Nanoliter-scale, regenerable ion sensor: sensing with a surface functionalized microstructured optical fibre

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HTTP://PUBS.RSC.ORG/EN/CONTENT/ARTICLELANDING/2013/RA/C3RA40321A#!DIVABSTRACT

Overview

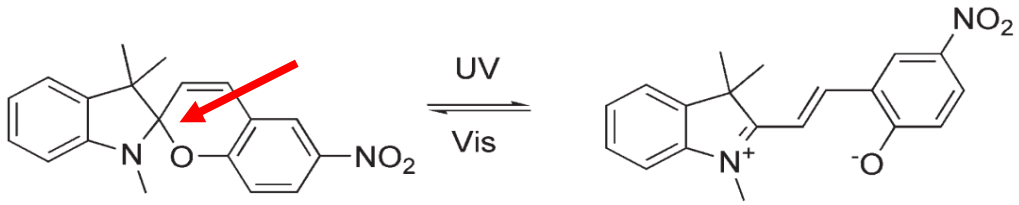
- Background
- Results
- Conclusion

Background

- Goal: develop a reusable metal ion sensor capable of continuous or repeat measurements
- Basic design elements:
  - Switch between active/passive state
  - Controlled by external stimuli: light
  - Nanoliter-scale detection
- Why?
  - Affordable, user-friendly & easily deployed
  - Affords rapid response
  - Remote application, biochemical studies & environmental studies

Background

- Sensing platform: optical fibre
- Microstructured optical fibres (MOFs):
  - Air holes used to guide light
  - Small sample chambers: light interactions with materials in holes
  - These interactions controlled by manipulating the cross sectional geometry
- Integrate MOFs with a photoswitchable molecule to create a sensor
  - Spiropyran



SP (Closed)

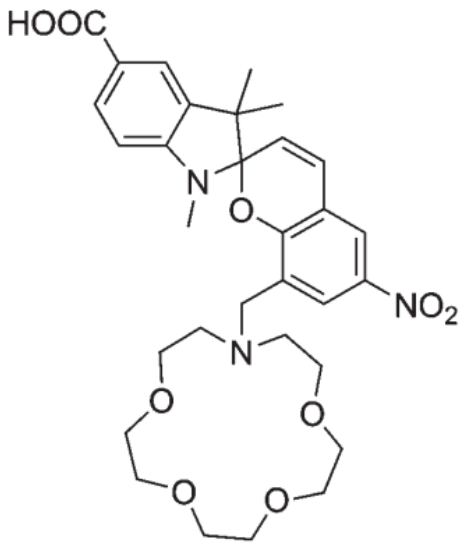
Colorless

MC (Opened)

Colored

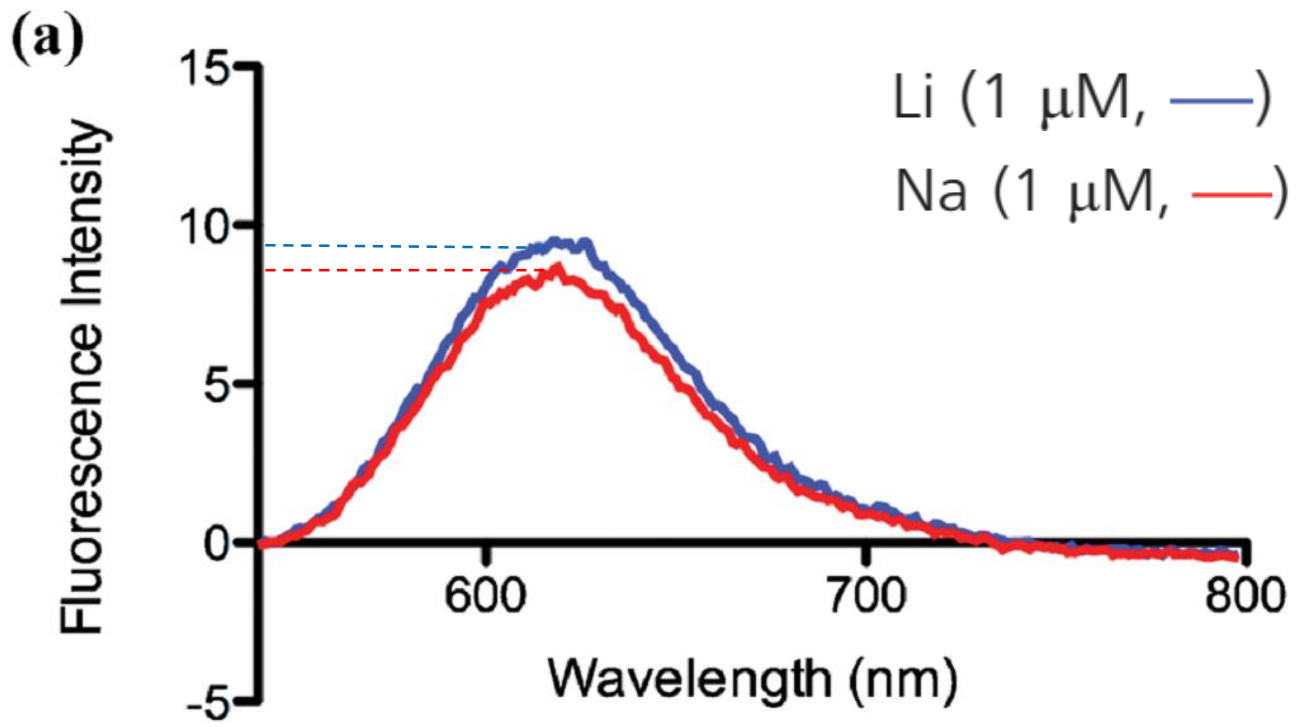
Background

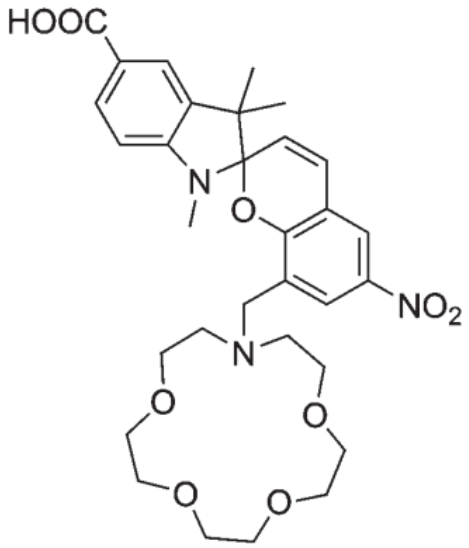
- Functionalize MOFs with SP1 (a monoazacrown bearing spiropyran)
- This crown incorporates a binding site a metal ion



