Development of Low-Cost colourimetric and pH sensors based on PMMA@Cyanine Polymers.

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Captions

Table 1. Photophysical data of the cyanine dyes **1** to **3** in acetonitrile.

Table 2. Stability association constants for the complexes formed with cyanines **1** to **3** with Cu^{2+} ions, in CH_3CN and 50%CH_3CN:50%H_2O* (σ is an estimate of the average experimental error). Minimal detection (LOD) and quantification (LOQ) amounts (μM) of Cu^{2+} metal ions (M) by dyes **1** to **3.** [LOD and LOQ were measured by absorption at 484 and 500 nm for **1**, 803 nm for **2** and 774 nm for **3**, in CH_3CN and 50% CH_3CN:50% H_2O, respectively].

Figure 1. General workflow of the preparation of PMMA polymers doped with cyanine derivative, followed by photophysical characterization and acidity assays.

Figure 2. Synthetic approach to the preparation of the unsymmetrical cyanine dye **1.**

Figure 3. (Top) Chemical structure of cyanine derivative **1**-**3**. (Bottom) (A) Absorption and (B) emission spectra of cyanine derivatives **1** to **3** in acetonitrile. Inset: (A) naked-eye images of the cyanine derivatives (**1**-**3**) in acetonitrile and (B) under UV-lamp (**1***-**3***). [**1**-**3**]$_{Abs.}$= 1 ×10^{-5} M, [**1**-**3**]$_{emis.}$ = 1×10^{-6} M;, λ_{exc1}= 484 nm, λ_{exc2}= 803 nm, λ_{exc3}= 774 nm.

Figure 4. Spectrophotometric (A, C, E) and spectrofluorimetric (B, D, F) titrations of dyes **1** (A, B), **2** (C, D) and 3 (E, F) with the addition of Cu^{2+} in acetonitrile. The inset represents the absorption (A, C, E) at 500 nm (A), 803 nm (C) and 774 nm (E) with the fitting determined by HypSpec Program; and the emission intensity (B, D, F) at 541 nm (B), 823 nm (D) and 800 nm (F) as function of [Cu^{2+}]/[**1**] (A, B), [Cu^{2+}]/[**2**] (C, D) and [Cu^{2+}]/[**3**] (E, F). [**1**] = 9.2 ×10^{-6} M, [**2**] = 1.8 ×10^{-6} M, [**3**] = 2.5×10^{-6} M, λ_{exc1}=484 nm, λ_{exc2}=803 nm, λ_{exc3}=774 nm, T = 298 K).

Figure 5. Spectrophotometric (A, C, D) and spectrofluorimetric (B) titrations of dyes **1** (A, B), **2** (C) and **3** (D) with the addition of Cu^{2+} in aqueous solution (CH_3CN:miliQ water,

1:1). The inset represents the absorption (A, C, D) at 500 nm (A), 803 nm (C) and 774 nm (D) with the fitting determined by HypSpec Program; and the emission intensity (B) at 543 nm as function of $[Cu^{2+}]/[\mathbf{1}]$ (A, B), $[Cu^{2+}]/[\mathbf{2}]$ (C) and $[Cu^{2+}]/[\mathbf{3}]$ (D). [**1, 2**] = 3×10^{-6} M, [**3**] = 1×10^{-6} M, λ_{exc1}= 500 nm, λ_{exc2}=803 nm, λ_{exc3}=774 nm, T = 298 K).

Figure 6. Naked-eye and under UV-light images of PMMA polymers doped with cyanine dyes **1** to **3** and their copper complexes.

Figure 7. Naked-eye and under UV-light images of PMMA_**2** and PMMA_**2**@Cu^{2+} before and after heat. Emission intensities at 660 nm and 824 nm for PMMA_**2** (A) and PMMA_**2**@Cu^{2+} (D) as a function of temperature.

Figure 8. Naked-eye and under UV-light images of PMMA_**3** and PMMA_**3**@Cu^{2+} before and after heat. Emission intensities at 550 nm and 824 nm for PMMA_**3** (A) and PMMA_**3**@Cu^{2+}(D) as a function of temperature.

Figure 9. Emission spectra and naked-eye and under UV-light (365 nm) images of PMMA_**1** and PMMA_**1**@Cu^{2+}polymers, after immersion in 12 M HCl solutions, for 15 to 180 min. Insets represent emission variations of PMMA_**1** at 543 nm and PMMA_**1**@Cu^{2+} at 543 nm and 592 nm.

