Supporting Information

pH-responsive polymer-supported pyrene-based fluorescent dyes for CO_2 detection in aqueous environments

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1. General information and abbreviations

1.1. Materials

1-Aminopyrene (97%), 1-Bromopyrene (98%), Triethylamine (TEA), Cupper (I) Iodide, (98%), 3-Butyn-1-ol (97%), Methacrylic Acid (250 ppm MEHQ, 99%), Methacryloyl chloride (250 ppm MEHQ, 97%), N,N-Dimethylacrylamide (DMAm, 99%, 500 ppm MEHQ), 4-(Dimethylamino) pyridine (DMAP) (≥99%), 4,4'-Azobis(4-cyanovaleric acid) (ACVA, 98%), Acetonitrile (MeCN, ≥99.9%), Methyl Iodide (99%), Ethyl Iodide (99%), and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPAD) were obtained from Sigma-Aldrich. 1-(3-dimethylaminopropyl)-3 ethylcarbodiimide hydrochloride (EDC-HCl, 98+%) was acquired from Acros-Organics. 1,4-Dioxane (99%), Ethyl acetate (EtOAc, ≥99%), Hexane (Hex, ≥95%), Chloroform ($CHCl_3$, 99%) Dichloromethane (DCM, 99%), and Na_2SO_4 anhydrous (99+%, Extra Pure) were obtained from Fischer Scientific.1kg CP Carbon dioxide-cylinder and pure Nitrogen was obtained from BOC. Spectrum Spectra/Por dialysis tubing with either 1 kDa or 6–8 kDa MWCO was supplied by Fischer Scientific. Deionized and 18.2 MΩ·cm ultrapure water was obtained from a Triple Red Alto purification system and was used in all experiments unless stated otherwise.

1.2. Characterization techniques

NMR Spectroscopy. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 MHz on a Bruker DPX-400 spectrometer, using Dimethylsulfoxide-d_6 (DMSO-d_6) as the solvent. Chemical shifts of protons are reported as δ in parts per million (ppm) and are relative to solvent residual peaks.

High Resolution Mass Spectra (HR-MS). Were obtained by using Bruker UHR-Q-ToF MaXis spectrometer with electrospray ionization.

Dynamic Light Scattering. Dynamic light scattering (DLS) experiments were performed using either a Malvern Zetasizer Nano S or ZSP system equipped with a 633 nm He-Ne laser at either 4 mW or 10 mW, respectively. All size measurements were made using samples of concentration 0.1 mg mL-1 in 0.3 M NaCl(aq) (pH = 8.0) at 15 °C, with light scattering detected at an angle of 173° (back-scattering). Hydrodynamic diameters (D_h) were determined using the Stokes-Einstein equation, which assumes perfectly monodisperse non-interacting spheres, and averaged over 4 consecutive runs with at least 10 measurements recorded for each run. All samples of the pH studies were prepared at concentration of 0.3 mg/ml and different buffers solutions.

Transmission Electron Microscopy. Dry-state-stained transmission electron microscopy (TEM) imaging was performed on a JEOL JEM-1400 microscope at an acceleration voltage of 80 kV. All samples were diluted with deionized water to appropriate analysis concentration and then deposited onto formvar-coated copper grids. After approximately 1 min, excess sample was blotted from the grid and the grid was stained using an aqueous 1 wt % uranyl acetate (UA) solution for 1 min prior to blotting, drying and microscopic analysis. Average

particle diameters (D_{ave}) were determined by measuring 100 particles per sample using the ImageJ software.

Fluorescence Spectroscopy. All steady state emission and excitation were obtained with an Edinburgh Instruments FS5 Spectrofluorometer in matched quartz 3.5 mL cuvettes (Starna Cell, Type: 3/Q/10), and analyzed in Fluoracle (Edinburgh Instruments) and Origin Pro 2022 (Origin Labs). All samples of the pH studies were prepared at concentration of 0.3 mg/ml and different buffers solutions.

Fourier-Transform Infrared Spectroscopy. Fourier-Transform Infrared (FTIR) spectroscopy was carried out using an Agilent Technologies Cary 630 FTIR spectrometer. 16 Scans from 600 to 4000 cm^{-1} were taken at a resolution of 4 cm^{-1}, and the spectra were corrected for background absorbance.

Size Exclusion Chromatography. Molecular weight distributions were determined using aqueous size exclusion chromatography (SEC) on an Agilent PL50 instrument fitted with an Agilent PL aquagel-OH MIXED-M column (300 × 7.5 mm × 5 µm) and an aquagel guard column. The mobile phase used was DMF containing 4.6 mM of NH_4BF_4, at a flow rate of 1.0 mL min^{-1}, a column temperature of 40 °C and detection by refractive index (RI). 80 µL of sample were injected for each measurement and eluted for 35 min. Samples were prepared at a concentration of 1 mg mL^{-1} and filtered using a 0.45 µm nylon filter prior to analysis. Calibration was carried out in the molecular weight range 100-30000 Da using EasiVial polyethylene glycol (PEG) standards supplied by Agilent Technologies.

UV-Vis Spectroscopy. UV-Vis spectroscopy was performed using a Thermo Scientific Evolution 350 UV-Vis spectrophotometer equipped with a Xenon flash lamp light source and a dual-matched silicon photodiode detector. Quartz cells (360–2500 nm) from Hellma with two polished sides were used for examining the transmittance spectral data by using Thermo

INSIGHT-2. All samples were prepared at concentration of 0.3 mg/ml and different buffers solutions.