SP1

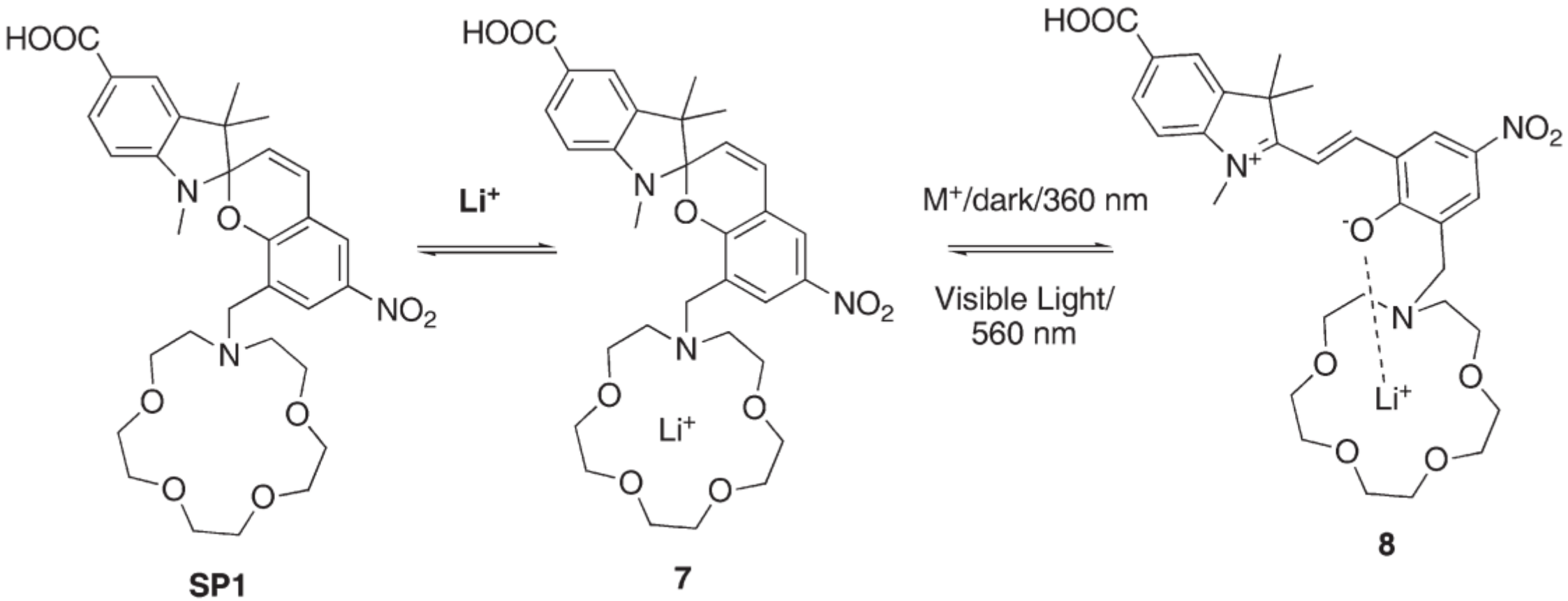
Results



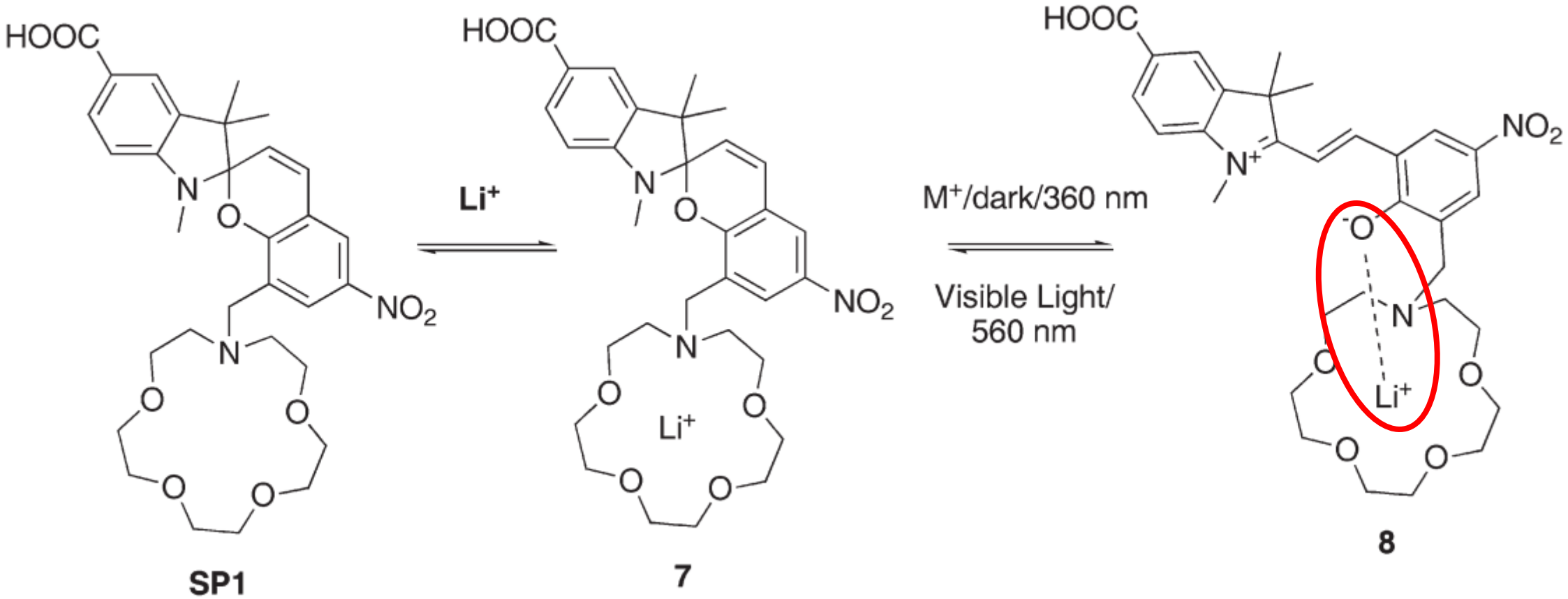


SP1 (10 μM)

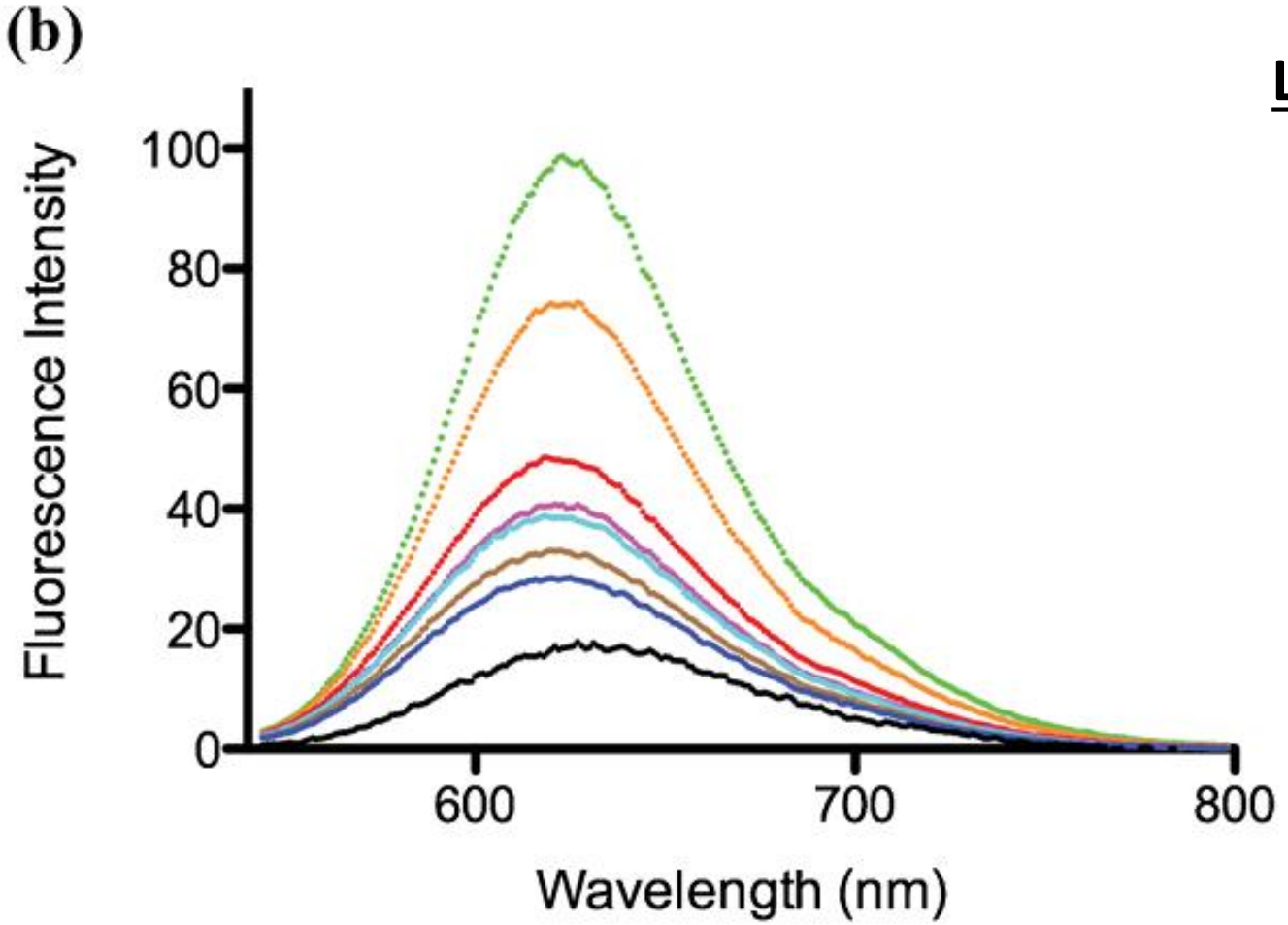
Results


HOOC
N
O
NO2
N
O
O
O
O
O
SP1
Li+
HOOC
N
O
NO2
N
O
O
Li+
O
O
O
7
M+/dark/360 nm
Visible Light/
560 nm
HOOC
N+
NO2
-O
N
O
O
Li+
O
O
O
8