Figure 10. Naked-eye and under UV-light (365 nm) images of PMMA_**3** and PMMA_**3**@Cu^{2+} polymers, after immersion in 12 M HCl solutions, for 15 to 180 min.

Table 1.

Dyes	$\lambda_{Abs.}$ (nm)	$\lambda_{Emis.}$ (nm)	$\Delta\lambda$ (nm)	ϕ (%)	ε ($M^{-1}.cm^{-1}$)
1	484	541	57	0.01	4.17×10^{4}
2	803	823	20	0.12[9]	2.06×10^{5}
3	774	800	26	0.11[26]	1.28×10^{5}

Table 2.

Dye (L)	Metal (M)	Association constants ($LogK_{ass.}$) ± σ for L:M = 1:1		LOD (µM)		LOQ (µM)	
1		5.38±0.01	5.48±0.01*	1.6	1.5*	3.1	3.1*
2	Cu^{2+}	6.76±0.01	5.57±0.01*	0.9	0.3*	1.6	0.6*
3		6.19±0.04	5.58±0.02*	5.0	1.5*	6.3	4.6*

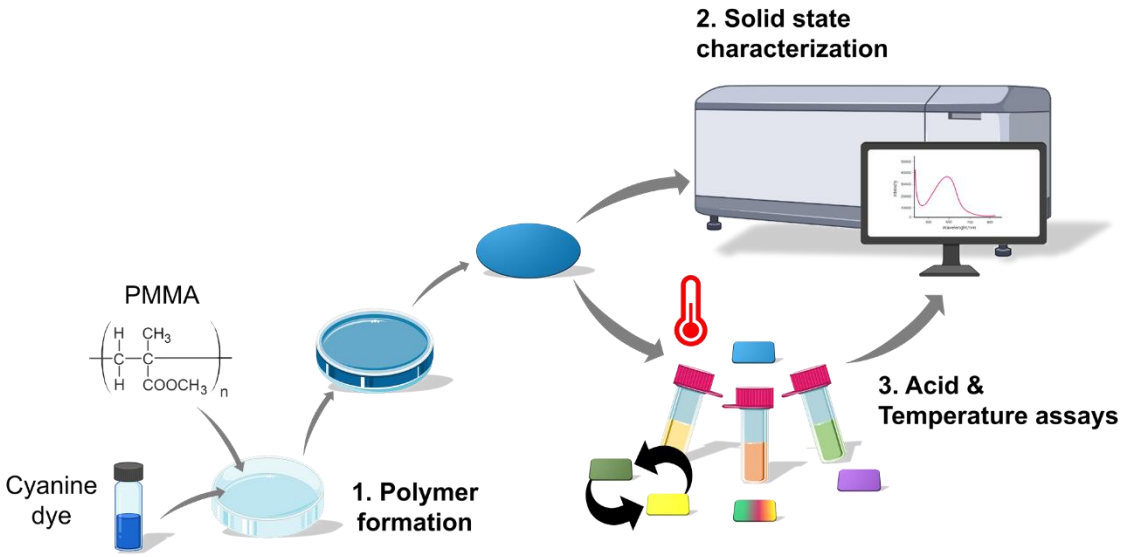

Figure 1.

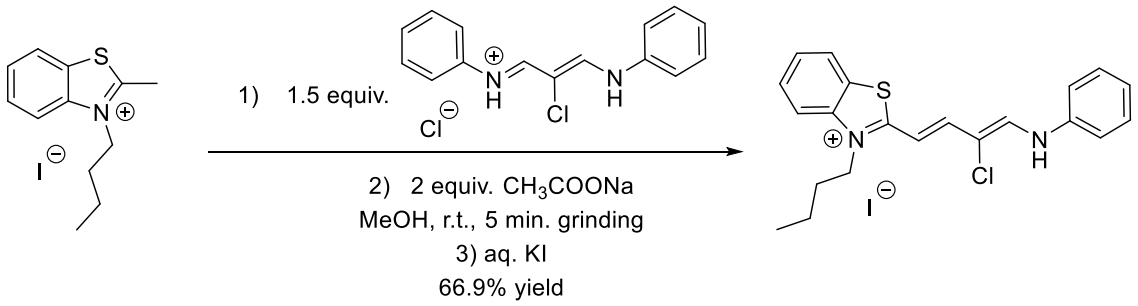

Figure 2.

