.18	97.44 %	1.60
1 % AA, 1 % BSP-A	67.33 %	1.85	100.45 %	0.64
2 % AA, 1 % BSP-A	59.37 %	4.26	96.48 %	1.34
5 % AA, 1 % BSP-A	49.10 %	4.73	97.35 %	1.93
2 % AA, 2 % BSP-A	61.31 %	5.20	83.69 %	1.27
5 % AA, 2% BSP-A	45.50 %	5.33	82.69 %	3.33
5 % AA, 3 % BSP-A	77.22 %	1.12	76.44 %	1.46

Hydrogel 5-1

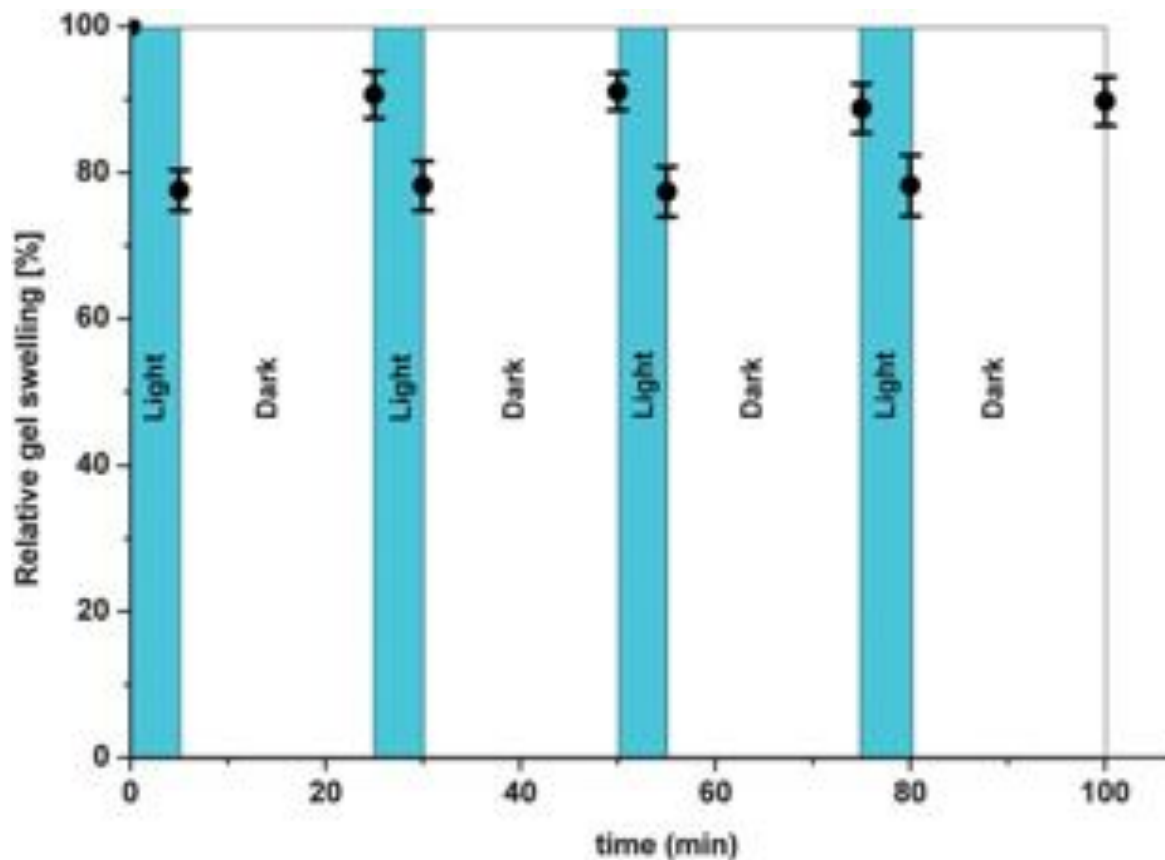


$$\begin{aligned} x &= 5 \\ y &= 1 \\ z &= 100 \end{aligned}$$



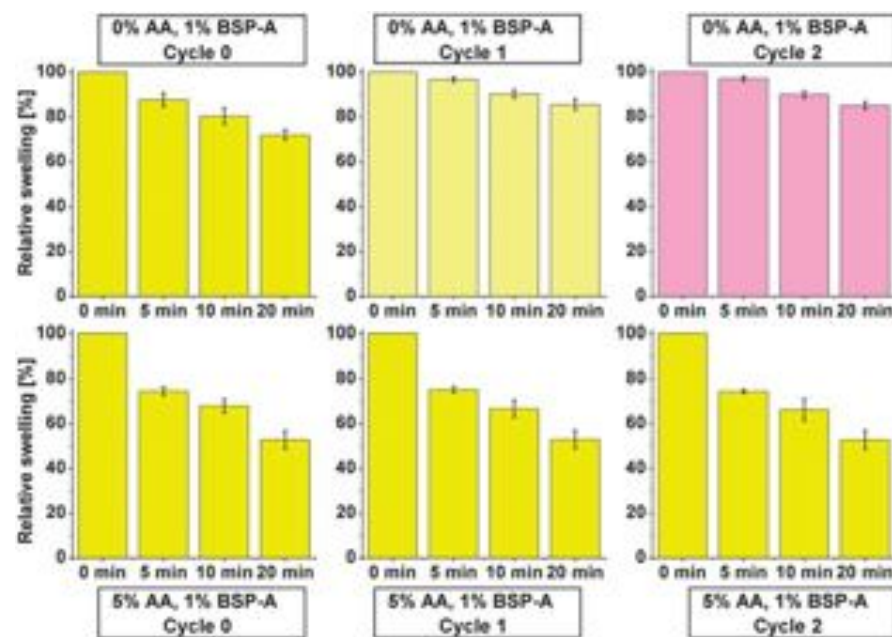
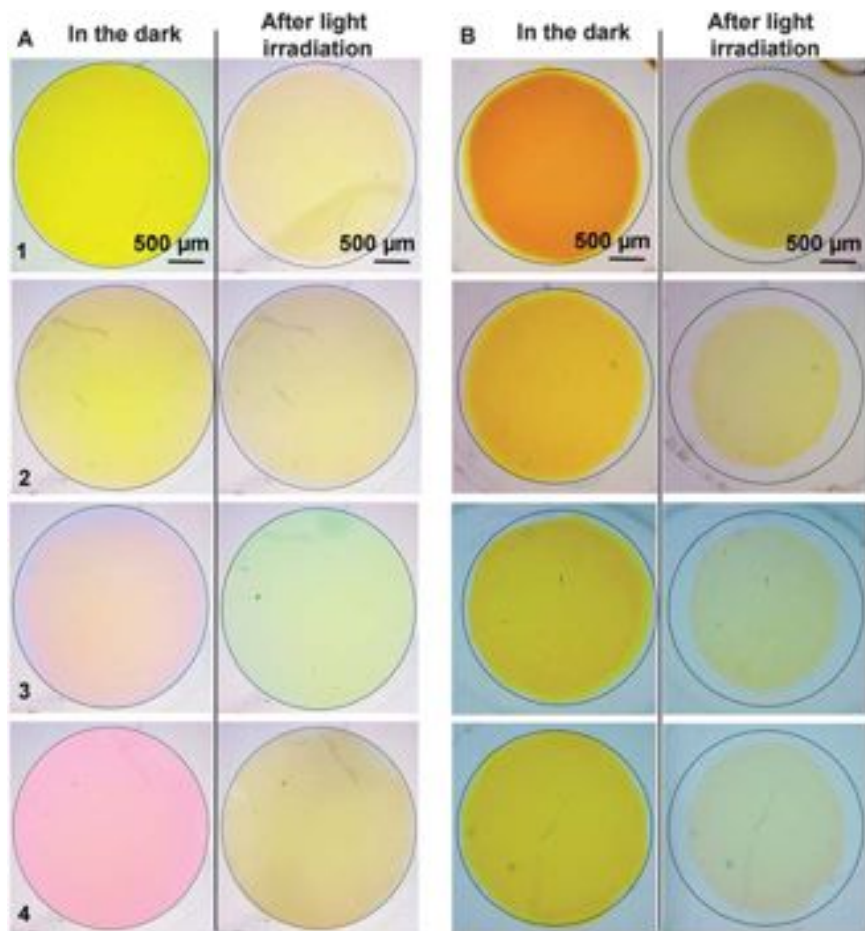
Reproducible actuation