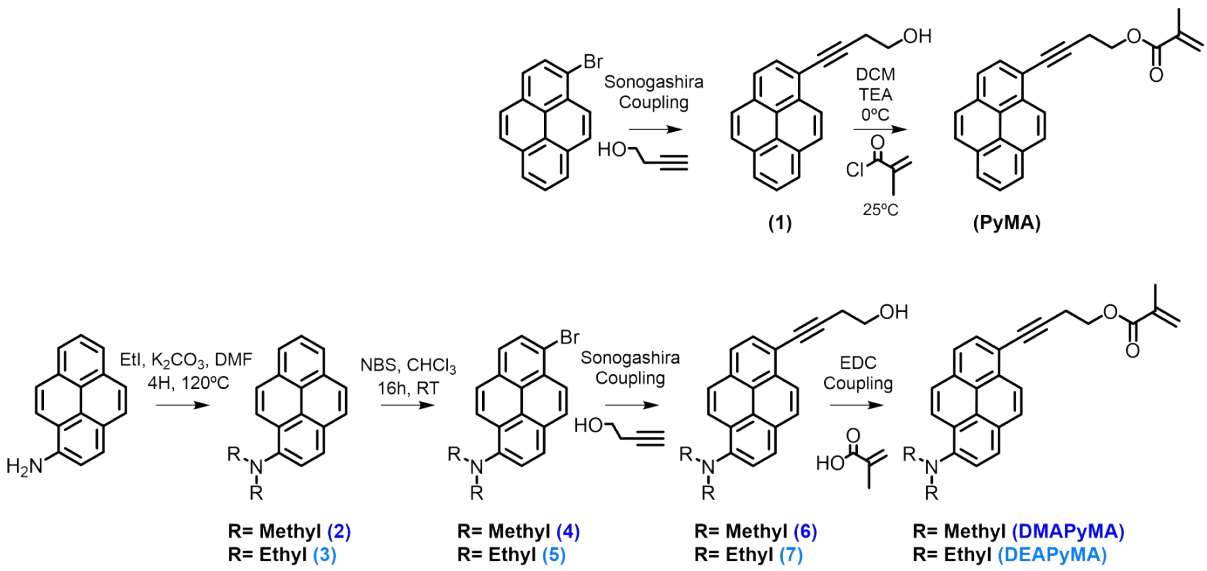
CO_2 bubbling experiments procedure. In a 50 mL round-bottom flask (RBF), an aqueous solution containing 10 ppm of P(DMAm-*co*-DEAPyMA) polymer is prepared by dissolving 0.4 mg of the polymer in 40 mL of deionized (DI) water. The flask is sealed with a septum, and CO_2 from a 1 kg cylinder (BC) is bubbled into the solution while stirring continuously. This process is conducted at a pressure of 1 bar and a constant flow rate of 50 cm^3/min for a duration typically not exceeding 10 minutes. Samples are taken at different time intervals and their fluorescence is measured in an Edinburgh Instruments FS5 Spectrofluorometer.

Air exposure experiments procedure. A previously CO_2-bubbled (10 min) 10 ppm P(DMAm-*co*-DEAPyMA) solution is exposed to air while rigorously stirring for 1 hour. Samples are taken at different time intervals and their fluorescence is measured in an Edinburgh Instruments FS5 Spectrofluorometer.

2. Synthetic methods

2.1. Synthesis of pyrene-derived monomers

Scheme S1. Synthetic routes for different pyrene monomers (PyMA, DMAPyMA and DEAPyMA)



(1). In a dry RBF, and with the previous vacuum/nitrogen cycles done. 1-bromopyrene (1.00 g, 3.6 mmol) was dissolved in THF (30 mL) and Et_3N (3.0 mL, 21.4 mmol) was added under inert atmosphere. CuI (27 mg) and $Pd[Ph_3P]_2Cl_2$ (65 mg) were added, followed by 3-butyn-1-ol (0.4 mL, 5.3 mmol). The reaction mixture was heated to reflux and stirred for 18 h. The reaction mixture was heated to reflux and stirred for 24 h. TLC (hexane/ethyl acetate 1:1) showed the disappearance of starting material. The crude was filtered through celite and washed with DCM. The solvent was removed in vacuo and the residue was loaded on silica gel (3.5 g) and was purified by column chromatography on previously deactivated silica gel in hexane/ethyl acetate (100% hexane to 1:1) and Compound **1** was isolated as a red solid (129 mg, 35%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, J = 9.1 Hz, 1H), 8.21 (ddd, J = 8.9, 7.6, 1.1 Hz, 2H), 8.16 (d, J = 9.1 Hz, 1H), 8.10 (s, 2H), 8.08 – 8.00 (m, 3H), 3.99 (q, J = 6.2 Hz, 2H), 2.95 (t, J = 6.3 Hz, 2H), 1.96 (t, J = 6.3 Hz, 1H).

PyMA. Compound **(1)** (0.30 g. 1.12 mmol) was dissolved in 5 mL dry DCM and triethylamine (TEA, 0.19 mL, 1.34 mmol) was added to the solution at 0 ºC. Then methacryloyl chloride dissolved in 5 mL of dry DCM was added to the above mixture dropwise at 0 ºC under argon. The mixture was allowed to reach the room temperature overnight. The crude solution was washed with dilute HCl aqueous solution (3%) (3×10 mL) and brine (3×10 mL) separately to remove water-soluble side products. The DCM phase was dried over anhydrous magnesium sulphate. Then concentrated the DCM solution to about 3 mL by rotary evaporation. The crude product was chromatographed on a silica gel using petroleum ether/ethyl acetate (9:1, v/v) to afford the pure **PyMA** as an orange/yellow solid (0.120 g, yield: 32%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 9.1 Hz, 1H), 8.20 (ddd, *J* = 9.1, 7.6, 1.2 Hz, 2H), 8.13 (d, *J* = 9.2 Hz, 1H), 8.11 – 8.06 (m, 3H), 8.05 – 8.00 (m, 2H), 6.26 (dq, *J* = 2.1, 1.0 Hz, 1H), 5.64 (p, *J* = 1.6 Hz, 1H), 4.52 (t, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H), 2.03 (dd, *J* = 1.6, 1.0 Hz, 3H), 1.53 (s, 1H). ^{13}C NMR (400 MHz, Chloroform-*d*) δ 167.43, 136.35, 132.14, 131.38, 131.20, 131.11, 129.74, 128.27, 128.09, 127.36, 126.31, 126.11, 125.67, 125.60, 125.58, 124.58, 124.57, 124.46, 118.16, 91.44, 81.22, 62.90, 20.64, 18.51, 1.17. TOF MS (ES+) m/z [M]: 339.138, calculated 339.138.

(2). Triethylamine (4.2 ml, 32 mmol) was added to a mixture of 1-aminopyrene (3.0 g, 13.8 mmol) and K_2CO_3 (4.19 g, 30 mmol) previously dissolved in 30 ml DMF under an argon atmosphere. To this stirring solution, methyl iodide (4.3 ml, 69 mmol) was added dropwise. The reaction mixture was heated at 120 °C for 4 h. The reaction was followed by TLC. After 4 h, TLC analysis showed the completion of the reaction; therefore, it was allowed to cool down to room temperature, and the reaction mixture was evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed twice with saturated aq. $NaHCO_3$. The combined aq. phase was extracted with ethyl acetate. The combined organic phase was dried with Na_2SO_4 and evaporated to dryness. The residue was loaded on silica gel (5 g) and purified by column chromatography in hexane/ethyl acetate (99:1 to 9:1) yielding **(2)** as a yellow solid (2.01 g, 60%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)8.38 (d, *J* = 9.2 Hz, 1H),

8.20 (td, *J* = 8.7, 2.3 Hz, 3H), 8.14 (d, *J* = 9.2 Hz, 1H), 8.05 (t, *J* = 9.3 Hz, 1H), 8.00 (dd, *J* = 8.3, 4.3 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 1H), 2.99 (s, 6H).

