Supporting Information

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

Joana Galhano [a], Gonçalo A. Marcelo [a], Atanas Kurutos [b], Emilia Bértolo [c], Jose Luis Capelo-Martinez [a,d], Carlos Lodeiro*[a,d] and Elisabete Oliveira*[a,d]

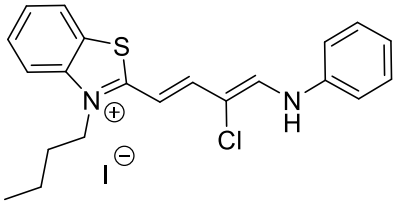
[a] BIOSCOPE Research Group, LAQV-REQUIMTE, Chemistry Department, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal;

[b] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 9, Sofia, 1113, Bulgaria

[c] Section of Natural and Applied Sciences, Canterbury Christ Church University, Canterbury, CT1 1QU, United Kingdom

[d] PROTEOMASS Scientific Society. Rua dos Inventores. Madam Parque. Caparica Campus. 2829-516 Caparica. Portugal

* Corresponding authors: ej.oliveira@fct.unl.pt (EO) and cle@fct.unl.pt (CL).



3-butyl-2-methylbenzo[d]thiazol-3-ium iodide [21], [22] (1 equiv., 333 mg, 1 mmol) and the commercial product 2-chloro-3-(phenylamino)allylidene)benzenaminium chloride (1.5 equiv., 440 mg, 1.5 mmol) from ORGANICA Feinchemie GmbH Wolfen, were mixed with 5 mL methanol in a mortar with a pestle. After homogenization of the mixture, sodium acetate (2 equiv., 164 mg, 1 mmol) was added. The reaction mixture was grinded for 5 minutes at room temperature, which resulted in the crystallization of a solid product. The crude product was dissolved in 10 mL methanol and transferred to a beaker containing 200 mL of an aqueous solution of potassium iodide (3 equiv., 498 mg, 3 mmol). A precipitate formed, and was collected by filtration under reduced pressure. Analytical samples were obtained after repeated recrystallization from methanol, yielding 332 mg (66.9%) of dark red solid with metallic shine (m.p. = 213-215 ^{o}C). The chemical structure of the target dye **1** was confirmed by ^{1}H-NMR, ^{13}C-NMR and HRMS (ESI in both positive and negative modes).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.52 (s, 1H, NH), 8.75 (s, 1H), 8.30 – 8.24 (m, 2H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.69 (m, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.44 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.19 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.67 (d, *J* = 13.8 Hz, 1H), 4.63 (t, *J* = 7.5 Hz, 2H), 1.89 – 1.64 (m, 2H), 1.55 – 1.31 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 169.2, 148.2, 145.6, 141.2, 139.6, 129.6, 128.7, 126.8, 126.4, 124.8, 123.8, 117.7, 115.3, 107.6, 100.7, 47.2, 29.9, 19.3, 13.6. HRMS-ESI(+): m/z: Found 369.1187 [M^+] $C_{21}H_{22}ClN_2S^+$; Requires [M^+] 369.1187 / HRMS-ESI(-) [I^-] Requires 126.9050 , m/z: Found 126.9037 [I^-].