- DI water
- No external proton source



Reproducible actuation

- Comparison between with 5-1 and 0-1 hydrogels



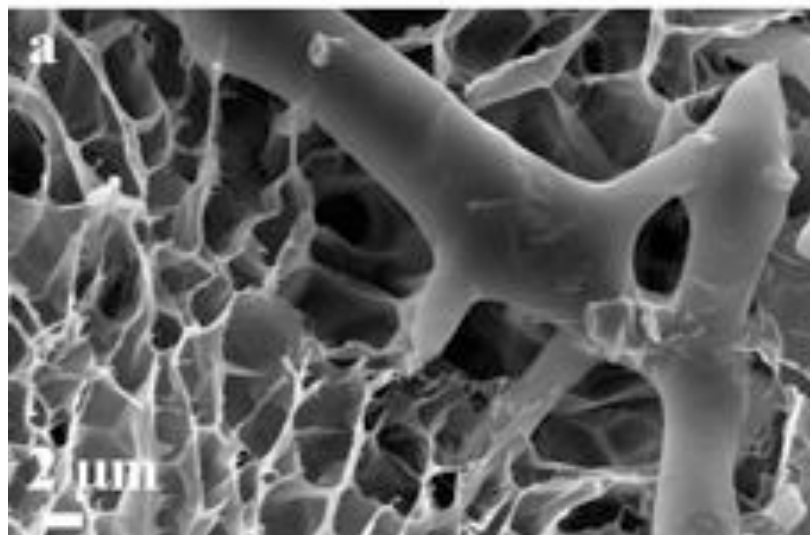
Improved actuation kinetics

- **5-1 Hydrogel**
- **poly(ethylene glycol) $M_w = 2000$ g/mol**
 $M_w = 20000$ g/mol

		Blank gel	2k gel	20k gel
AA	[mol %]	5	5	5
BSP	[mol %]	1	1	1
MBIS	[mol %]	3	3	3
PBPO	[mol %]	1	1	1
NIPAM	[mg]	200	200	200
PEG 2k	[mg]	-	400	-
PEG 20k	[mg]	-	-	200
Solvent	[μ L]	500	500	500