(4). Previously recrystallized 1-Bromo-2,5-pyrrolidinedione (NBS) (1.67 g, 9.4 mmol) was added slowly under stirring to a solution of **2** (2.012 g, 8.1 mmol) in $CHCl_3$ (29 mL) and stirred overnight at rt. After full conversion, which was followed by TLC (hexane/CH_2Cl_2 3:1) the mixture was diluted with 30 mL of CH_2Cl_2 and washed with water and brine, dried with Na_2SO_4. After removing the solvent, the residue was loaded on silica gel (5 g) and purified by column chromatography on silica gel in Hexane/CH_2Cl_2 (19:1 to 9:1) to obtain the product **4** (460 mg, 20%) as brown oil in yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.55 (d, *J* = 9.5 Hz, 1H), 8.40 (d, *J* = 9.5 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 3.07 (s, 6H).

(6). In a dry RBF, and with the previous vacuum/nitrogen cycles done. 6-bromo-N,N-dimethylpyren-1-amine **(4)** (0.46 g, 1.4 mmol) was dissolved in THF (13 mL) and Et_3N (1.2 mL, 8.3 mmol) was added under inert atmosphere. CuI (54 mg) and $Pd[Ph_3P]_2Cl_2$ (36 mg) were added, followed by 3-butyn-1-ol (0.2 mL, 2.1 mmol). The reaction mixture was heated to reflux and stirred for 18 h. The reaction mixture was heated to reflux and stirred for 24 h. TLC (hexane/ethyl acetate 1:1) showed the disappearance of starting material. The crude was filtered through celite and washed with DCM. The solvent was removed in vacuo and the residue was loaded on silica gel (2.5 g) and was purified by column chromatography on previously deactivated silica gel in hexane/ethyl acetate (100% hexane to 1:1) and Compound **6** was isolated as a yellow/orange viscous oil (195 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.52 (s, 2H), 8.11 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 8.01 – 7.95 (m, 2H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 3.99 (t, *J* = 6.2 Hz, 2H), 3.07 (s, 6H), 2.95 (t, *J* = 6.2 Hz, 2H).

DMAPyMA. A solution of EDC-HCl (0.17 g, 0.9 mmol) in dry DCM (10 mL) was added dropwise into a mixture of **(6)** (0.19 g, 0.6 mmol), DMAP (7 mg, 10 mol %), ET_3N (164 µl, 1.2 mmol) and methacrylic acid (500 µl, 0.6 mmol) in dry DCM (15 mL) at 0 ºC. The reaction was allowed to reach room temperature for 24h. The crude was then diluted with DCM (50 mL), washed with brine (60 mL x 3), and dried over Na_2SO_4 anhydrous. The reaction mixture was concentrated under vacuum and the residue was loaded on silica gel (2 g) and was purified by column chromatography on previously deactivated silica gel in hexane/ethyl acetate (from 100% hexane to 5:1) as eluent to obtain compound **DMAPyMA** (101 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.50 (d, J = 2.6 Hz, 2H), 8.10 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 8.01 – 7.95 (m, 2H), 7.87 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 6.26 (dq, J = 1.9, 1.0 Hz, 1H), 5.64 (p, J = 1.6 Hz, 1H), 4.51 (t, J = 6.8 Hz, 2H), 3.07 (s, 6H), 3.04 (d, J = 6.8 Hz, 2H), 2.03 (dd, J = 1.6, 1.0 Hz, 3H). ^{13}C NMR (400 MHz, CDCl3) δ 167.45, 149.65, 136.36, 132.38, 131.72, 129.81, 128.09, 127.08, 126.10, 126.00, 125.87, 125.39, 125.18, 124.50, 124.44, 124.31, 123.96, 117.26, 116.75, 91.06, 81.41, 62.97, 45.78, 20.65, 18.53, 1.17. TOF MS (ES+) m/z [M]: 381.170, calculated 381.480.

(3). Triethylamine (2.7 ml, 19.2 mmol) was added to a mixture of 1-aminopyrene (1.90 g, 8.7 mmol) and K_2CO_3 (2.66 g, 19.2 mmol) previously dissolved in 18 ml DMF under an argon atmosphere. To this stirring solution, ethyl iodide (3.2 ml, 43.7 mmol) was added dropwise. The reaction mixture was heated at 120 °C for 4 h. The reaction was followed by TLC. After 4 h, TLC analysis showed the completion of the reaction; therefore, it was allowed to cool down to room temperature, and the reaction mixture was evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed twice with saturated aq. $NaHCO_3$. The combined aq. phase was extracted with ethyl acetate. The combined organic phase was dried with Na_2SO_4 and evaporated to dryness. The residue was loaded on silica gel (5 g) and purified by column chromatography in hexane/ethyl acetate (99:1 to 9:1) yielding **3** as a yellow

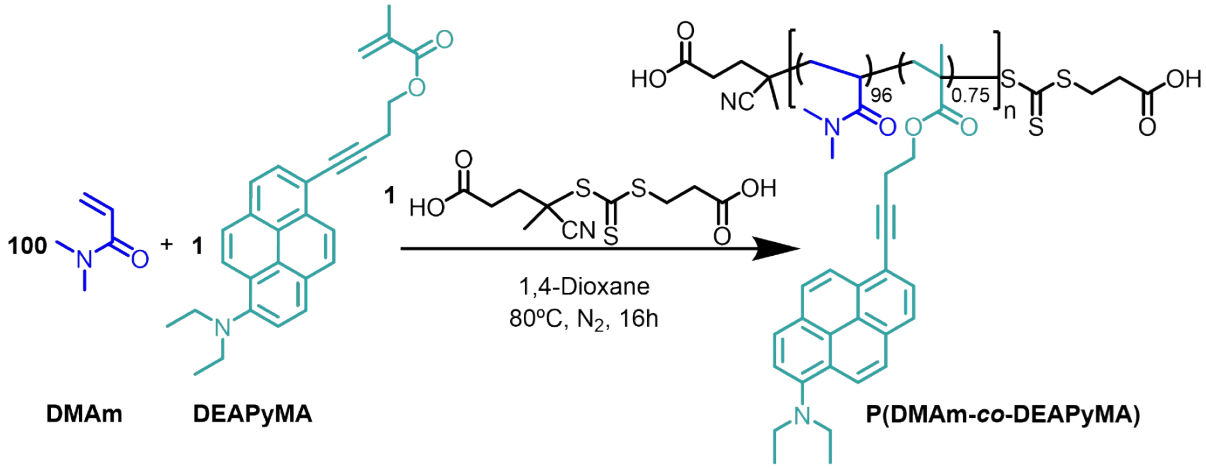
solid (1.18 g, 50%). %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.57 (d, *J* = 9.2 Hz, 1H), 8.16 – 8.08 (m, 3H), 8.05 (d, *J* = 9.3 Hz, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 3.35 (q, *J* = 7.1 Hz, 4H), 1.08 (t, J = 7.1 Hz, 6H).