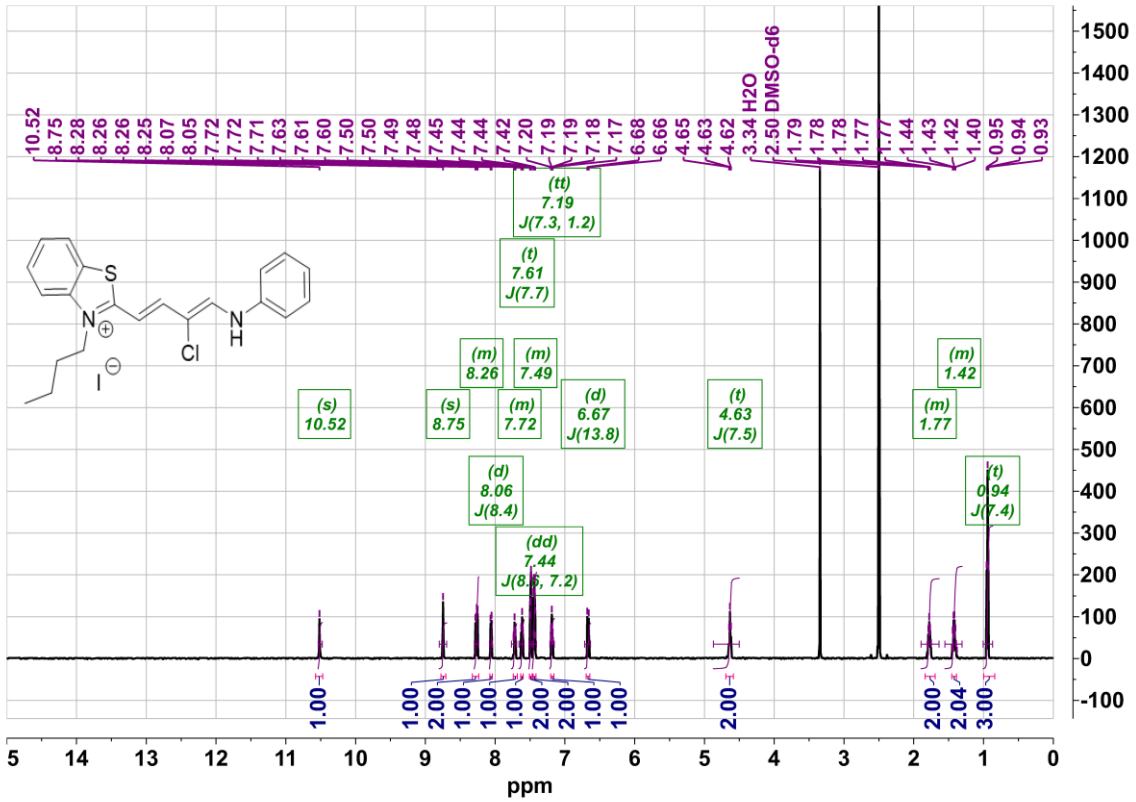


Figure S1. ^{1}H-NMR spectrum (whole spectrum between 0-15 ppm) of the cyanine dye **1** measured in DMSO-d_6.

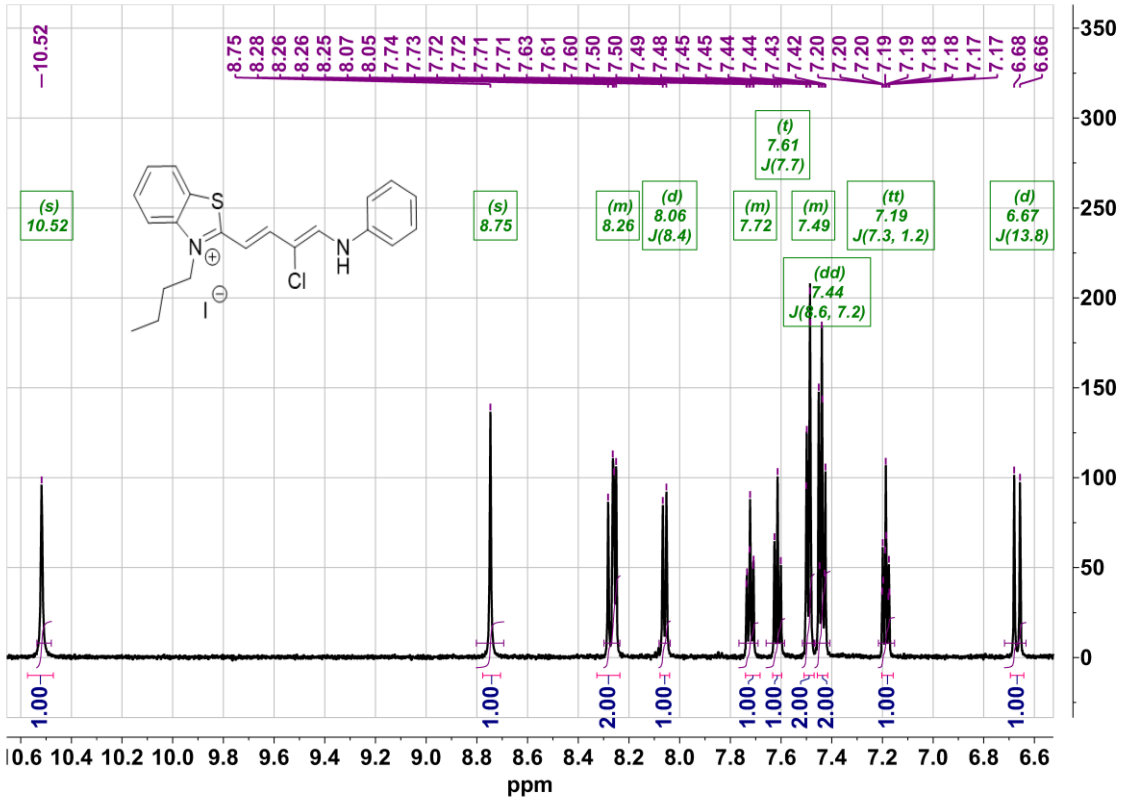


Figure S2. ^{1}H-NMR spectrum (expansion between 6.6-10.6 ppm) of the cyanine dye **1** measured in DMSO-d_6.