Results


HOOC
N
O
NO2
N
O
O
O
O
O
SP1
Li+
HOOC
N
O
NO2
N
O
O
Li+
O
O
7
M+/dark/360 nm
Visible Light/
560 nm
HOOC
N+
NO2
O-
N
Li+
O
O
O
O
O
8

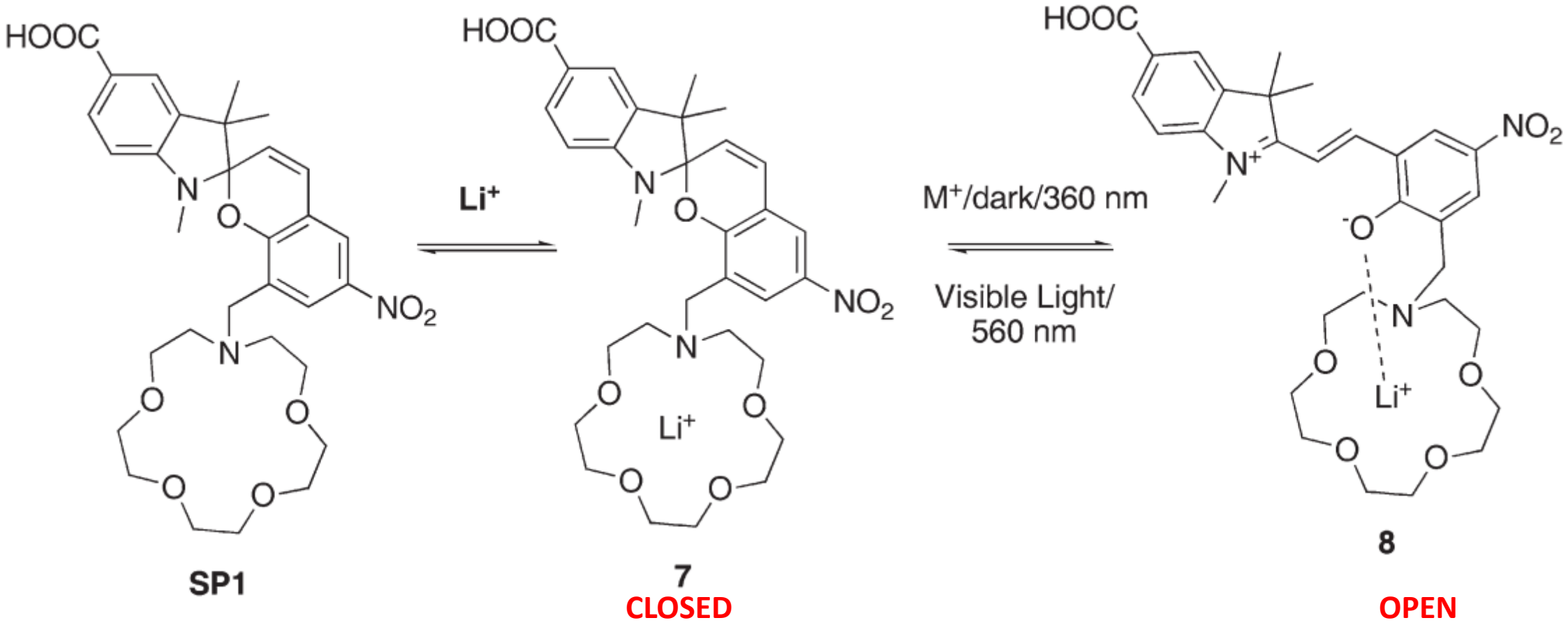
Results



Li^+ Concentration

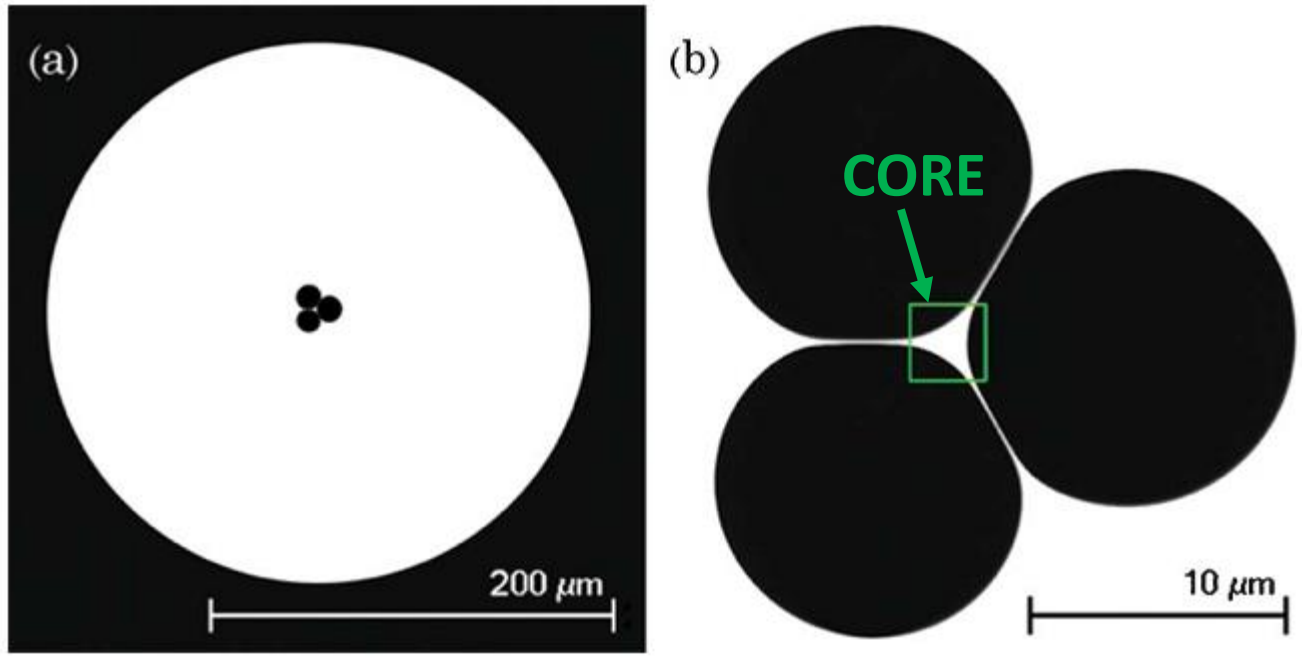
- 1 µM
- 0.8 µM
- 0.5 µM
- 0.4 µM
- 0.3 µM
- 0.2 µM
- 0.05 µM
- 0 µM

Results

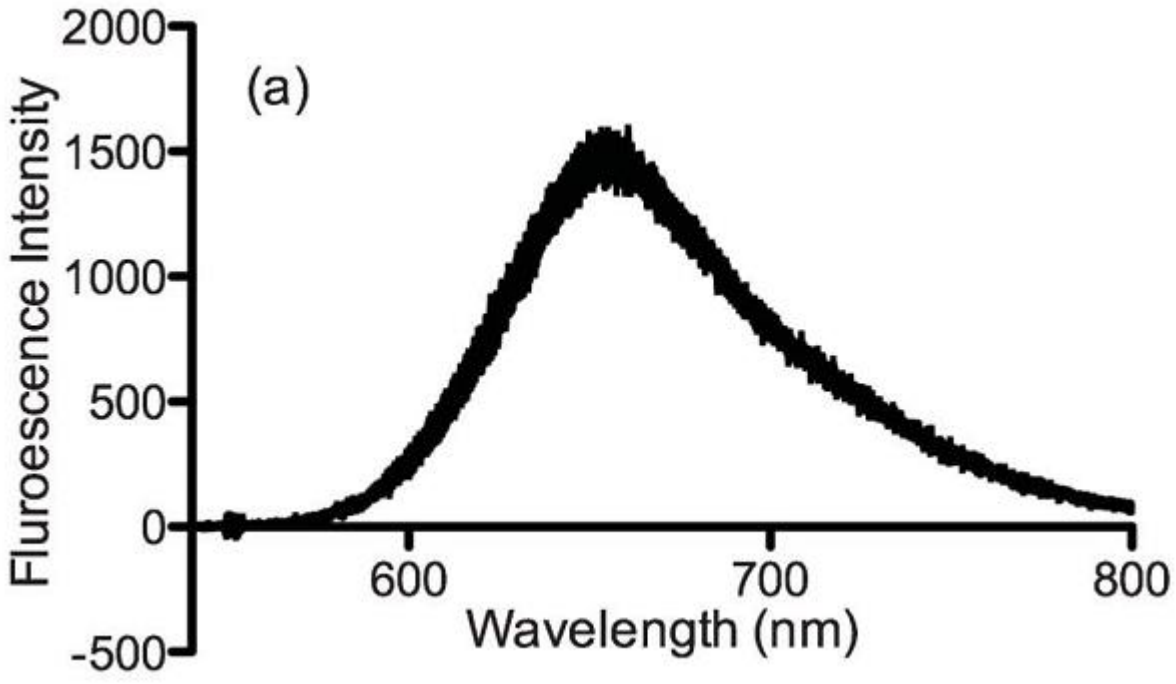

HOOC
N
O
NO2
N
O
O
O
O
O
SP1
Li+
HOOC
N
O
NO2
N
O
O
Li+
O
O
O
7
CLOSED
M+/dark/360 nm
Visible Light/
560 nm
HOOC
N+
NO2
-O
N
O
O
Li+
O
O
O
8
OPEN