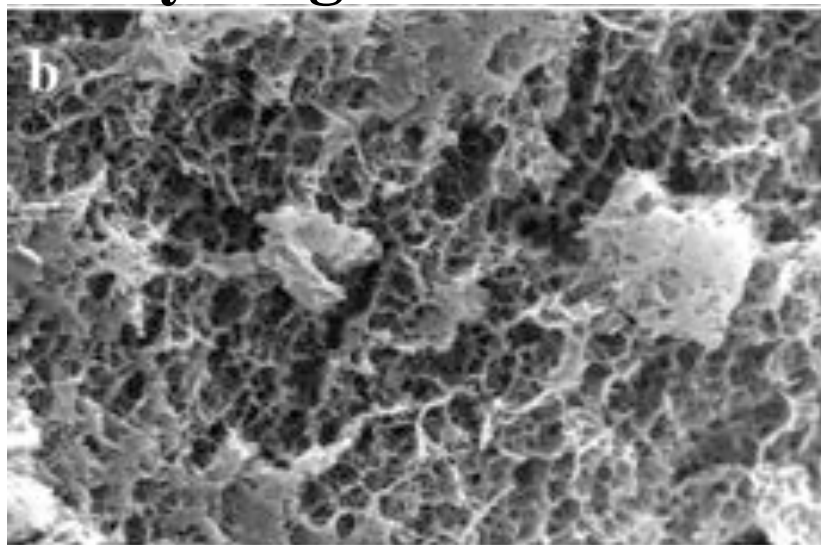


Porosity control

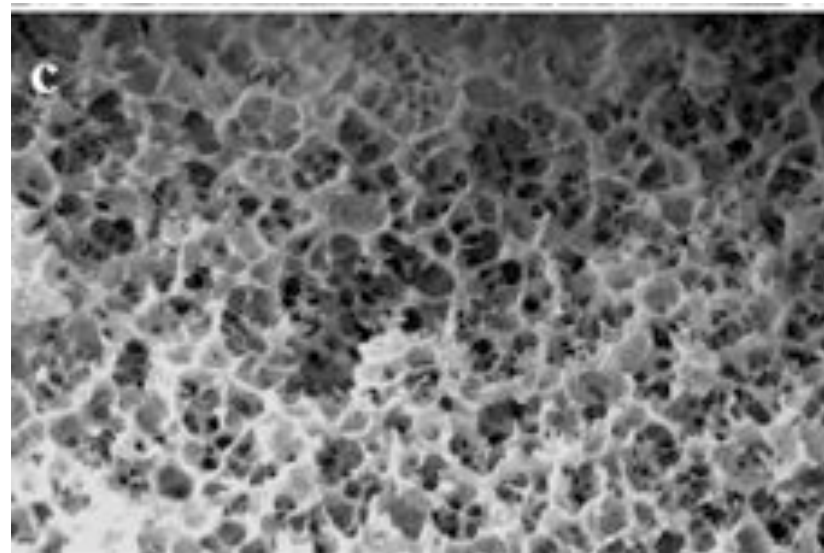


Blank hydrogel

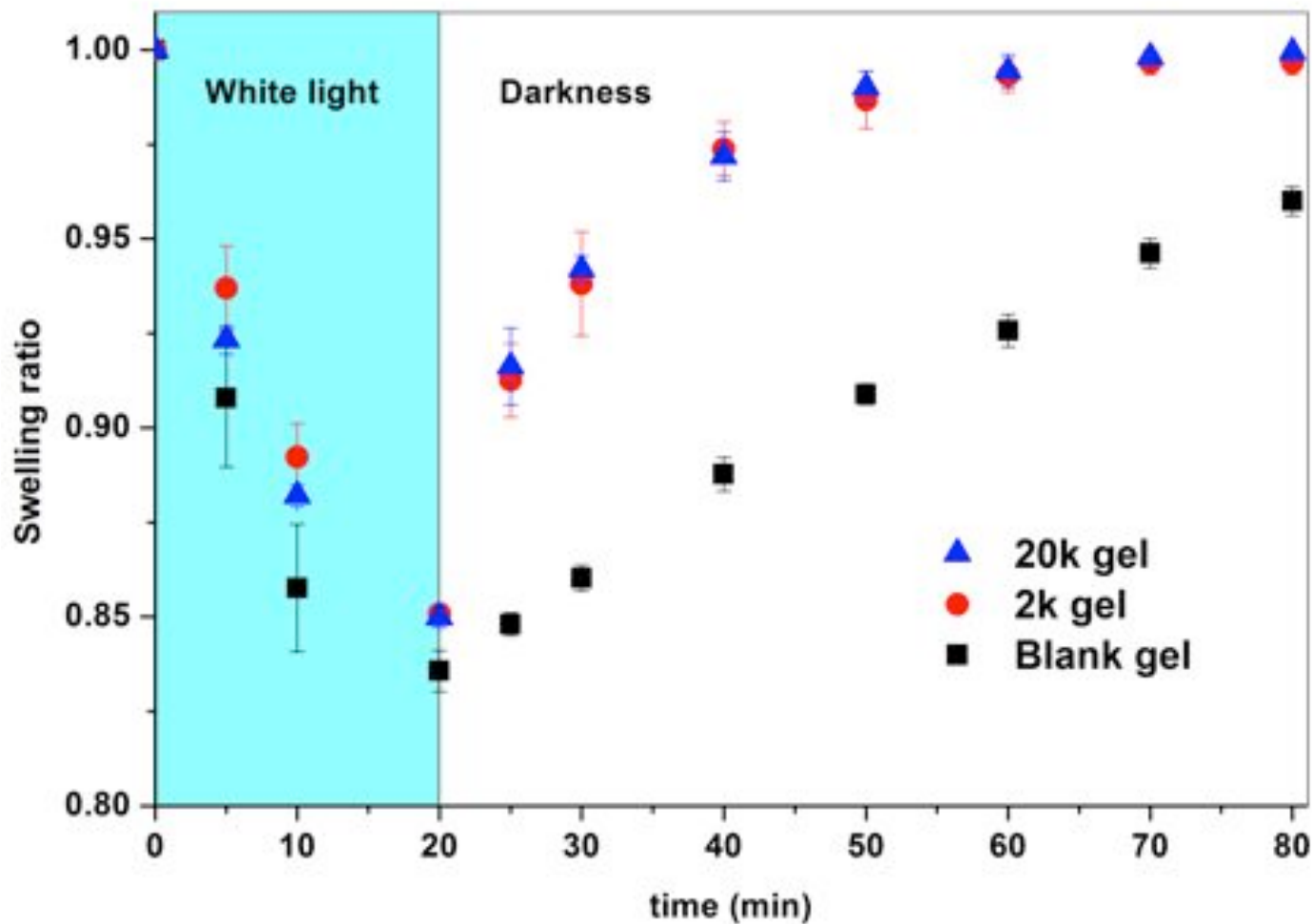
2k hydrogel



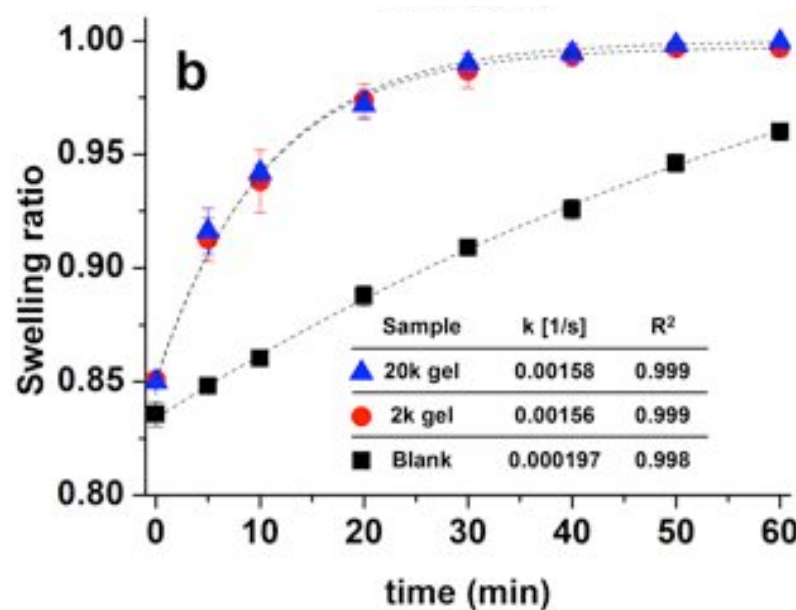
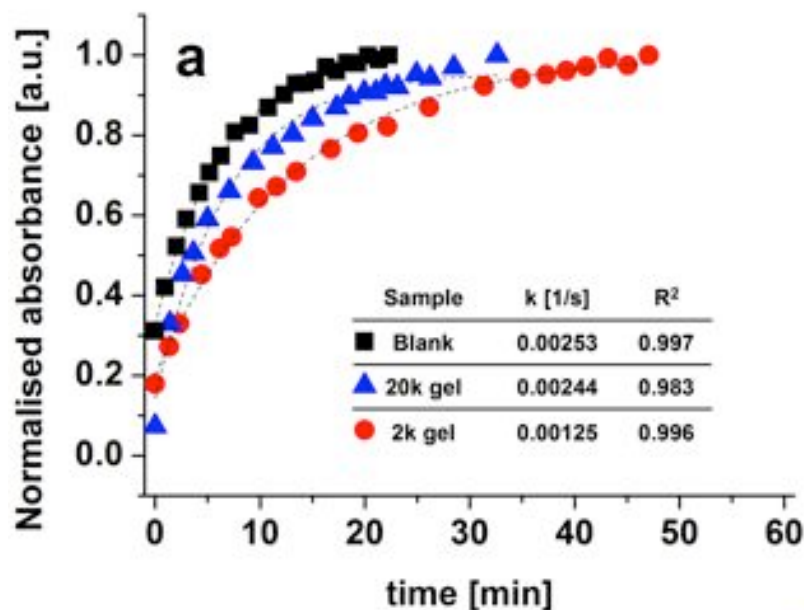
20k hydrogel



Shrinking/Reswelling Behaviour



Swelling and protonation kinetics



$$k_{\text{blank}} \sim 2.53 \times 10^{-3} \text{ [s}^{-1}\text{]}$$

$$k_{2k} \sim 1.25 \times 10^{-3} \text{ [s}^{-1}\text{]}$$

$$k_{20k} \sim 2.44 \times 10^{-3} \text{ [s}^{-1}\text{]}$$

$$k_{\text{blank}} \sim 2 \times 10^{-4} \text{ [s}^{-1}\text{]}$$

$$k_{2k} \sim 1.6 \times 10^{-3} \text{ [s}^{-1}\text{]}$$

$$k_{20k} \sim 1.6 \times 10^{-3} \text{ [s}^{-1}\text{]}$$



Conclusions



- ✓ **Self-protonating hydrogels**
- ✓ **Reproducible photo-actuation**
- ✓ **Capable of performing in DI water and neutral pH solutions**
- ✓ **Porous hydrogels for improved reswelling kinetics**



Acknowledgments



- **Jannick Theobald**
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Thank you!