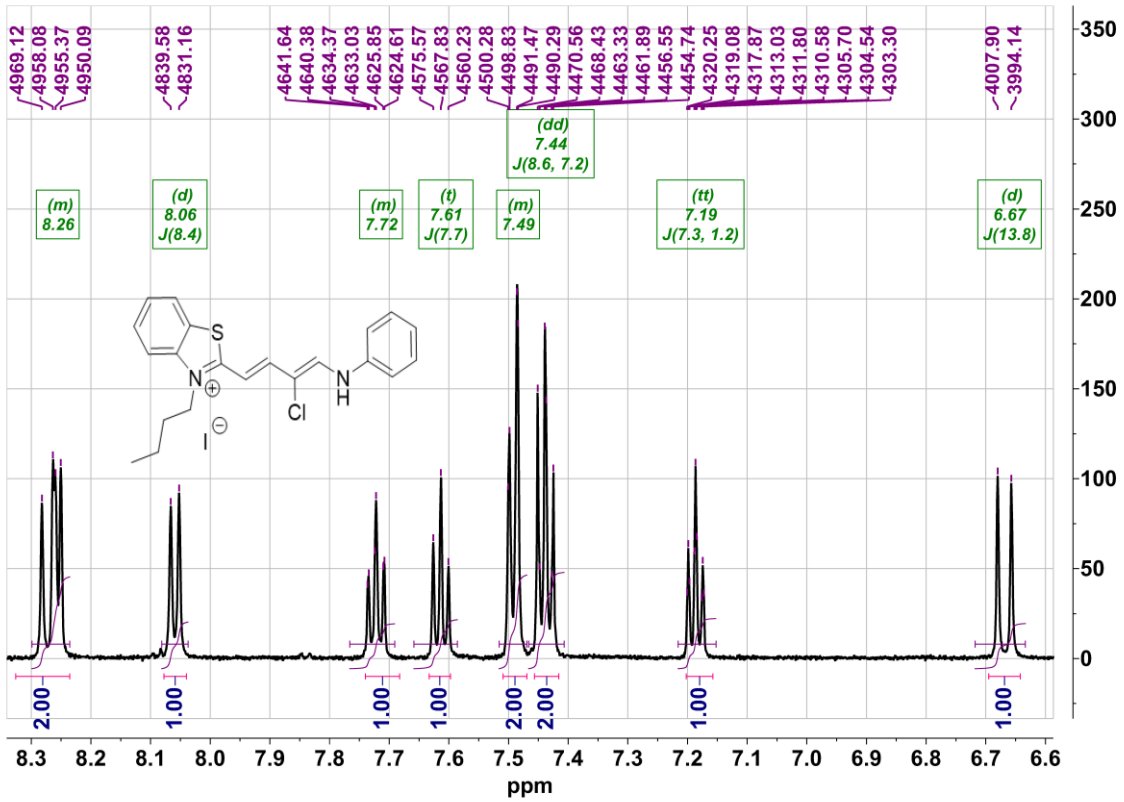


Figure S3. ^{1}H-NMR spectrum (expansion between 6.6-8.3 ppm) of the cyanine dye **1** measured in DMSO-d_6.

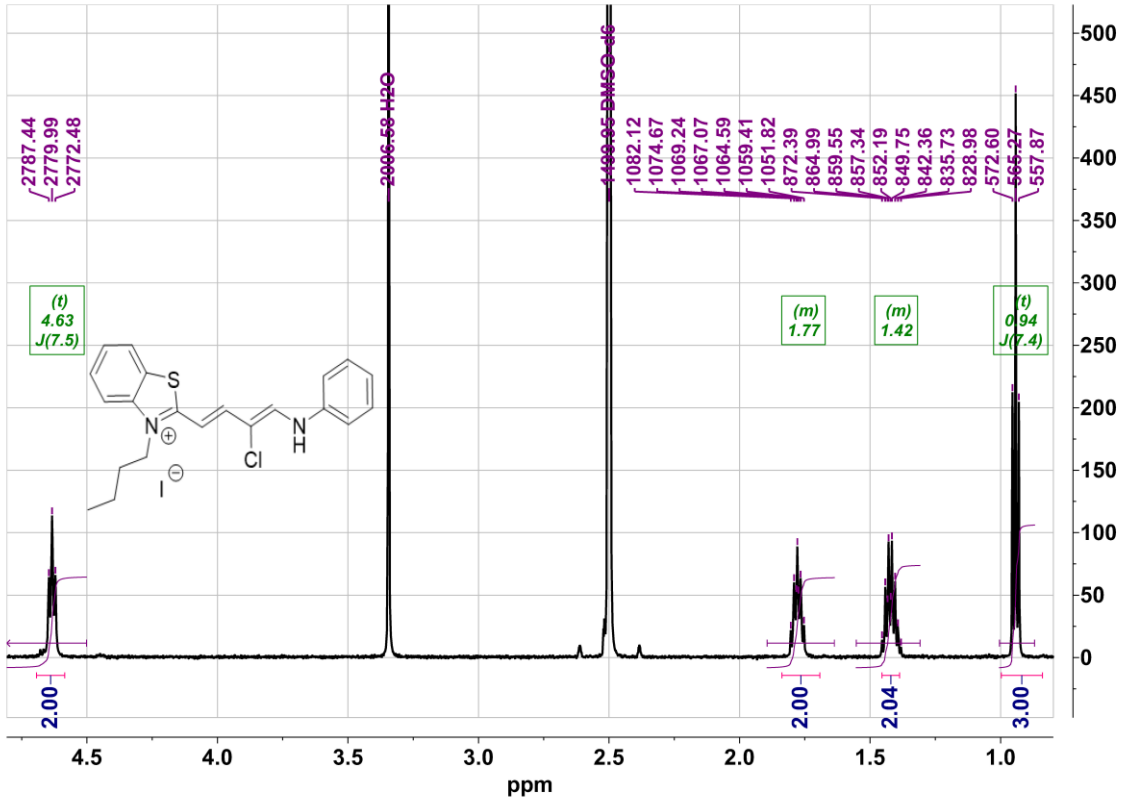


Figure S4. ^{1}H-NMR spectrum (expansion between 0.8-4.8 ppm) of the cyanine dye **1** measured in DMSO-d_6.