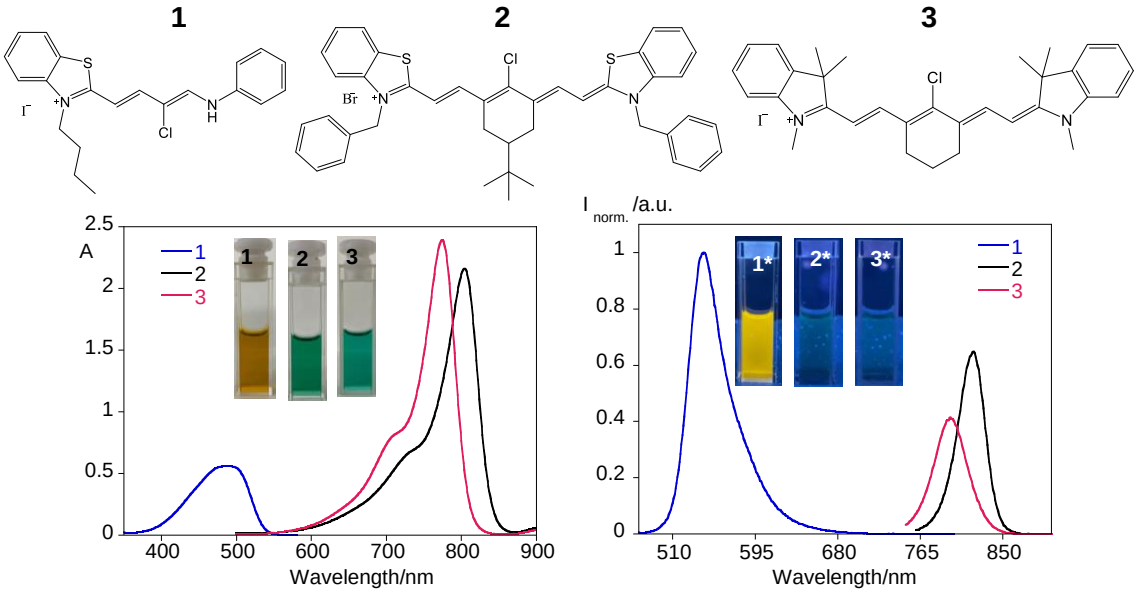
1
2
3
S
N
H
Cl
I⁻
Br⁻
+N
A
2.5
2
1.5
1
0.5
0
400
500
600
700
800
900
Wavelength/nm
1
2
3
I norm. /a.u.
1
0.8
0.6
0.4
0.2
0
510
595
680
765
850
Wavelength/nm
1*
2*
3*

Figure 3.