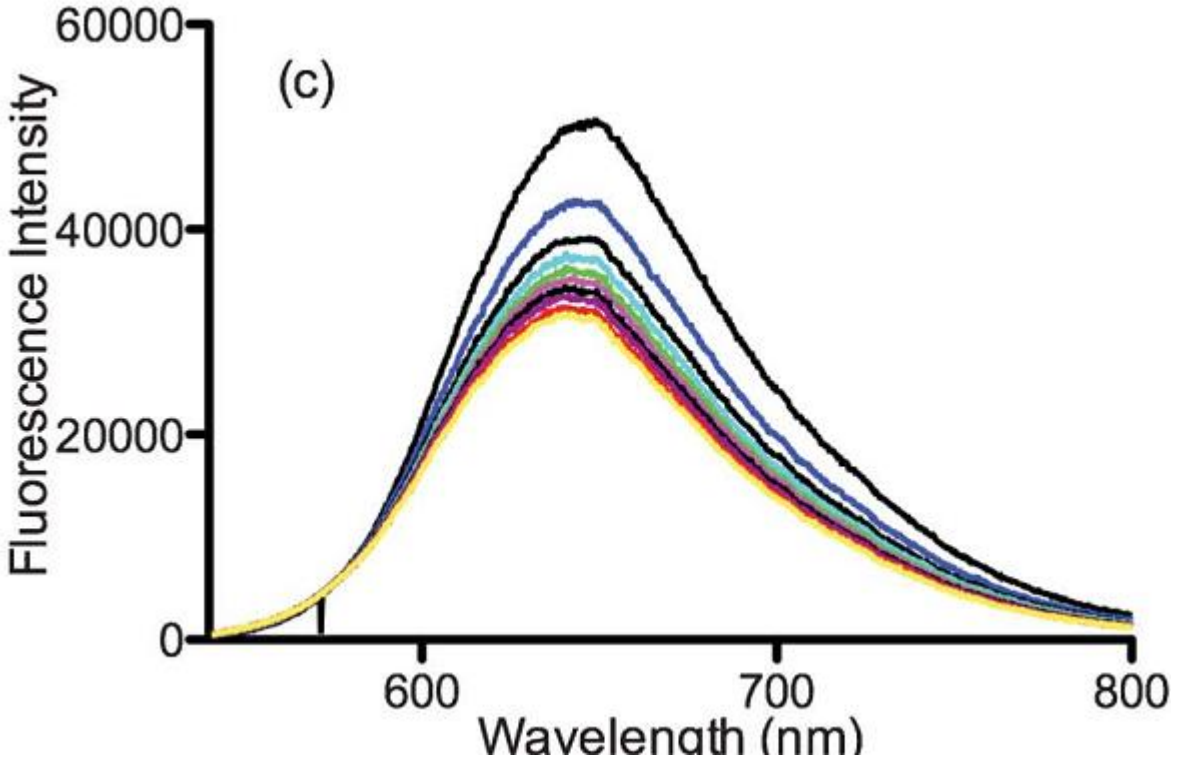
Results

- MOF fabricated using undoped high purity fused silica
  - High transmission properties in UV-Vis-NIR spectral range
- Fabricated 80m-long polymer coated fibre



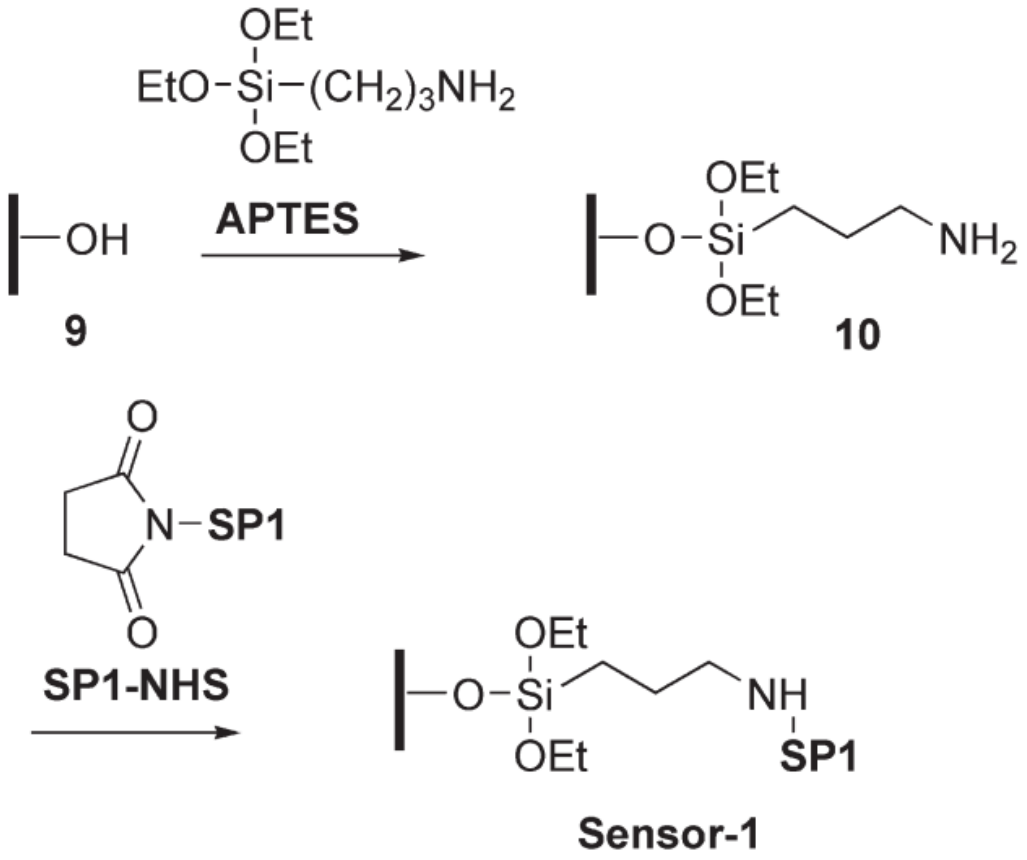
Results


(a)
Fluroescence Intensity
2000
1500
1000
500
0
-500
600
700
800
Wavelength (nm)