(5). Previously recrystallized 1-Bromo-2,5-pyrrolidinedione (NBS) (1.16 g, 6.5 mmol) was added slowly under stirring to a solution of **3** (1.18 g, 4.3 mmol) in $CHCl_3$ (15 mL) and stirred overnight at rt. After full conversion, which was followed by TLC (hexane/CH_2Cl_2 3:1) the mixture was diluted with 30 mL of CH_2Cl_2 and washed with water and brine, dried with Na_2SO_4. After removing the solvent, the residue was loaded on silica gel (4 g) and purified by column chromatography on silica gel in Hexane/CH_2Cl_2 (19:1 to 9:1) to obtain the product **5** (143 mg, 10%) as brown oil in yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.67 (d, *J* = 9.5 Hz, 1H), 8.40 (d, *J* = 9.5 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.9 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 3.36 (q, *J* = 7.1 Hz, 4H), 1.09 (t, *J* = 7.1 Hz, 6H).

DEAPyMA. In a dry RBF, and with the previous vacuum/nitrogen cycles done. 6-bromo-N,N-diethylpyren-1-amine **(5)** (130 mg, 0.4 mmol) was dissolved in THF (4 mL) and Et_3N (330 µL, 2.4 mmol) was added under argon atmosphere. CuI (3 mg) and $Pd[Ph_3P]_2Cl_2$ (7 mg) were added, followed by 3-butyn-1-ol (45 µL, 0.6 mmol). The reaction mixture was heated to reflux and stirred for 18 h. The reaction mixture was heated to reflux and stirred for 24 h. TLC (hexane/ethyl acetate 1:1) showed the disappearance of starting material. The crude was filtered through celite and washed with DCM. The solvent was removed in vacuo and the residue was loaded on silica gel (2.5 g) and was purified by column chromatography on previously deactivated silica gel in hexane/ethyl acetate (100% hexane to 1:1) and Compound **DEAPyMA** was isolated as a yellow/orange viscous oil (117 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.64 (d, *J* = 9.4 Hz, 1H), 8.50 (d, *J* = 9.4 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 2.6 Hz, 1H), 7.99 (d, *J* = 3.5 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.81

(d, J = 8.2 Hz, 1H), 3.99 (q, *J* = 6.3 Hz, 2H), 3.36 (q, *J* = 7.1 Hz, 4H), 2.96 (d, *J* = 6.2 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (400 MHz, CDCl3) δ 146.97, 136.36, 129.69, 128.03, 126.11, 125.78, 125.63, 124.79, 124.52, 123.97, 120.45, 62.99, 48.88, 20.65, 18.52, 12.85. TOF MS (ES+) m/z [M]: 410.212, calculated 410.212.

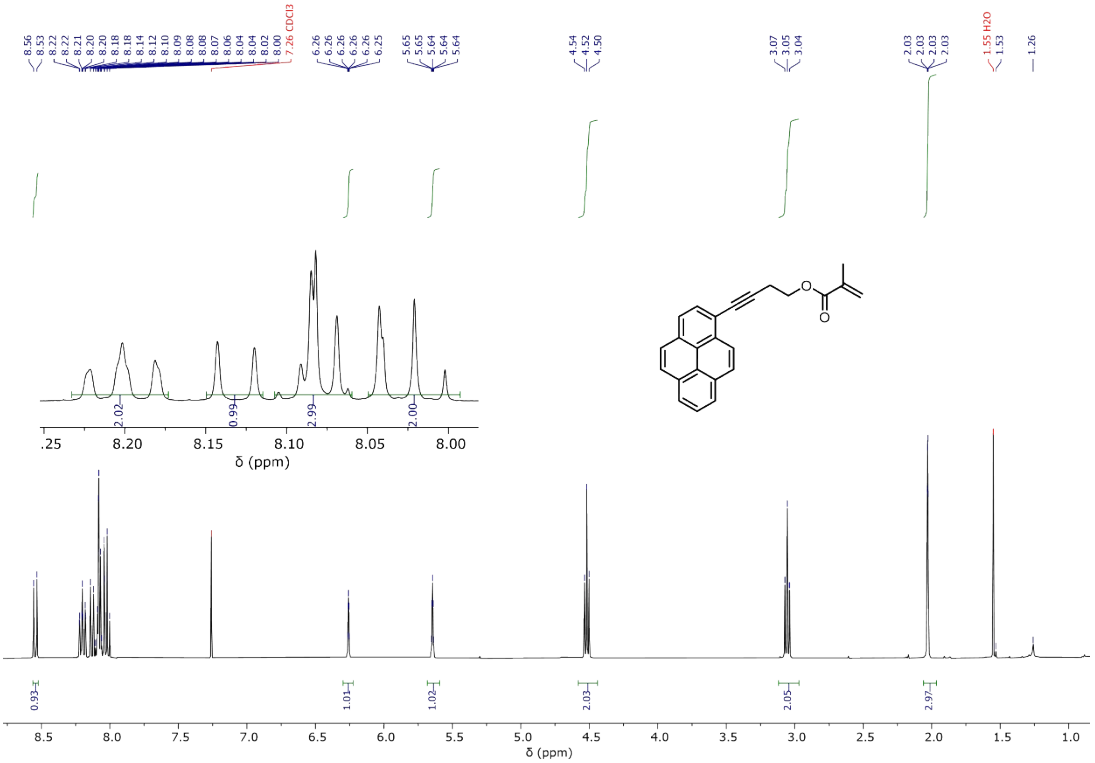
2.2. Scheme S2. Synthesis of Poly(N,N′-Dimethylacrylamide-co-Diethylaminopyrene methacrylate) P(DMAm-co-DEAPyMA)