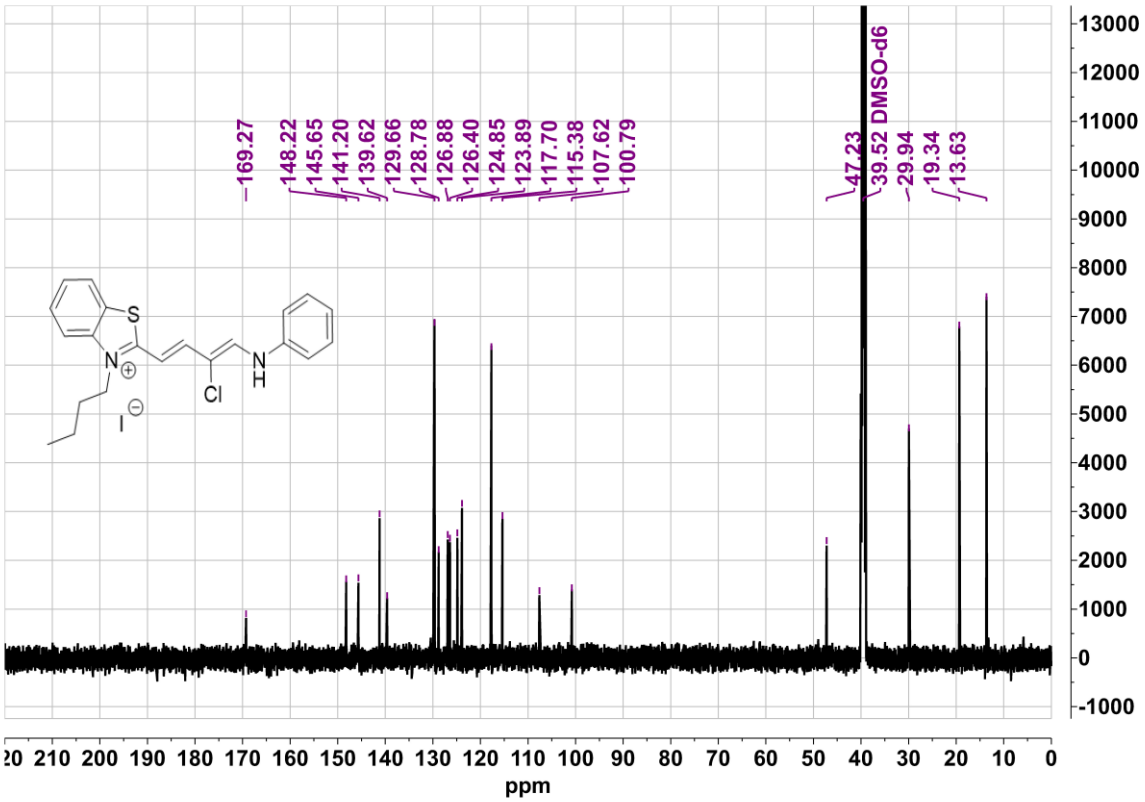


Figure S5. ^{13}C-NMR spectrum (whole spectrum between 0-220 ppm) of the cyanine dye **1** measured in DMSO-d_6.

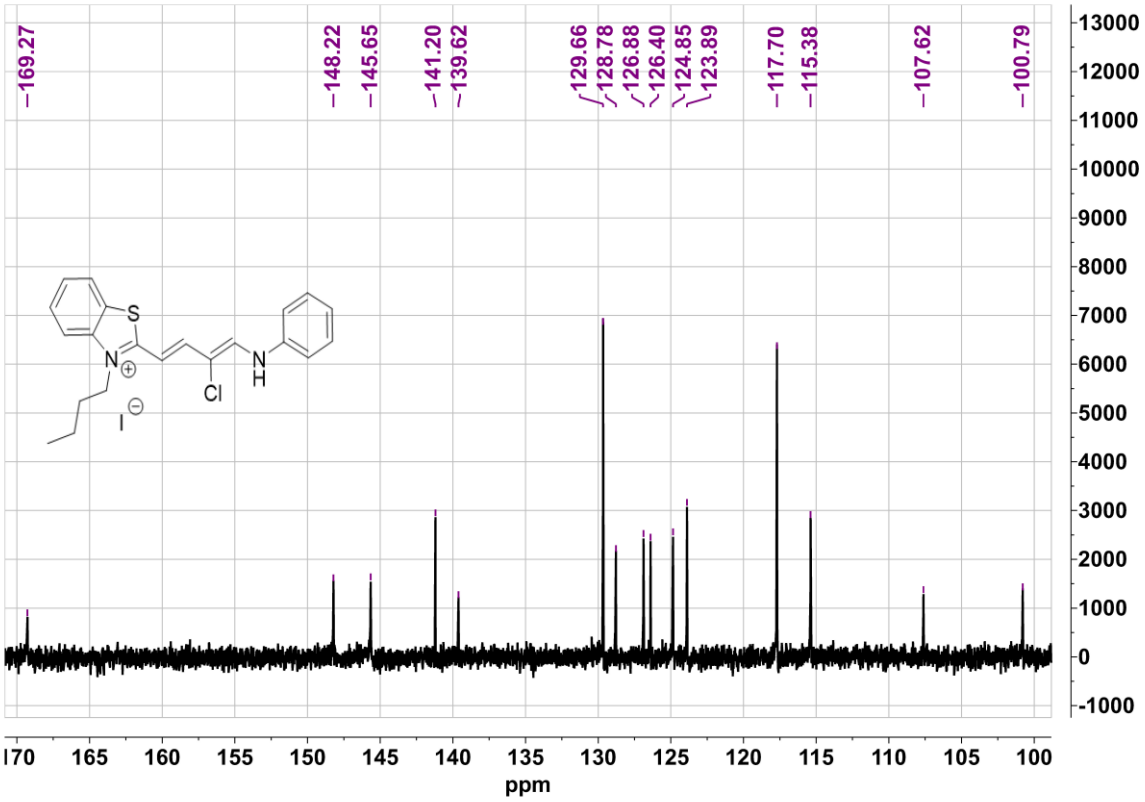


Figure S6. ^{13}C-NMR spectrum (expansion between 100-170 ppm) of the cyanine dye **1** measured in DMSO-d_6.