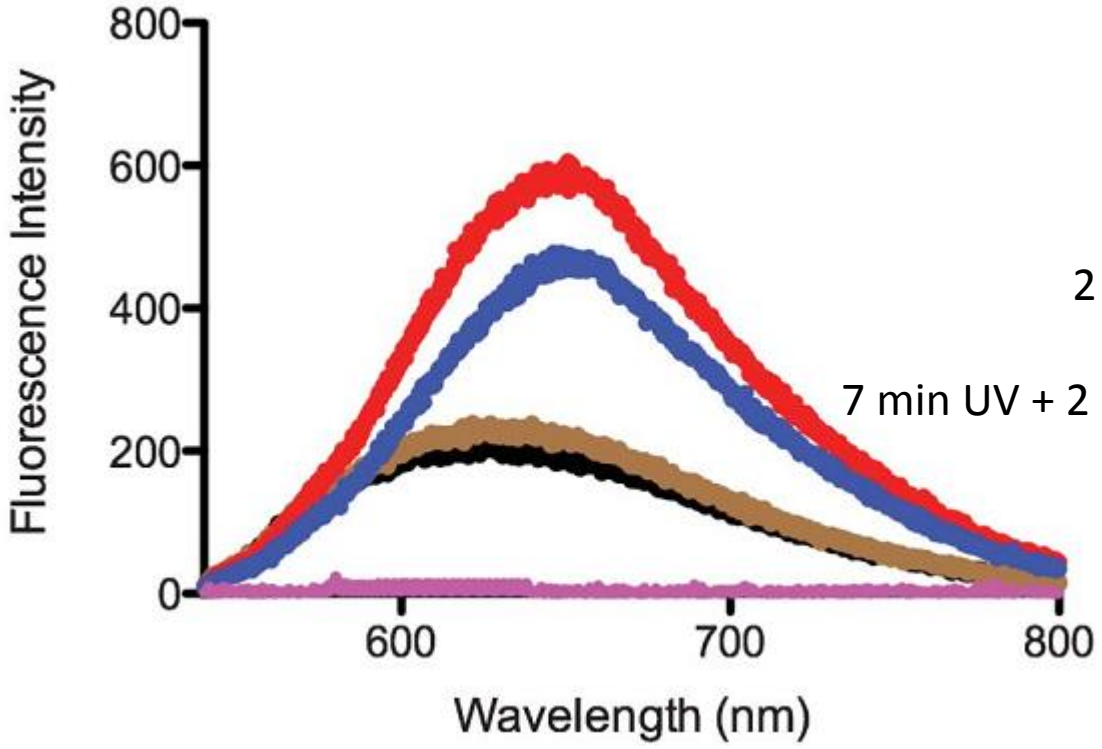

(c)
Fluorescence Intensity
60000
40000
20000
0
600
700
800
Wavelength (nm)

Results

- Fibres sealed into metal chamber
- Force solutions through using nitrogen gas
- Coat fibres in 5% **APTES** in toluene
- Rinse fibres by flushing with toluene, then dry with nitrogen, then flush with Millipore water, then dry again with nitrogen
- Coat fibres with 2mM SP1-NHS in acetonitrile
- Flush with acetonitrile, air and water



Results

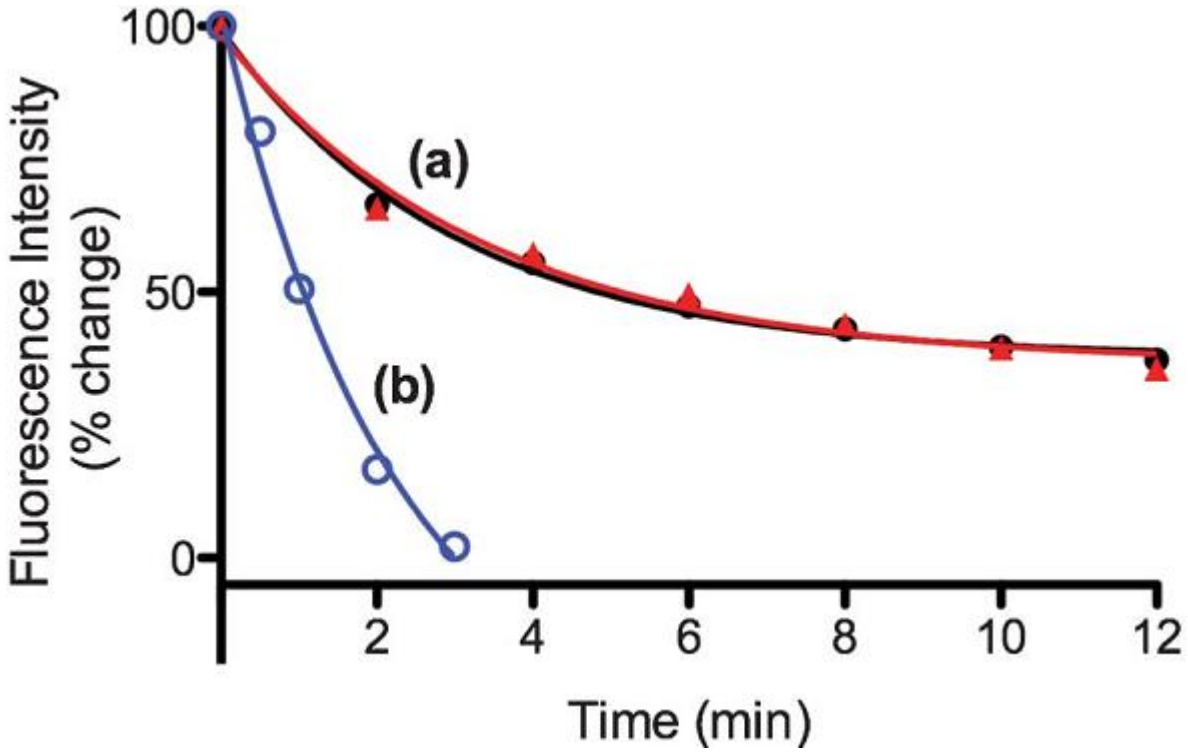


7 min UV
- FF, filled with 1 µM Li^+ in ACN
- FF, filled with 100 nM Li^+ in ACN

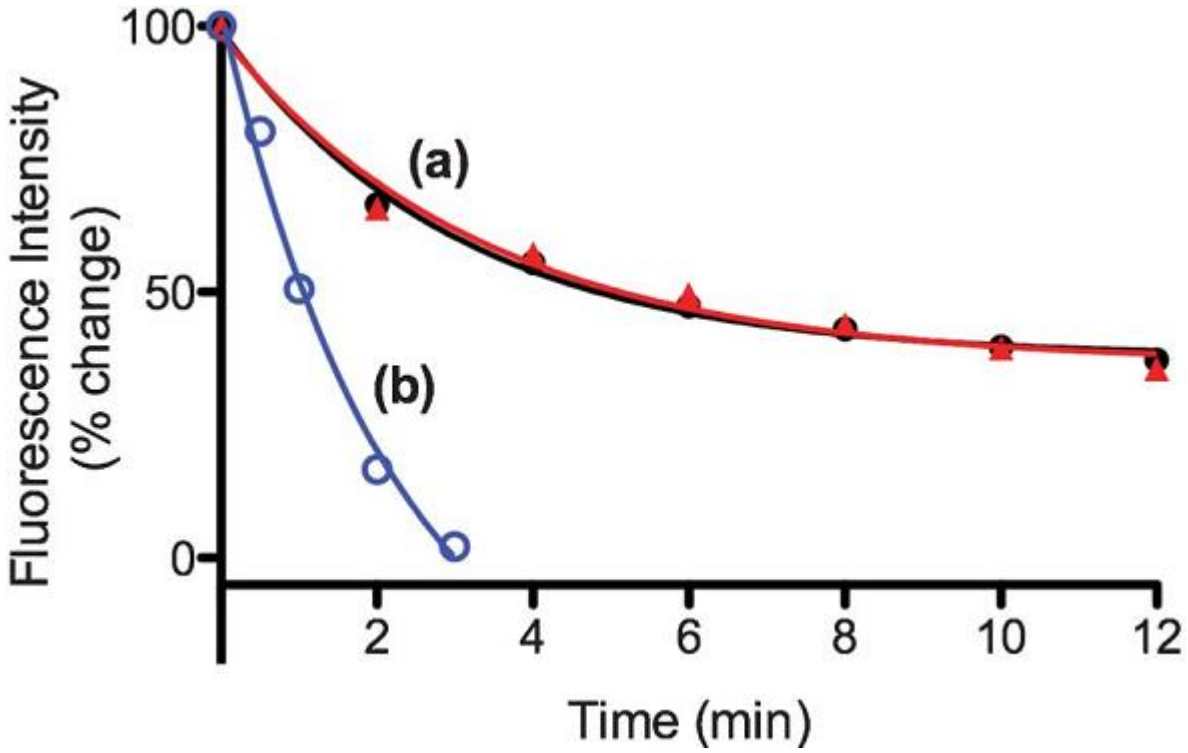
2 min white
- FF, filled with 100 nM and 1 µM Li^+ in ACN