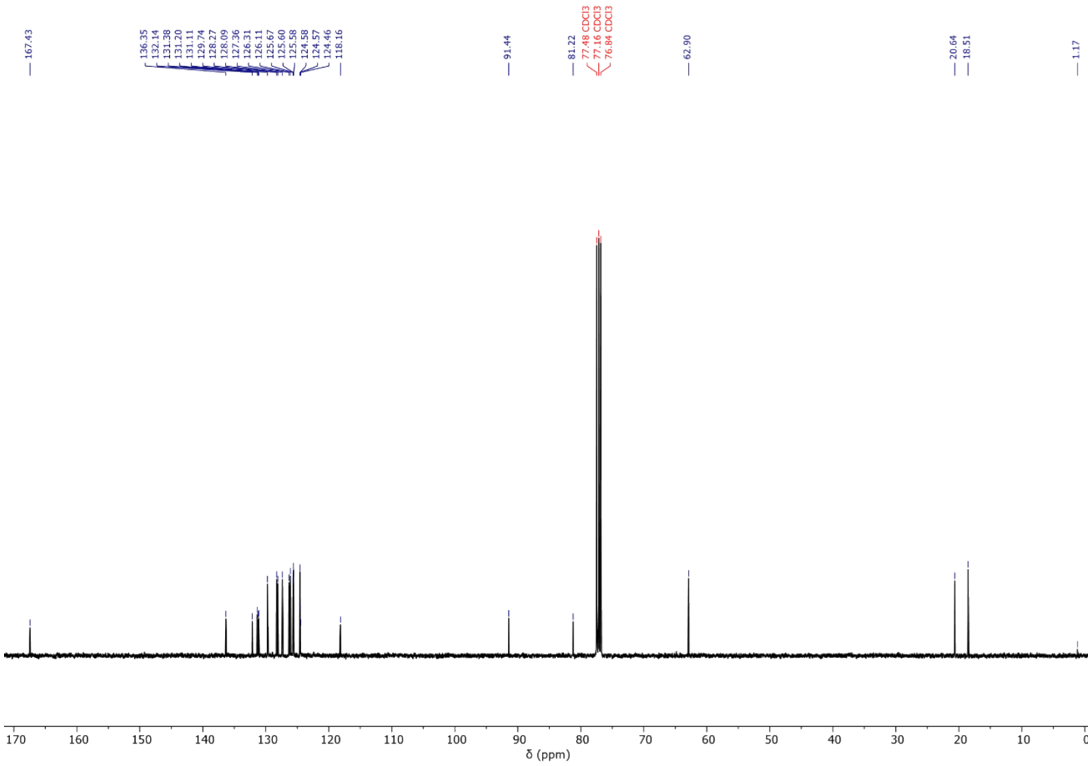
N,N′-Dimethylacrylamide (DMAm) monomer (65 mg, 0.65 mmol, 100 equiv), 4-((((2-Carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid chain-transfer agent (CTA) (2.0 mg, 65 µmol, 1 equiv), 4-(6-(diethylamino)pyren-1-yl)but-3-yn-1-yl methacrylate (2.66 mg, 065 µmol, 1 equiv) and 4,4′-azobis(4- cyanovaleric acid) (ACVA) radical initiator (1.0 mg, 06 µmol, 0.1 equiv) were dissolved in 1,4-dioxane (3 mL). After transferring the solution to an ampoule equipped with a magnetic stir bar, the solution was degassed by purging with N_2(g) for 30 min under rapid stirring. The polymerization reaction was initiated upon immersion of the ampoule in an oil bath heated at 80 °C, and the polymerization mixture was stirred at this temperature for 16 h to ensure full monomer conversion. The polymerization reaction was then terminated upon cooling and exposing the polymerization mixture to air. The resulting P(DMAm$_{96}$-*co*-DEAPyMA$_{0.75}$) polymer was purified by extensive dialysis against deionized water (MWCO = 1 kDa) and was recovered as a yellow solid by freeze drying (60 mg). The

resulting polymer was then characterized by ^{1}H-NMR spectroscopy and aqueous SEC analysis.^{1}H NMR (400 MHz, $CDCl_3$) conv ~96%, $M_{n,NMR}$ = 10.1 kDa. SEC ($CHCl_3$) $M_{n,SEC}$ = 8.01 kDa , $Đ_{SEC}$ = 1.4

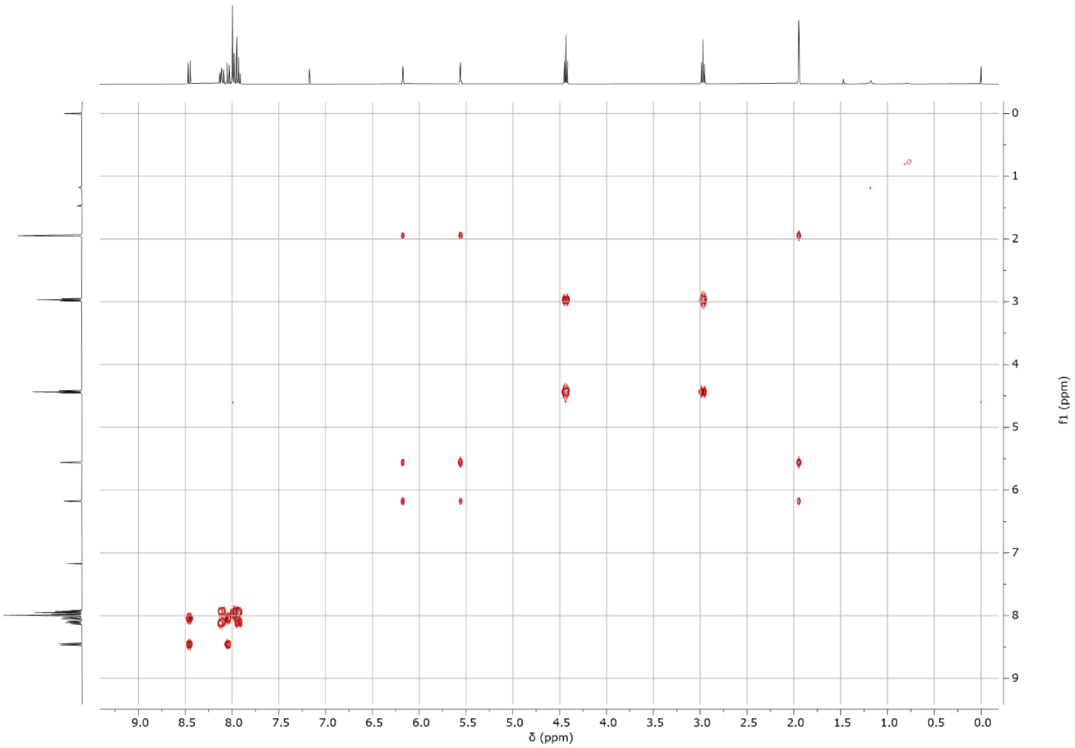
3. Monomer´s characterization



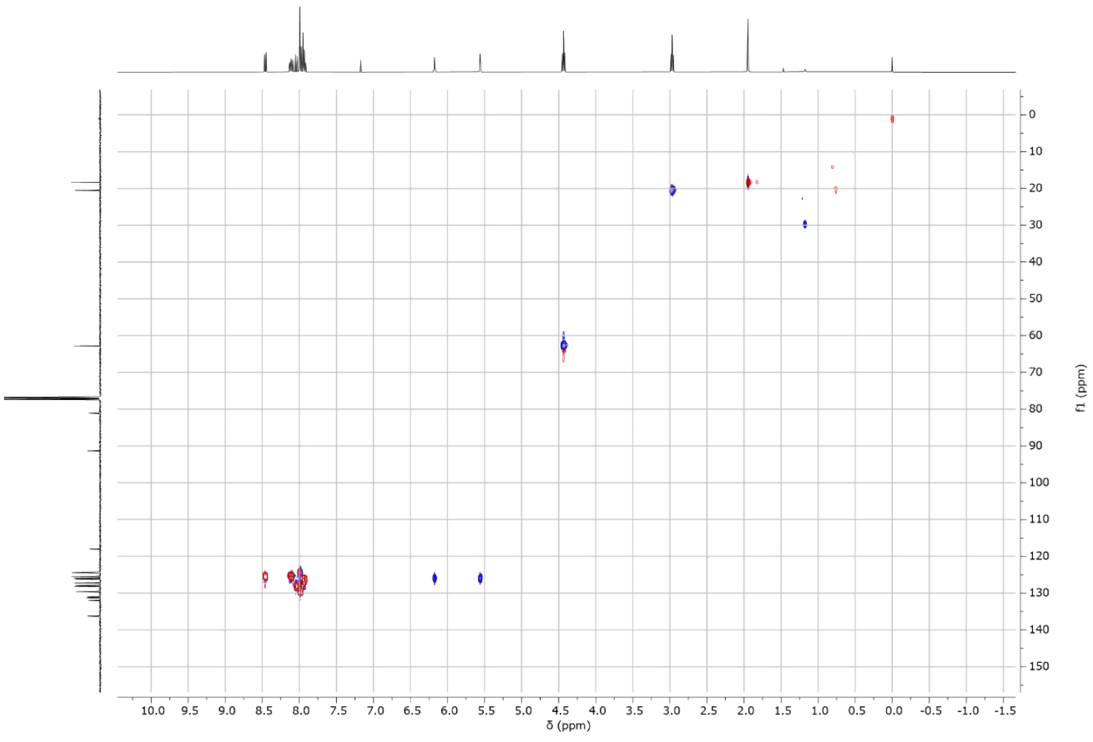
Spectrum S1. ^{1}H NMR spectrum of PyMA in $CDCL_3$