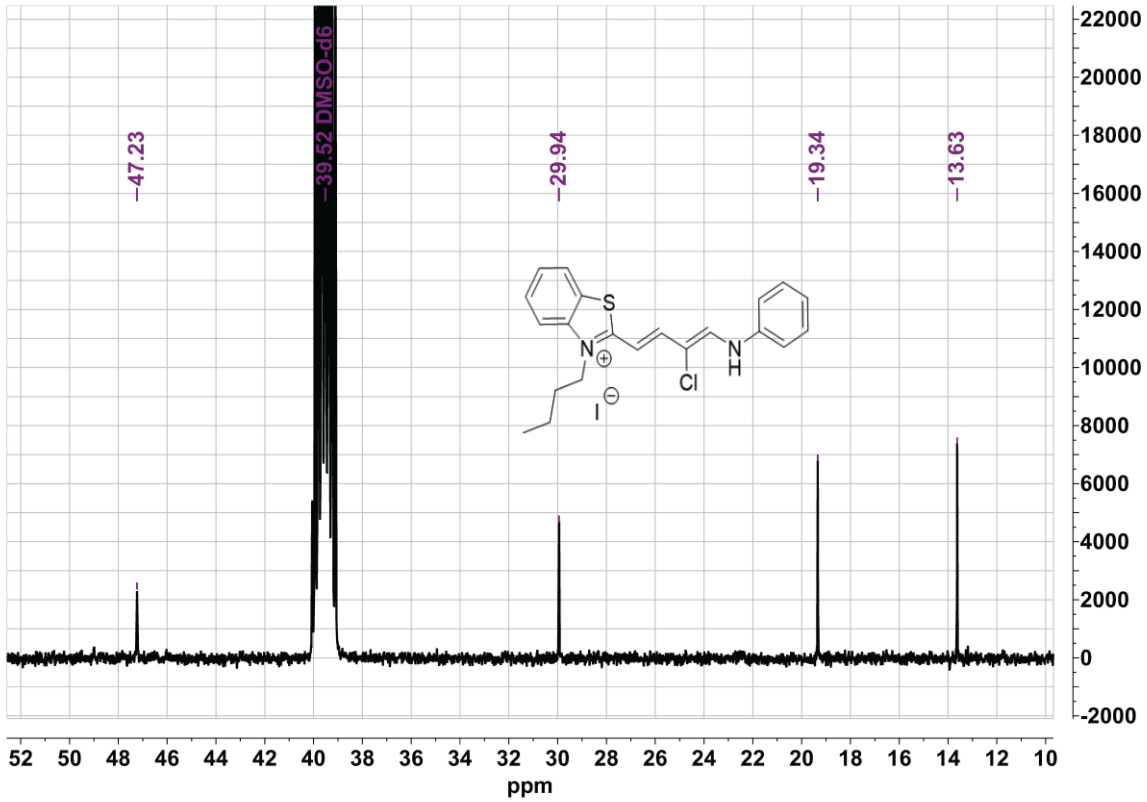


Figure S7. ^{13}C-NMR spectrum (expansion between 10-50 ppm) of the cyanine dye 1 measured in DMSO-d_6.