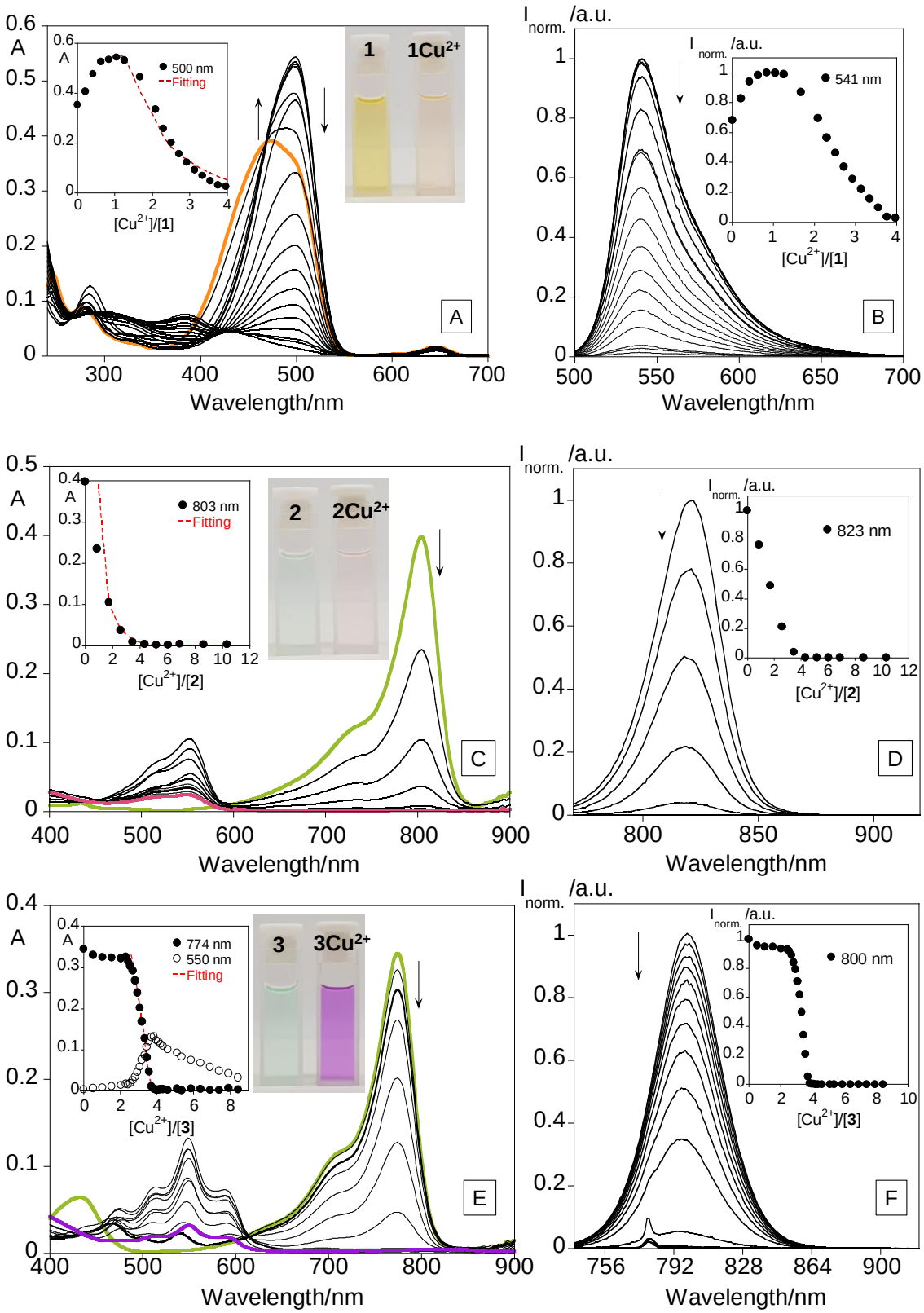
A
500 nm
Fitting
[Cu2+]/[1]
1
1Cu2+
Wavelength/nm
B
I norm. /a.u.
541 nm
[Cu2+]/[1]
C
803 nm
Fitting
2
2Cu2+
[Cu2+]/[2]
D
823 nm
[Cu2+]/[2]
E
774 nm
550 nm
Fitting
3
3Cu2+
[Cu2+]/[3]
F
800 nm
[Cu2+]/[3]

Figure 4.