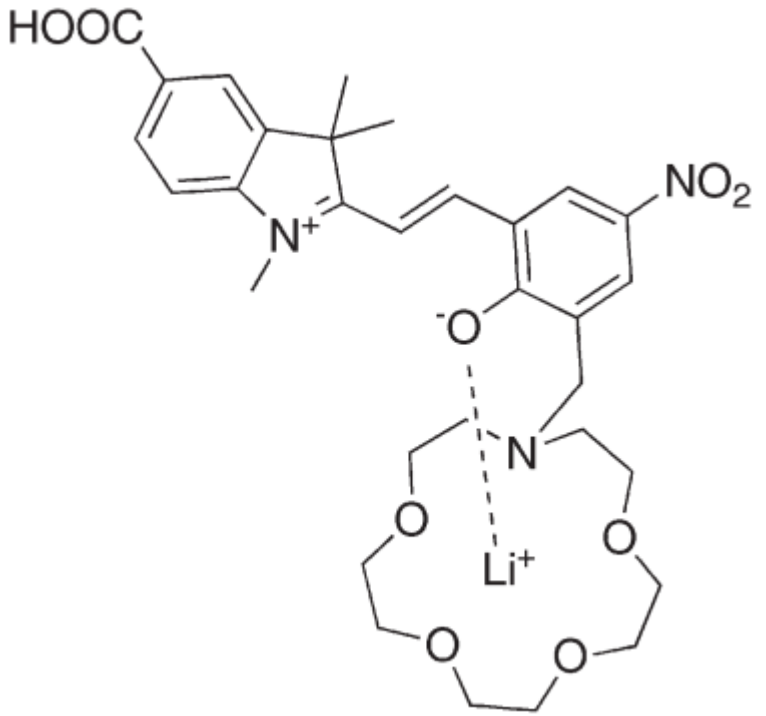
7 min UV + 2 min white
- functionalized fibre (FF), not filled with Li^+
- Empty fibre

Results

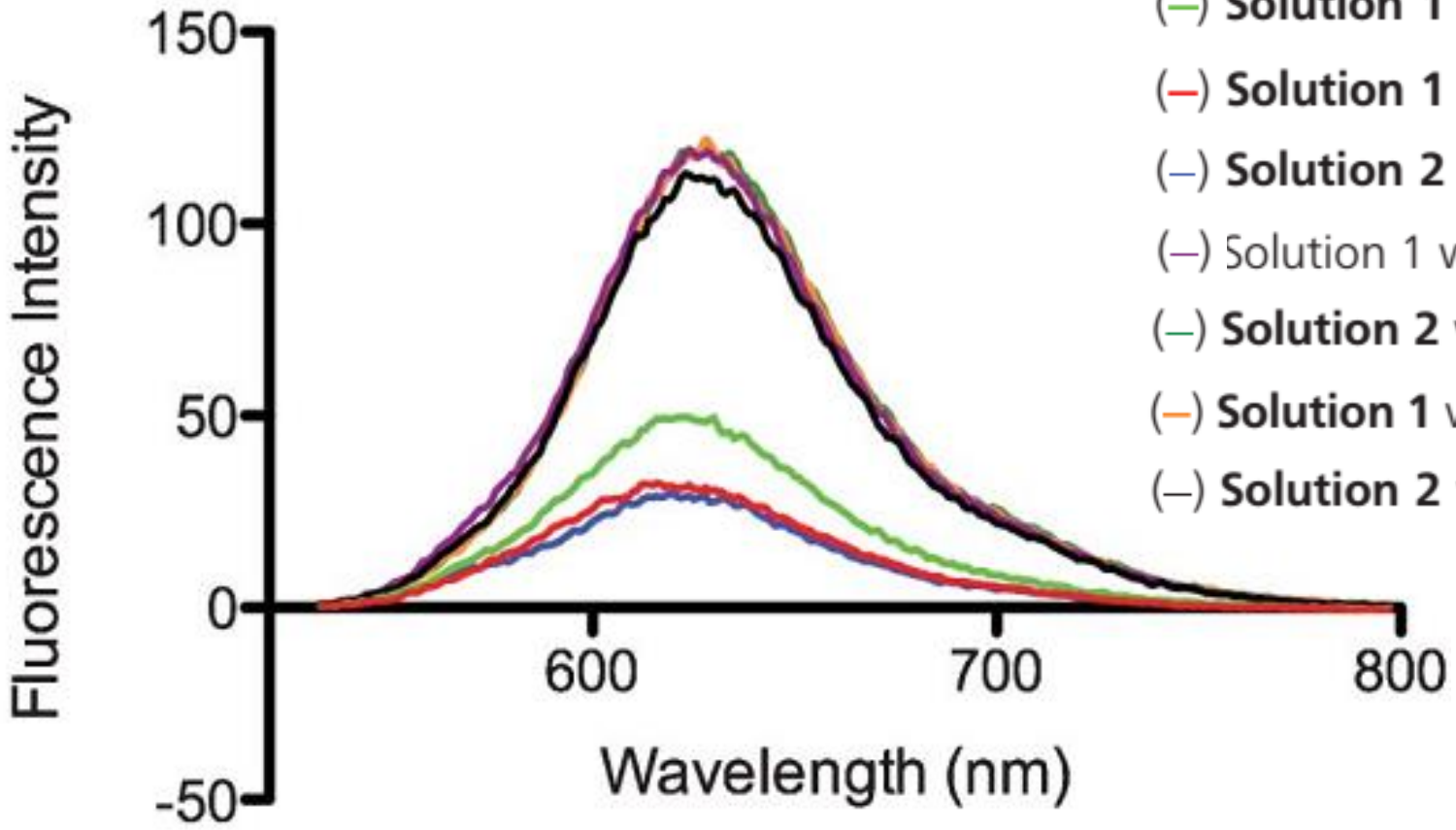

100
50
0
Fluorescence Intensity
(% change)
(a)
(b)
2
4
6
8
10
12
Time (min)

Results


100
50
0
Fluorescence Intensity
(% change)
(a)
(b)
2
4
6
8
10
12
Time (min)


HOOC
NO2
N+
-O
N
O
O
O
O
O
Li+

Results



(–) **Solution 1** prior to exposure to white light

(–) **Solution 1** exposed to white light for 2 min

(–) **Solution 2** exposed to white light for 2 min

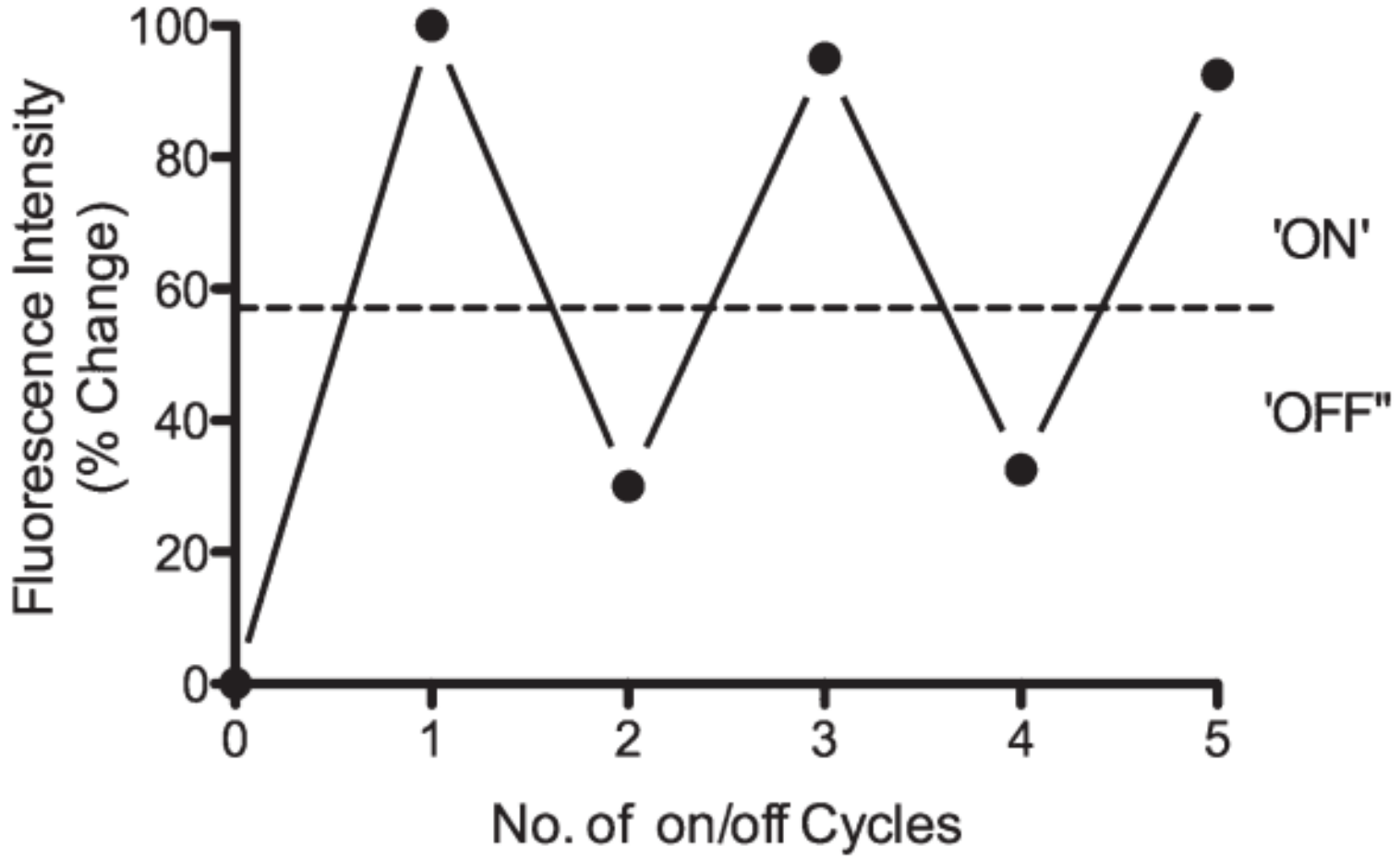
(–) Solution 1 with 1 μM Li^+ exposed to UV for 7 min