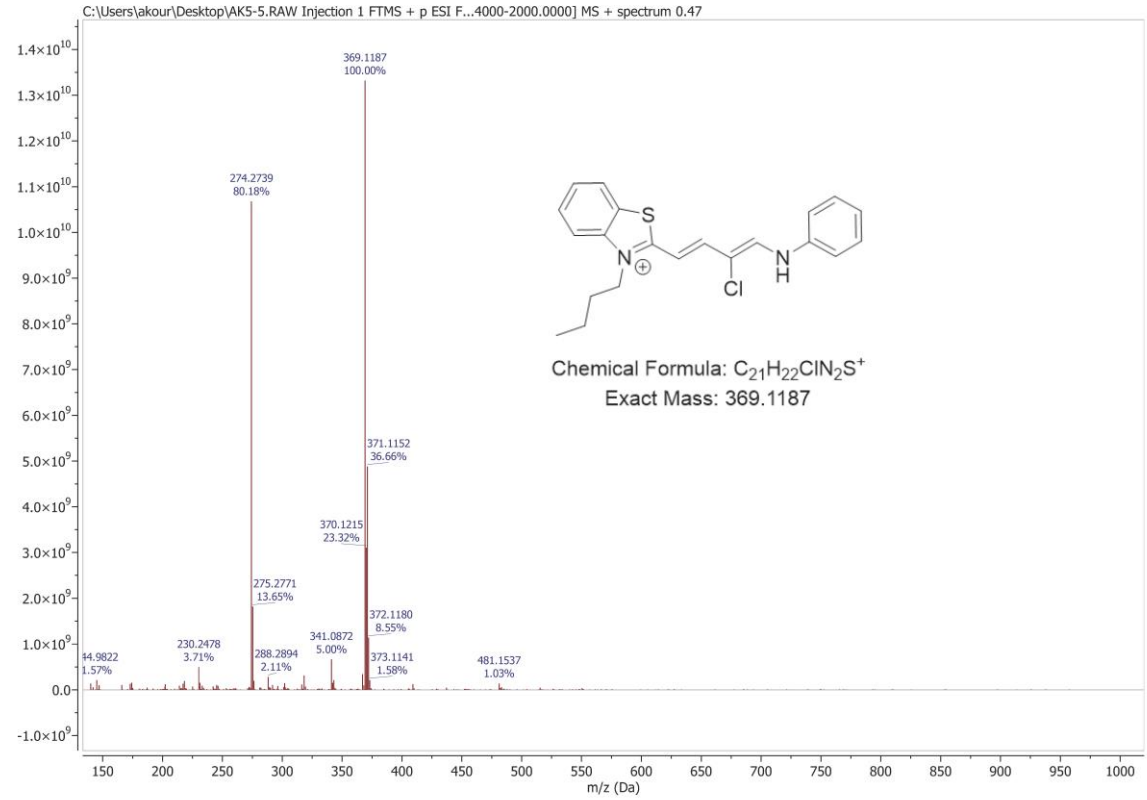


Figure S8. HRMS spectrum of the cyanine dye **1** measured in positive mode.

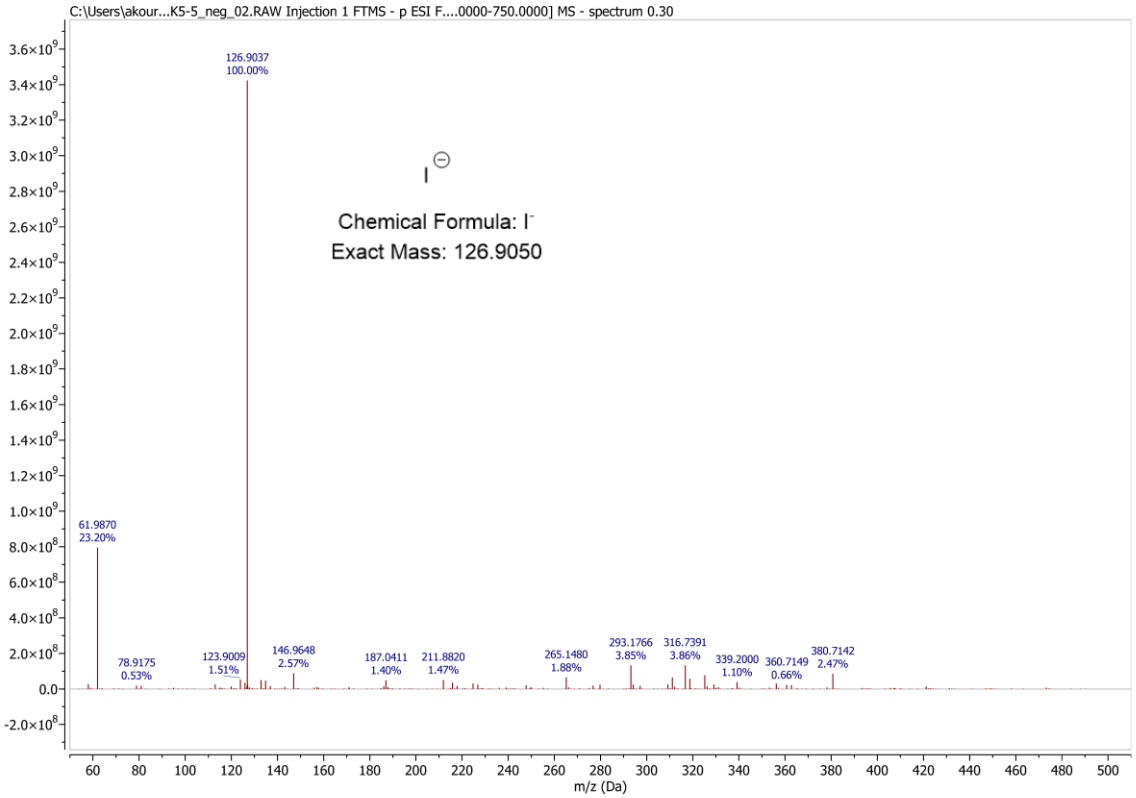


Figure S9. HRMS spectrum of the cyanine dye **1** measured in negative mode.