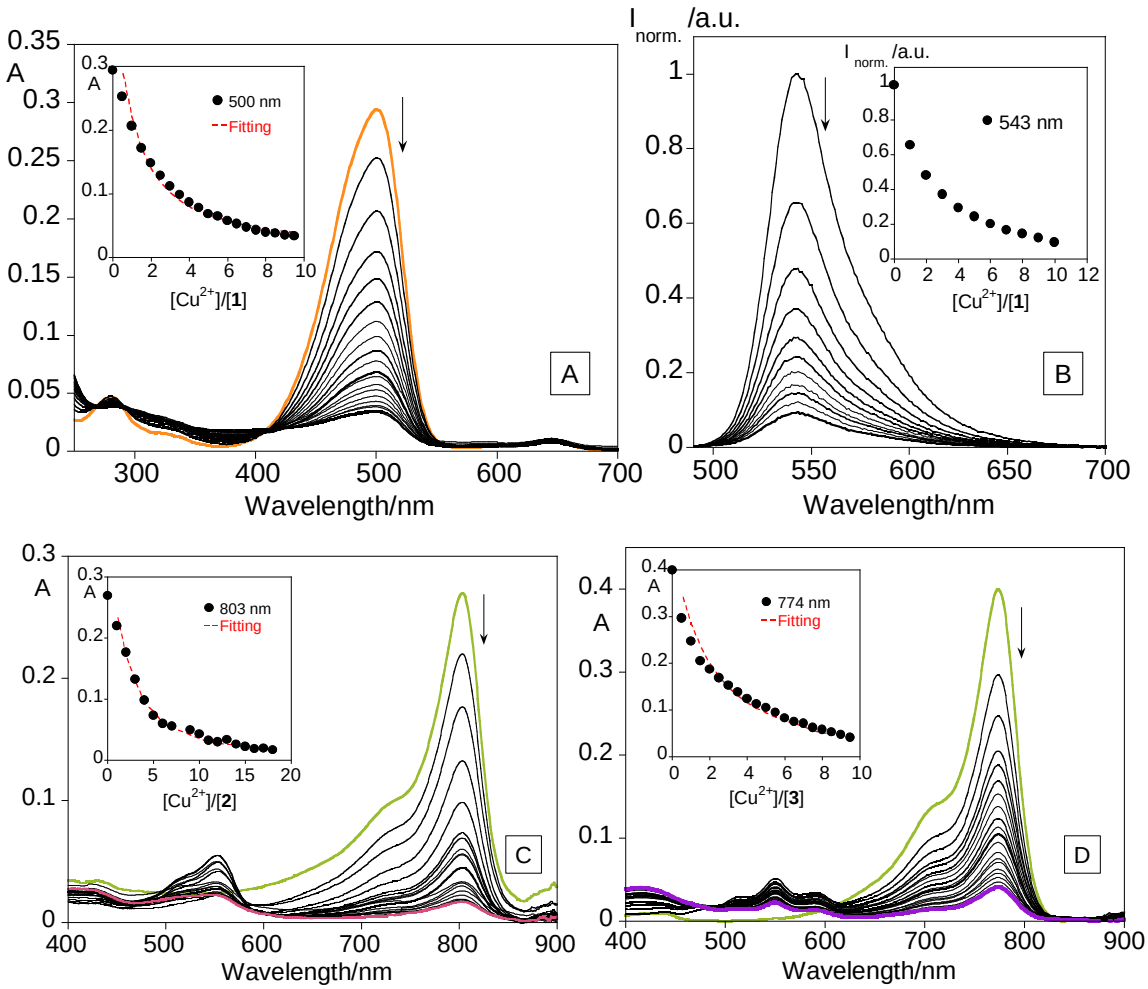
A
500 nm
Fitting
[Cu2+]/[1]
Wavelength/nm
B
I norm. /a.u.
543 nm
[Cu2+]/[1]
Wavelength/nm
C
803 nm
Fitting
[Cu2+]/[2]
Wavelength/nm
D
774 nm
Fitting
[Cu2+]/[3]
Wavelength/nm

Figure 5.

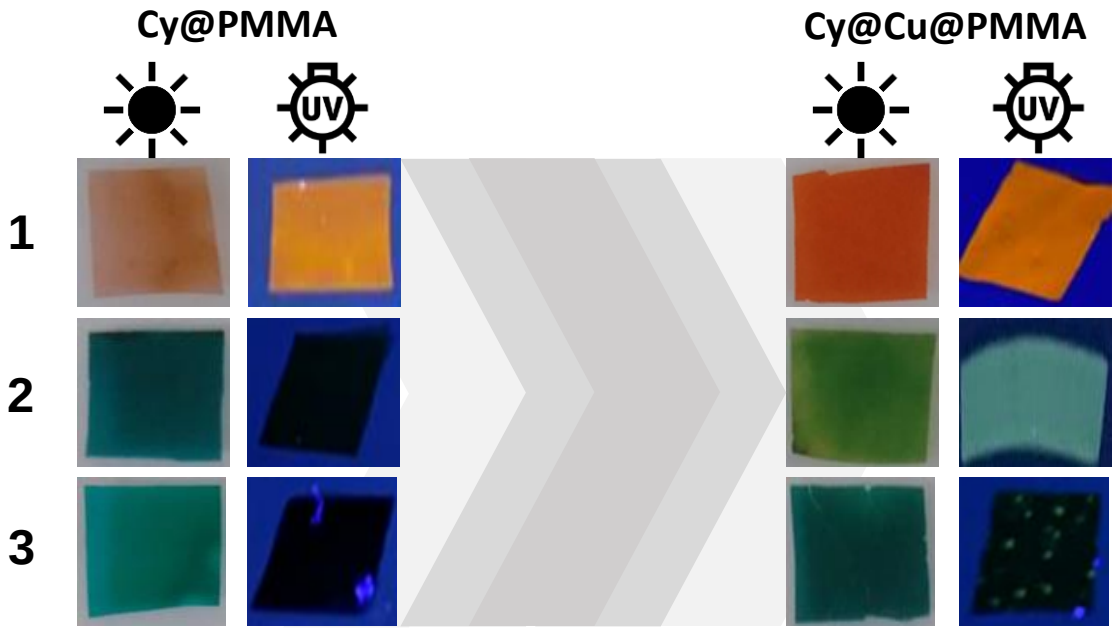

Figure 6.