(–) **Solution 2** with 1 μM Li^+ exposed to UV for 7 min,

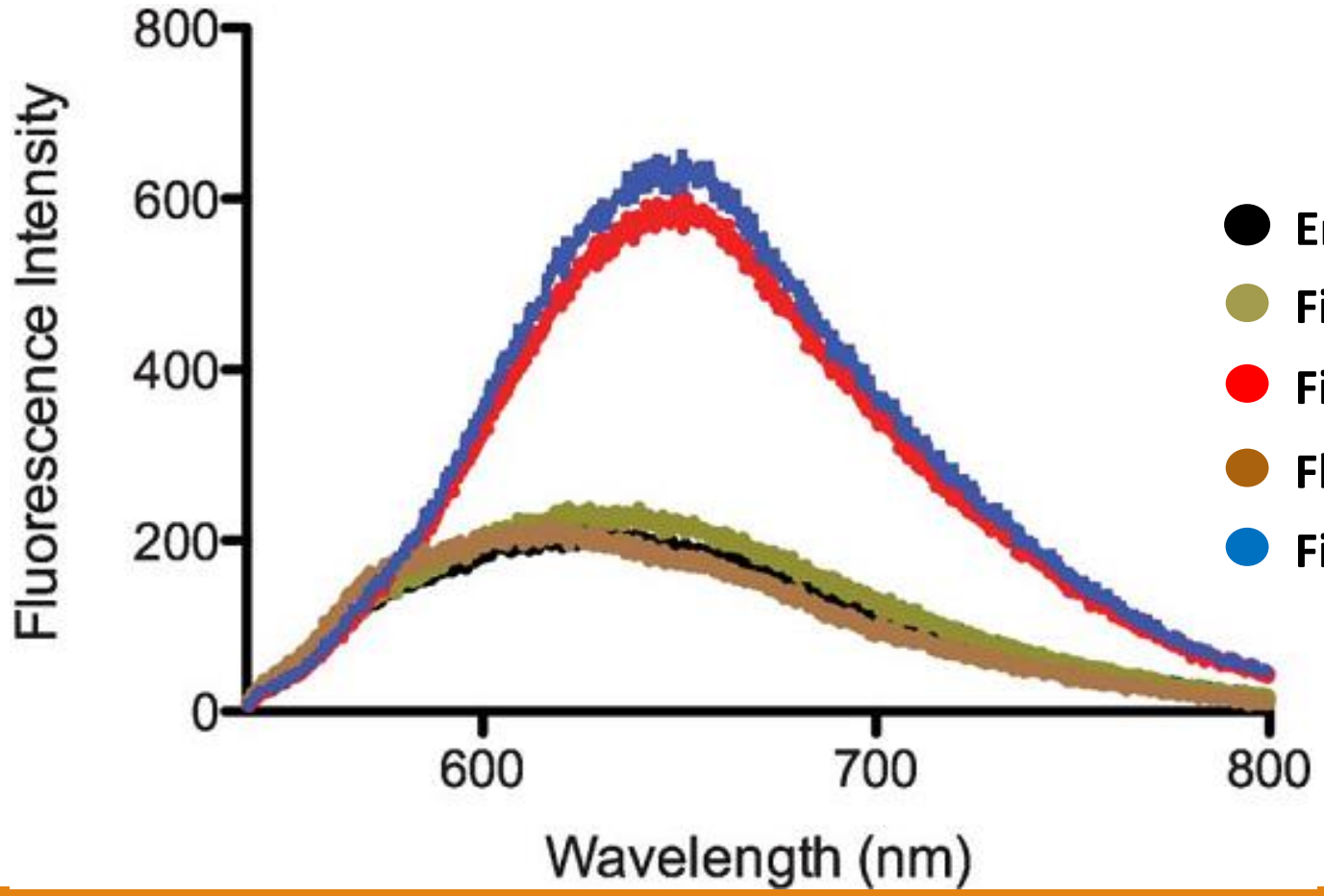
(–) **Solution 1** with 1 μM Li^+ exposed to white light for 2 min

(–) **Solution 2** with 1 μM Li^+ exposed to white light for 2 min

Results


Fluorescence Intensity
(% Change)
100
80
60
40
20
0
0
1
2
3
4
5
No. of on/off Cycles
'ON'
'OFF"