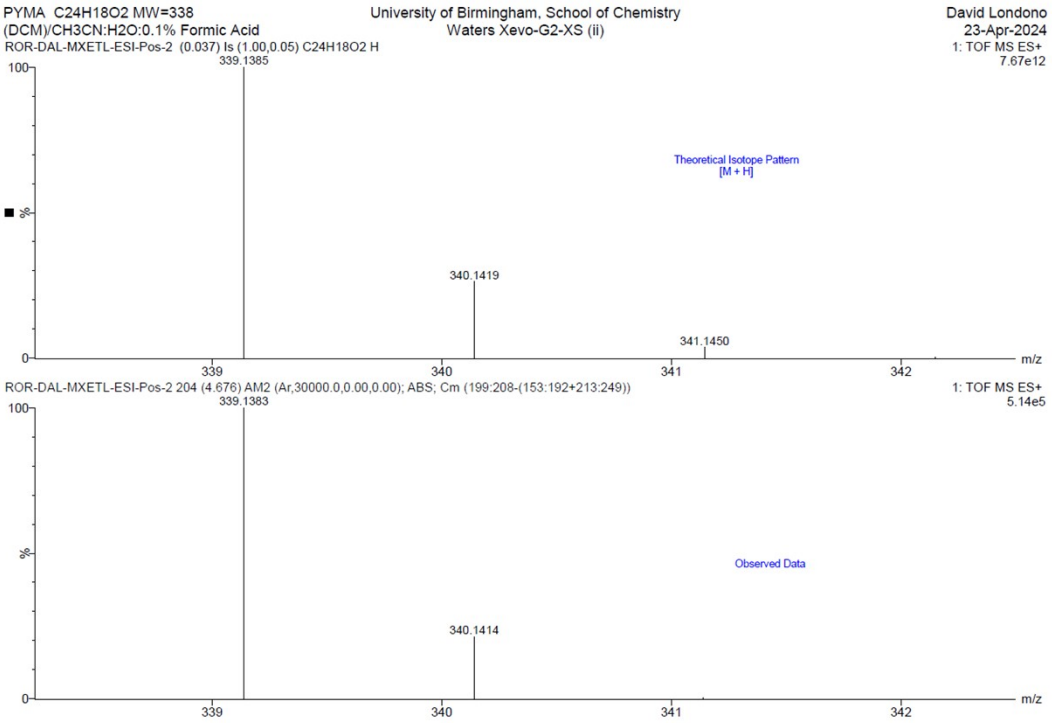
Spectrum S2. ^{13}C NMR spectrum of PyMA in $CDCL_3$



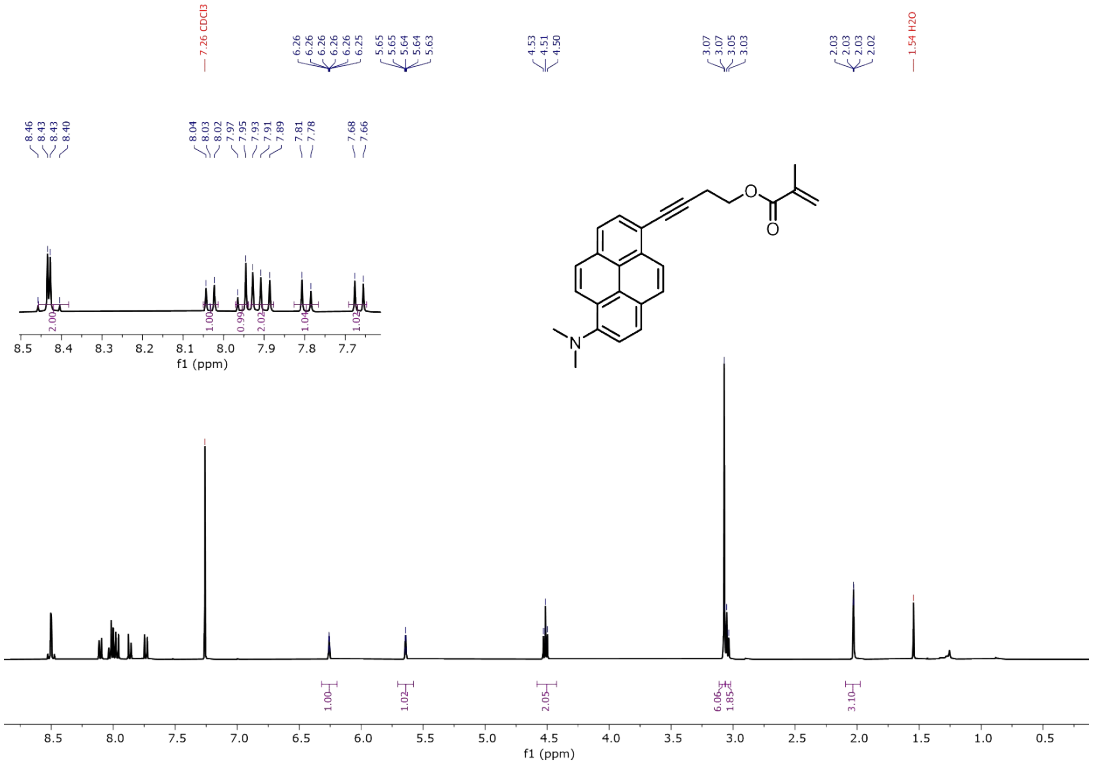
Spectrum S3. COSY 2D spectrum of PyMA in $CDCL_3$