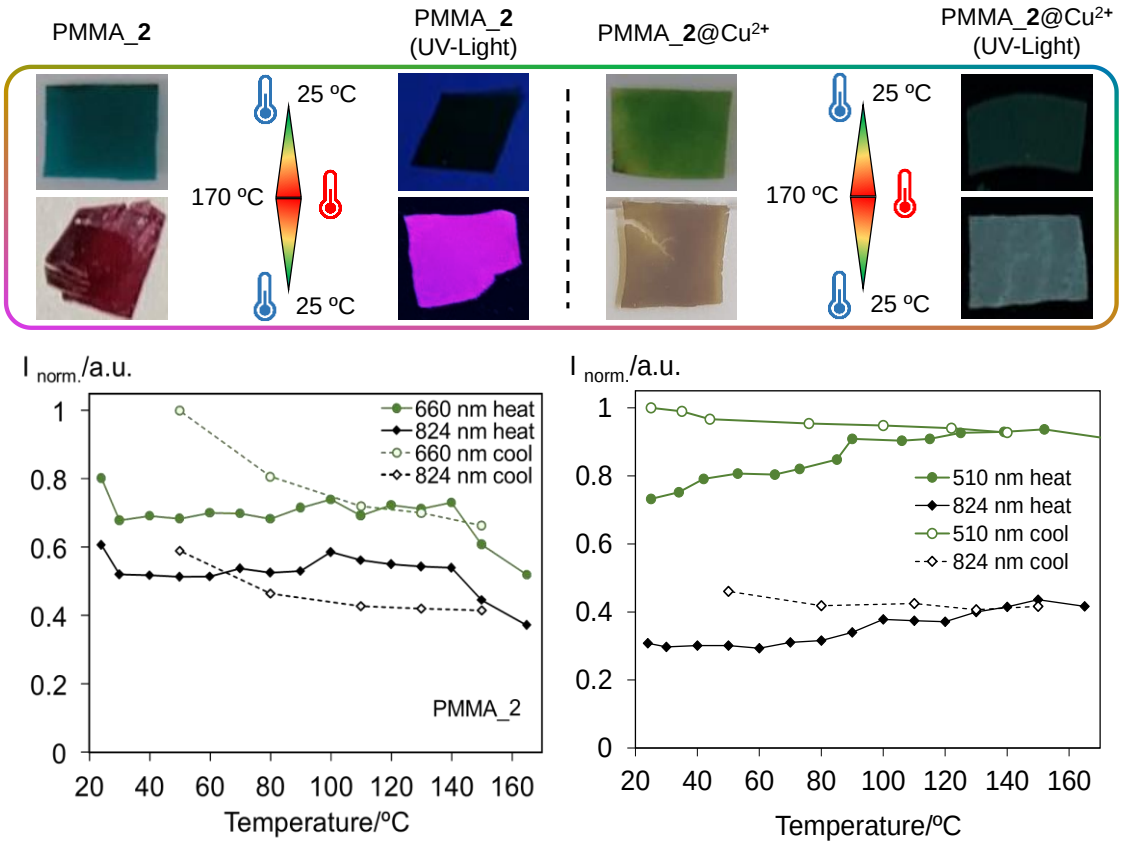
PMMA_2
PMMA_2
(UV-Light)
PMMA_2@Cu2+
PMMA_2@Cu2+
(UV-Light)
25 ºC
170 ºC
25 ºC
25 ºC
170 ºC
25 ºC
I norm./a.u.
660 nm heat
824 nm heat
660 nm cool
824 nm cool
PMMA_2
Temperature/ºC
I norm./a.u.
510 nm heat
824 nm heat
510 nm cool
824 nm cool
Temperature/ºC

Figure 7.