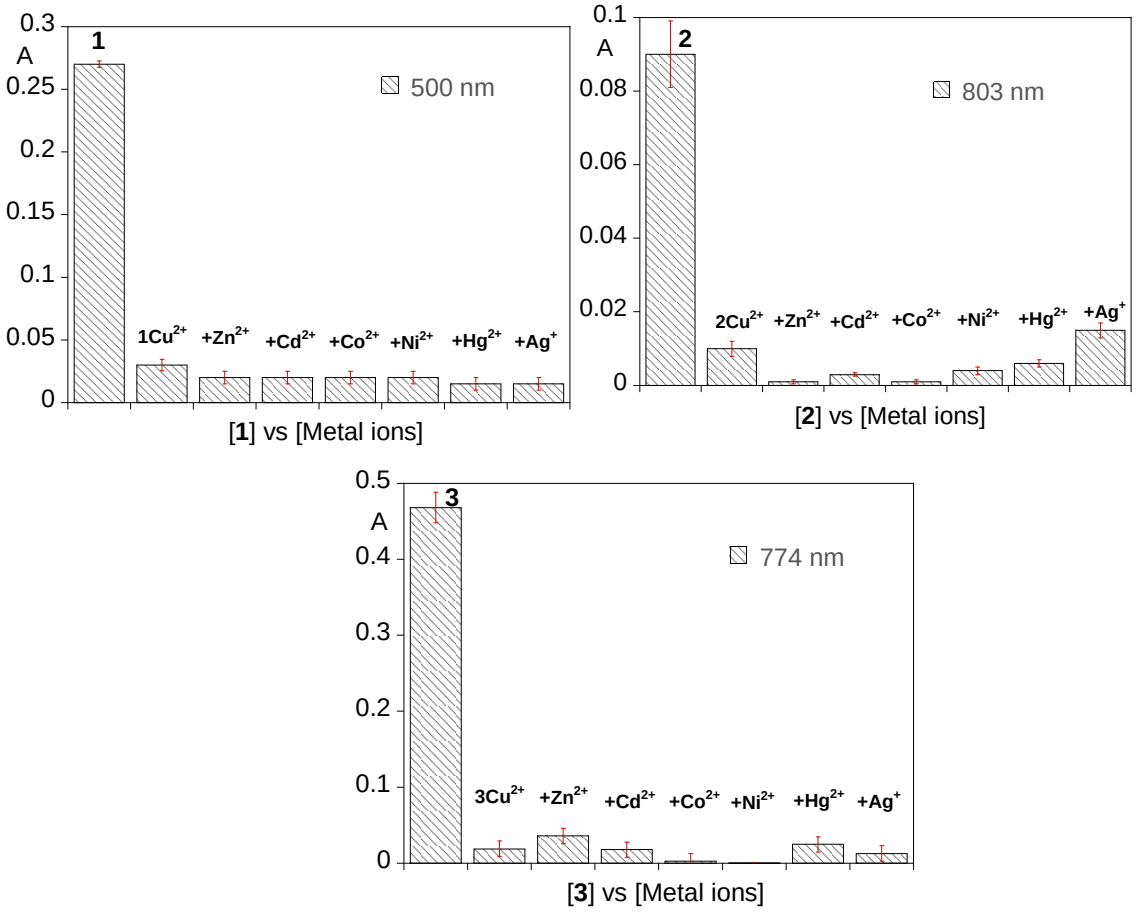


Figure S10. Absorption at 500 nm, 803 nm and 774 nm for dyes **1**, **2** and **3**, after addition of 2 equivalents of Cu^{2+} (**1**Cu^{2+}, **2**Cu^{2+}, **3**Cu^{2+}) ions, respectively. Effect of addition of different metal ions (10 equiv.) in the presence of **1**Cu^{2+}, **2**Cu^{2+} and **3**Cu^{2+}, respectively, in acetonitrile. [**1**] = [**2**] = [**3**] = 3 $\times 10^{-6}$ M.