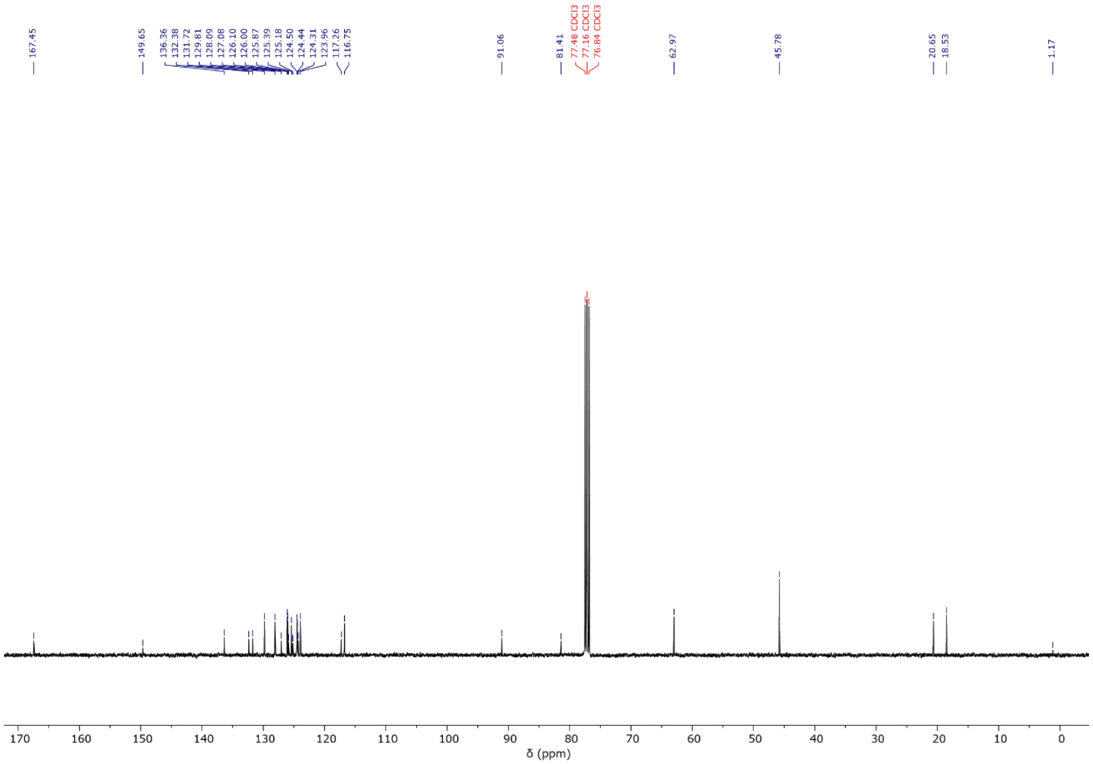
Spectrum S4. HSQC 2D spectrum of PyMA in $CDCL_3$



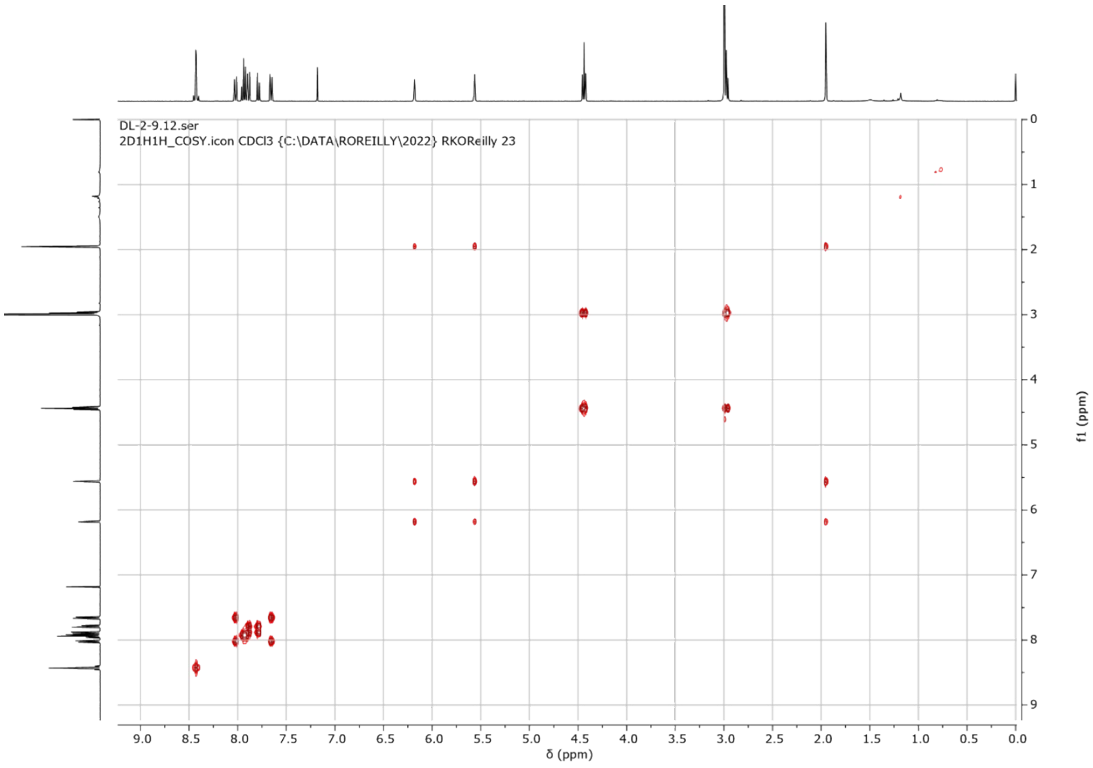
Spectrum S5. HSQC 2D NMR spectrum of PyMA in $CDCL_3$