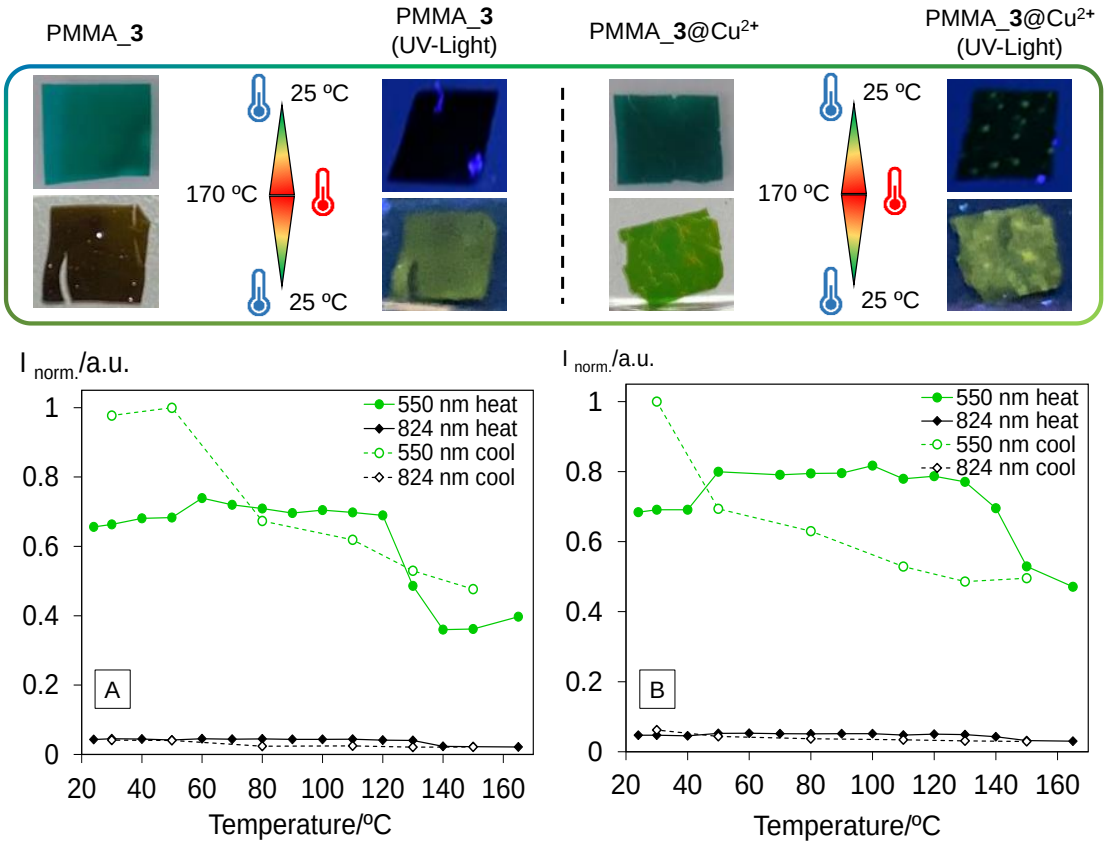
PMMA_3
PMMA_3
(UV-Light)
PMMA_3@Cu2+
PMMA_3@Cu2+
(UV-Light)
25 ºC
170 ºC
25 ºC
25 ºC
170 ºC
25 ºC
I norm./a.u.
550 nm heat
824 nm heat
550 nm cool
824 nm cool
A
Temperature/ºC
I norm./a.u.
550 nm heat
824 nm heat
550 nm cool
824 nm cool
B
Temperature/ºC

Figure 8.