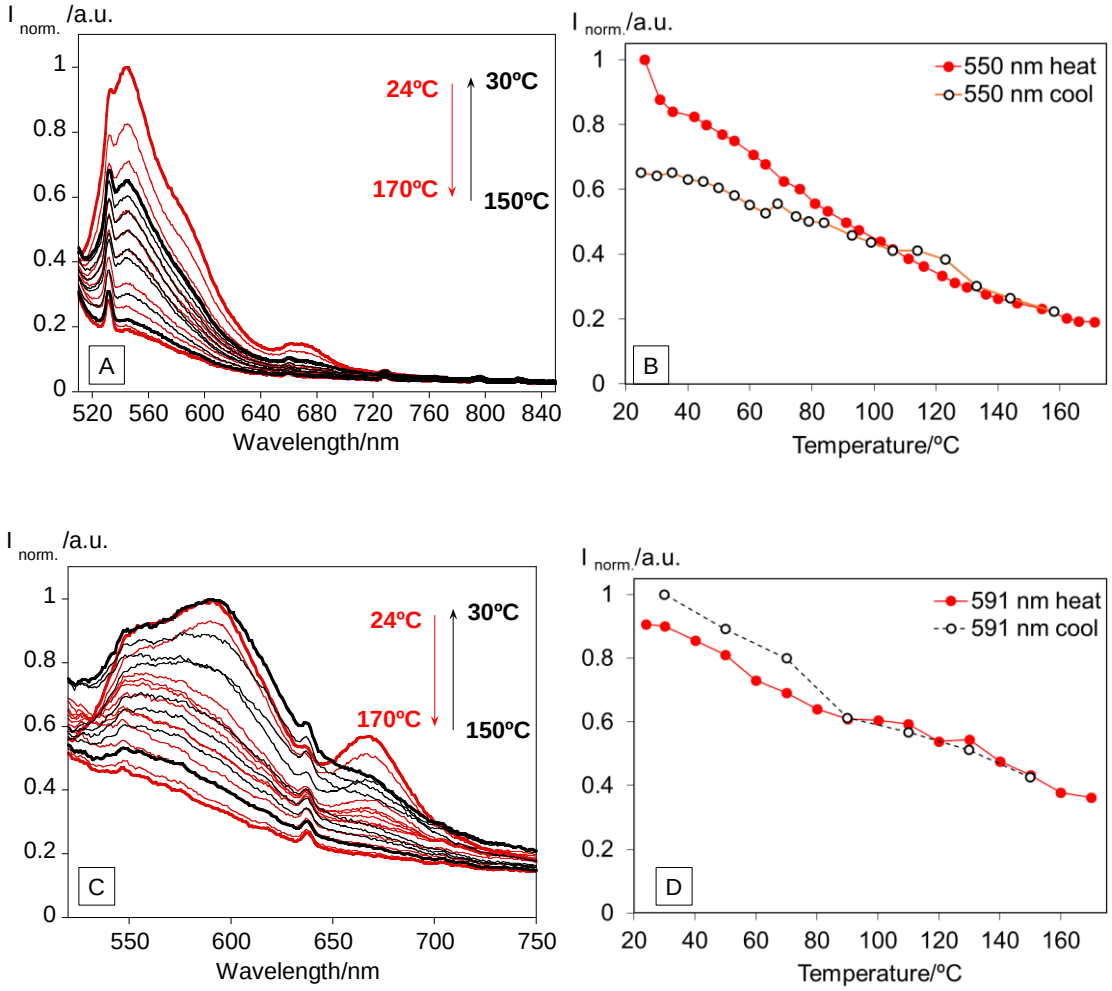


Figure S11. Normalised emission (A, C) spectra of the PMMA_**1** and PMMA_**1**@Cu^{2+}. Emission intensities at 550 nm (B) and 591 nm (D) as a function of temperature.

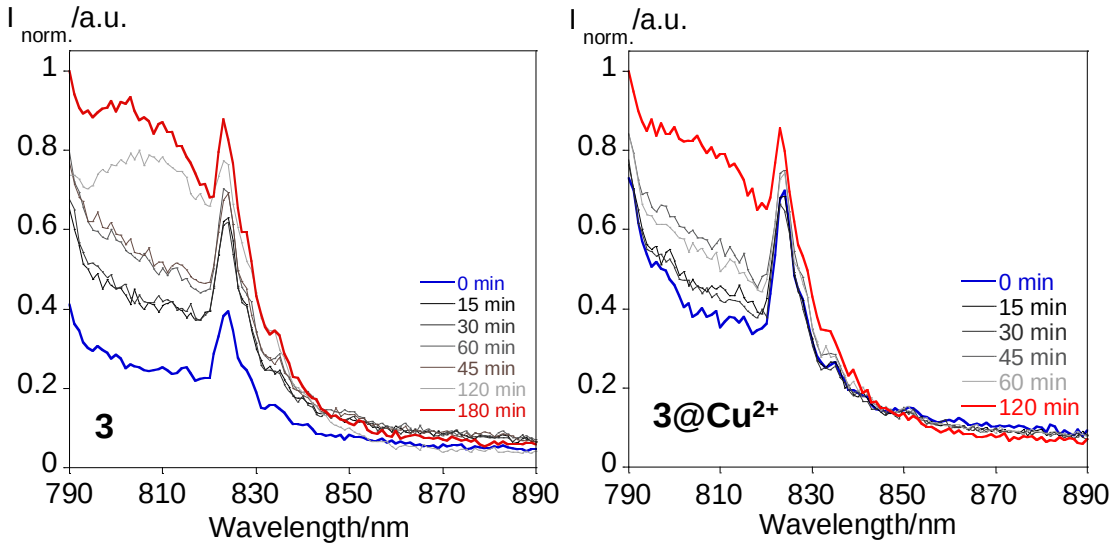


Figure S12. Emission spectra of PMMA_**3** and PMMA_**3**@Cu^{2+} polymers, after immersion in 12 M HCl solutions, for 15 to 180 min. Insets represent emission variations of PMMA_**3** and PMMA_**3**@Cu^{2+} at 805 nm.

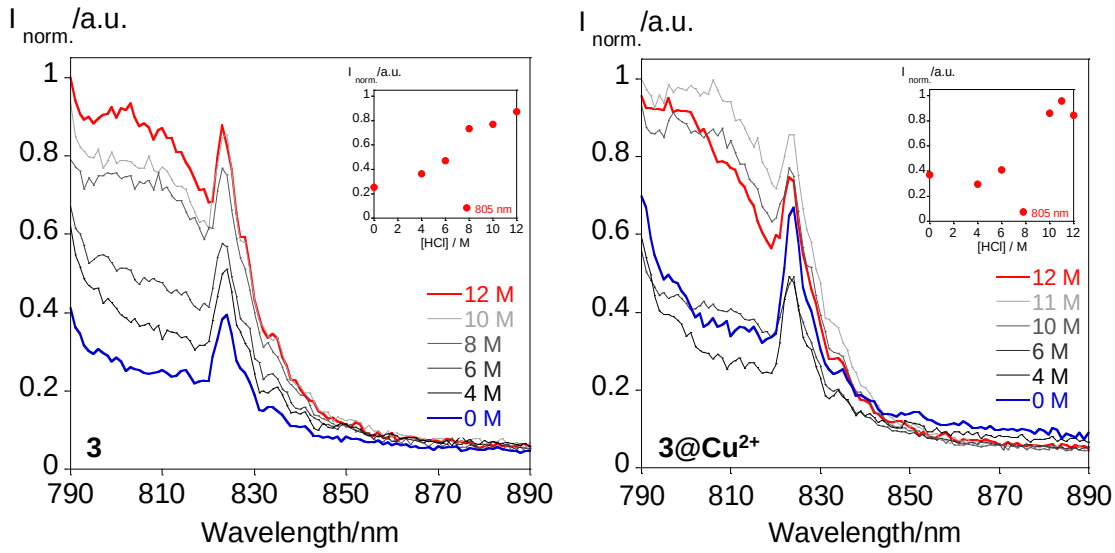


Figure S13. Emission spectra of PMMA_**3** and PMMA_**3**@Cu^{2+}, after a 10 mins immersion in a gradient of HCl concentrations, from 12 to 0 M aqueous solutions. Insets represent emission variations of PMMA_**3** and PMMA_**3**@Cu^{2+}.