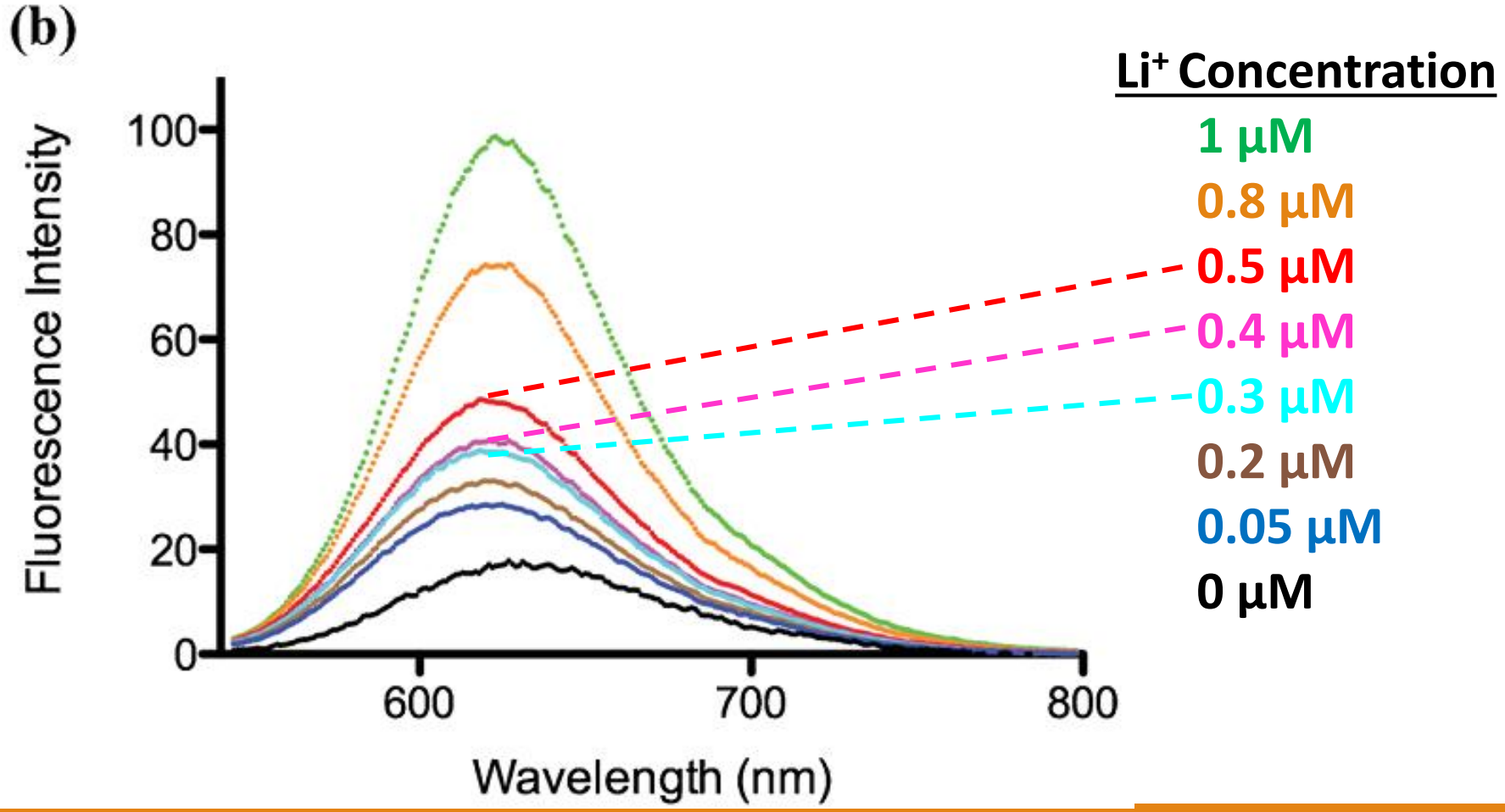
Results


800
600
400
200
0
Fluorescence Intensity
600
700
800
Wavelength (nm)
Empty Fibre
Fill with Li+/ACN (first time) – no UV
Fill with Li+/ACN (first time) – after UV
Flushed sensor
Fill with Li+/ACN (second time) – after UV

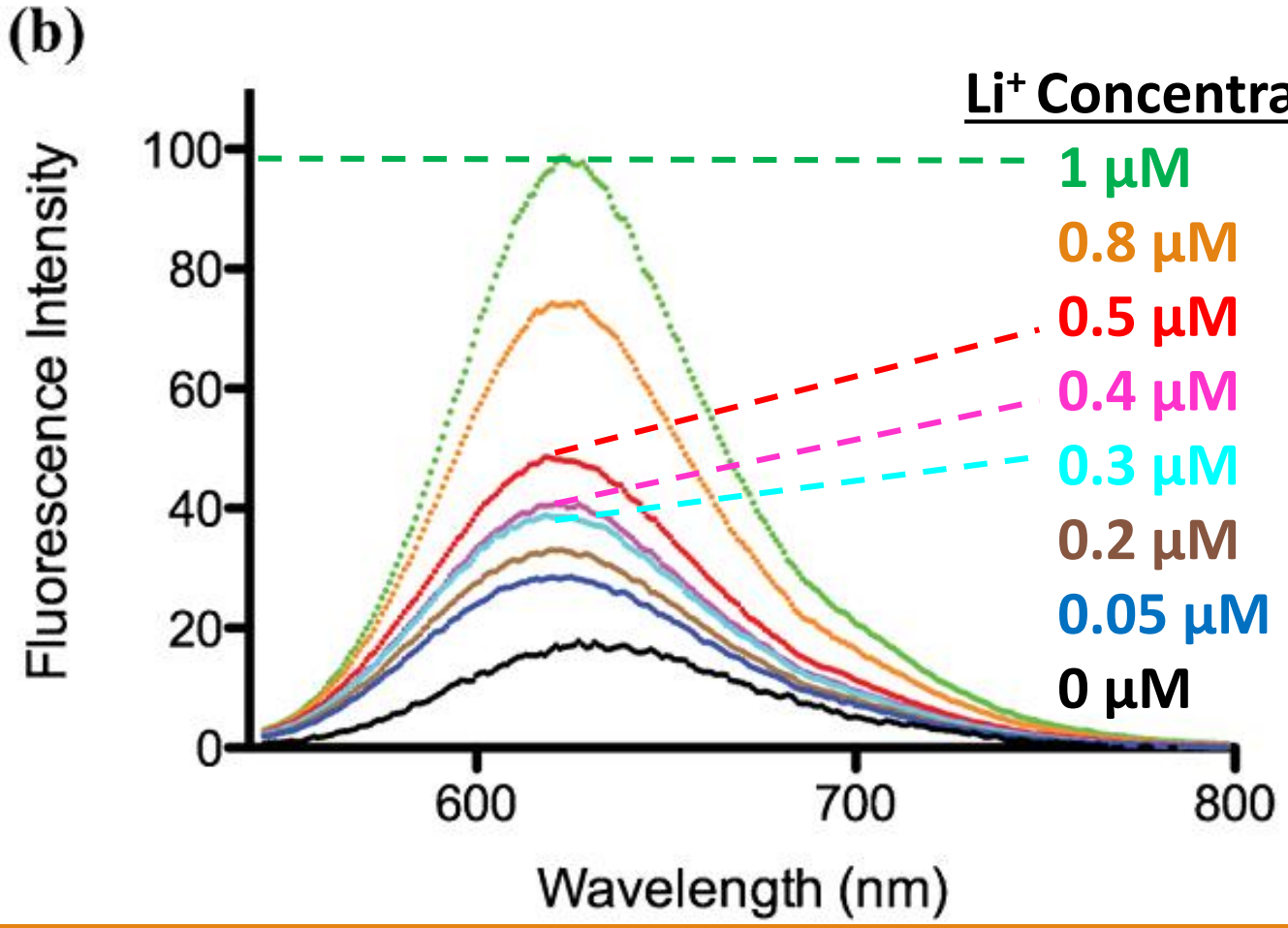
Conclusion

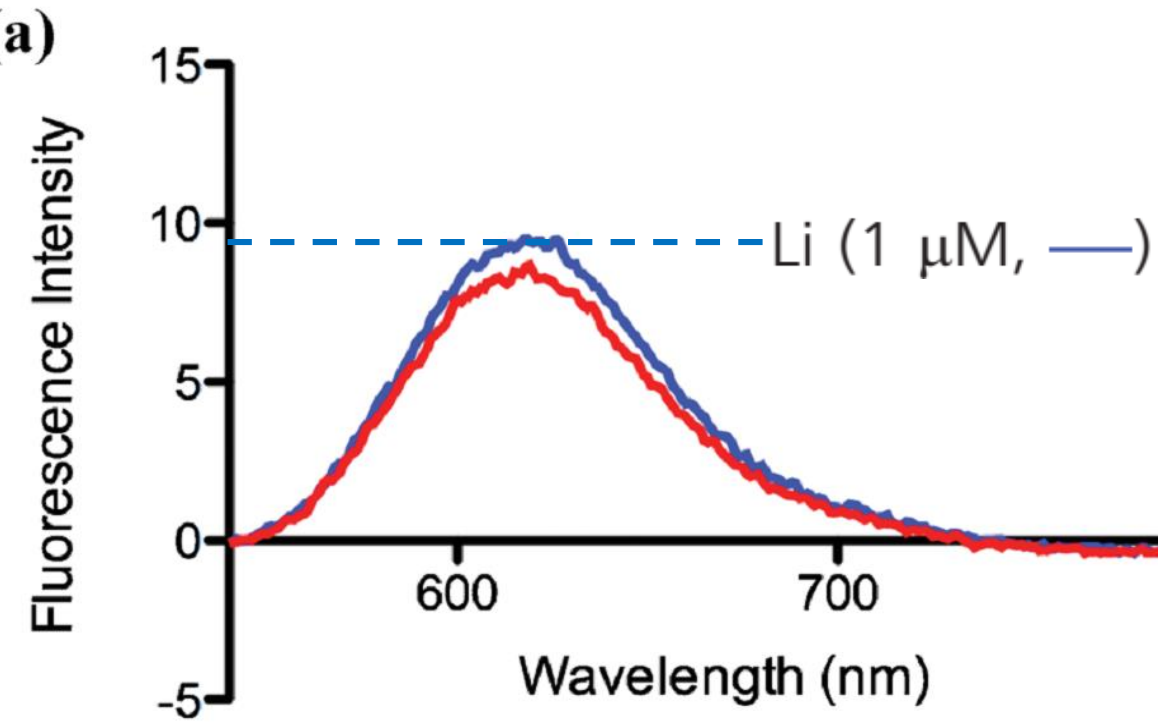
- Rapid and efficient metal ion detection has applications in:
  - Disease diagnosis & study
  - Environmental sensing
- Developed the first nano-liter scale, regenerable ion sensor based on a functionalized MOF

Results - Criticisms



Results - Criticisms





Additional Criticism

- Why are the figures missing legends?
- Why are the spectra plotted with different weighted lines?

Citation

S. Heng, M. Nguyen, R. Kostecki, T. Monro and A. Abell, *Royal Society of Chemistry*, 2013, **3**, 8308-8317