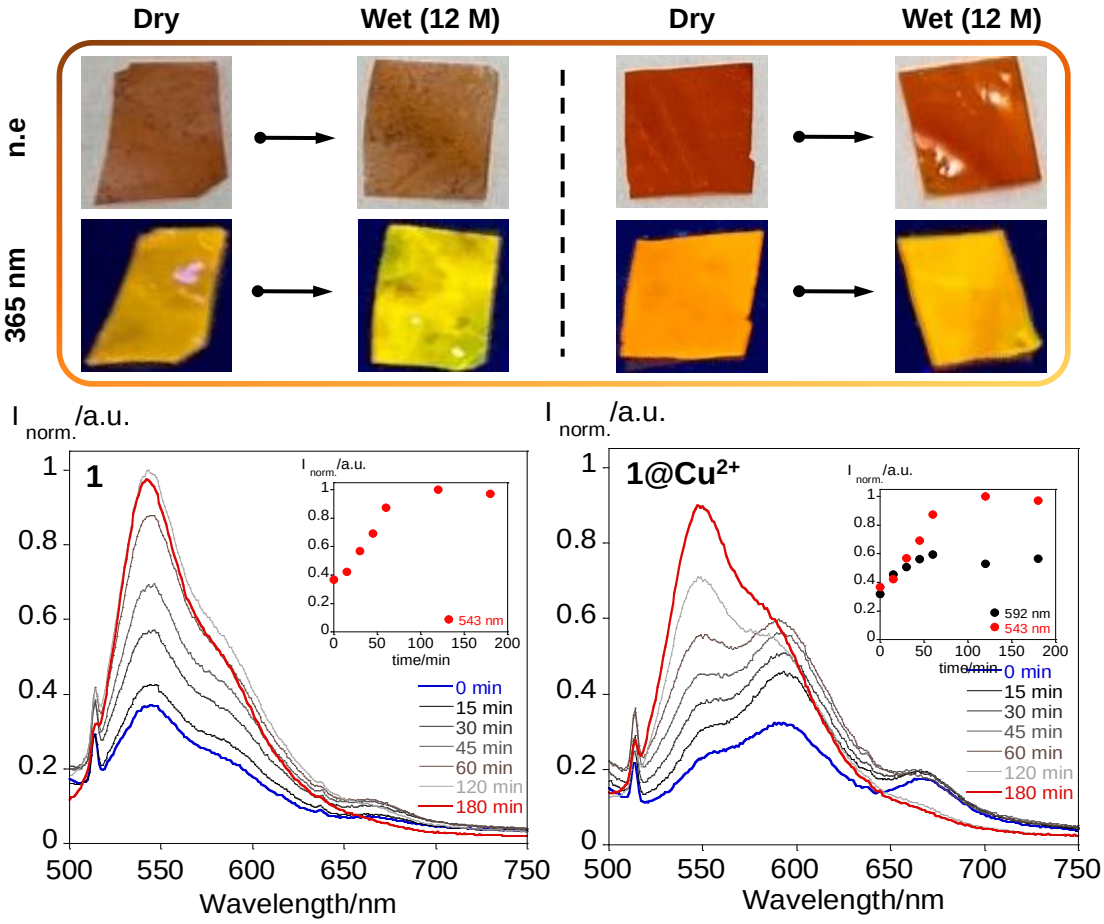
Dry
Wet (12 M)
Dry
Wet (12 M)
n.e
365 nm
I norm./a.u.
1
time/min
543 nm
0 min
15 min
30 min
45 min
60 min
120 min
180 min
Wavelength/nm
I norm./a.u.
1@Cu2+
time/min
592 nm
543 nm
0 min
15 min
30 min
45 min
60 min
120 min
180 min
Wavelength/nm

Figure 9.

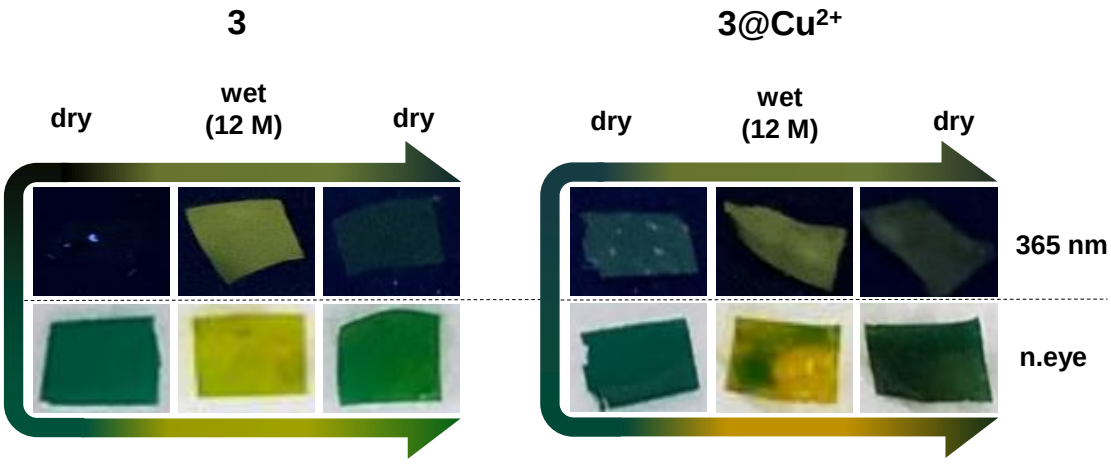

Figure 10.