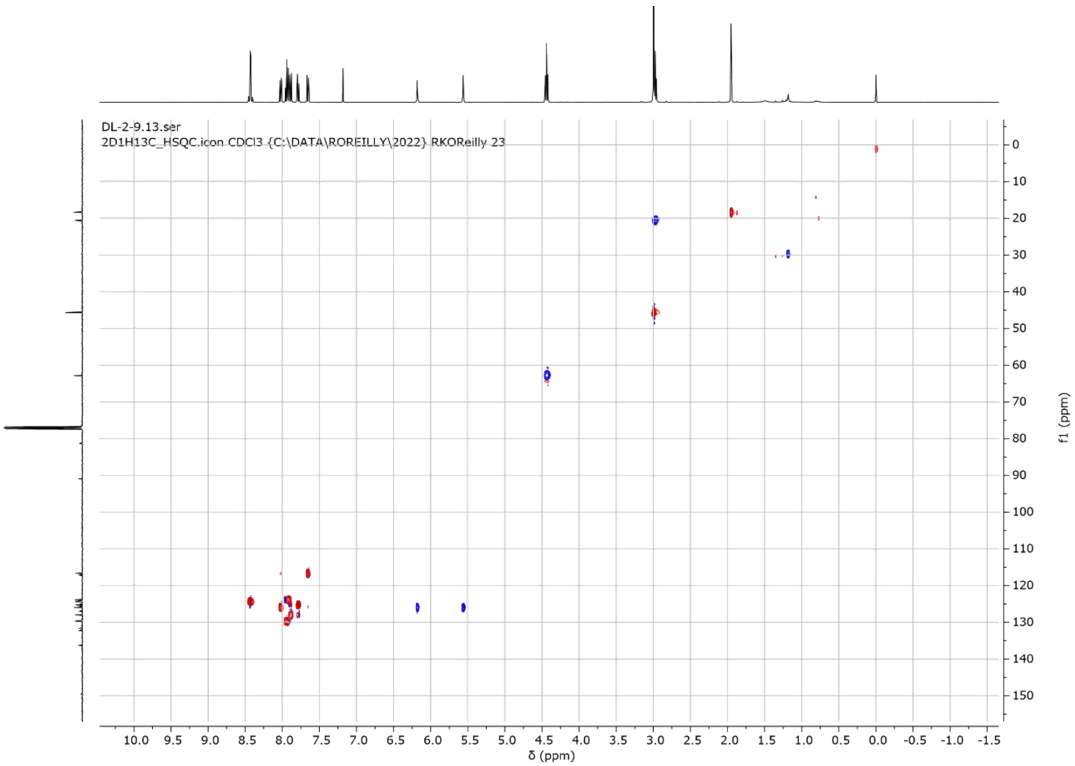
Spectrum S6. ^1H NMR spectrum of DMAPyMA in $CDCL_3$



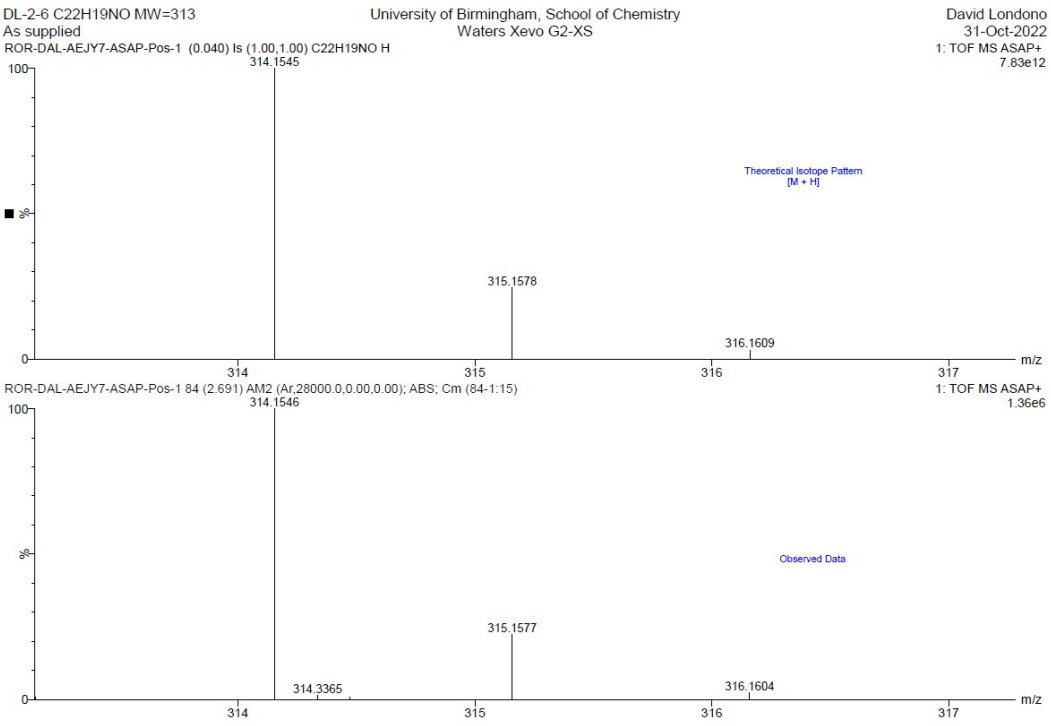
Spectrum S7. ^{13}C NMR spectrum of DMAPyMA in $CDCL_3$



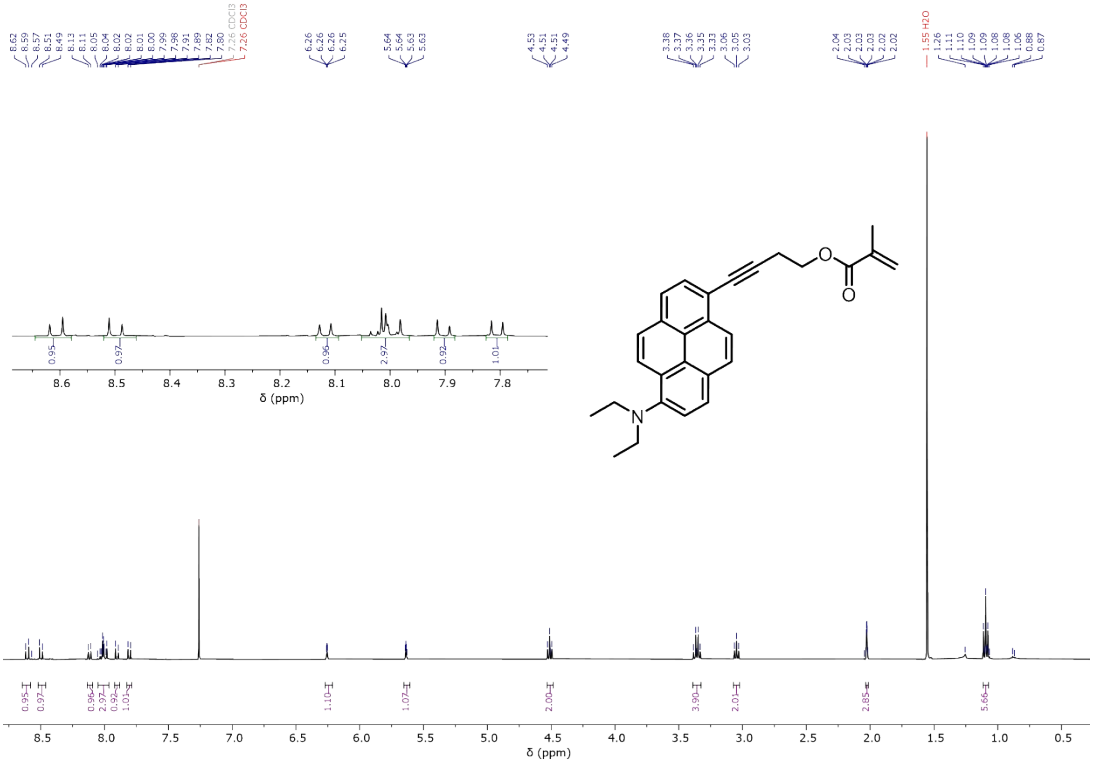
Spectrum S8. COSY 2D NMR spectrum of DMAPyMA in $CDCL_3$



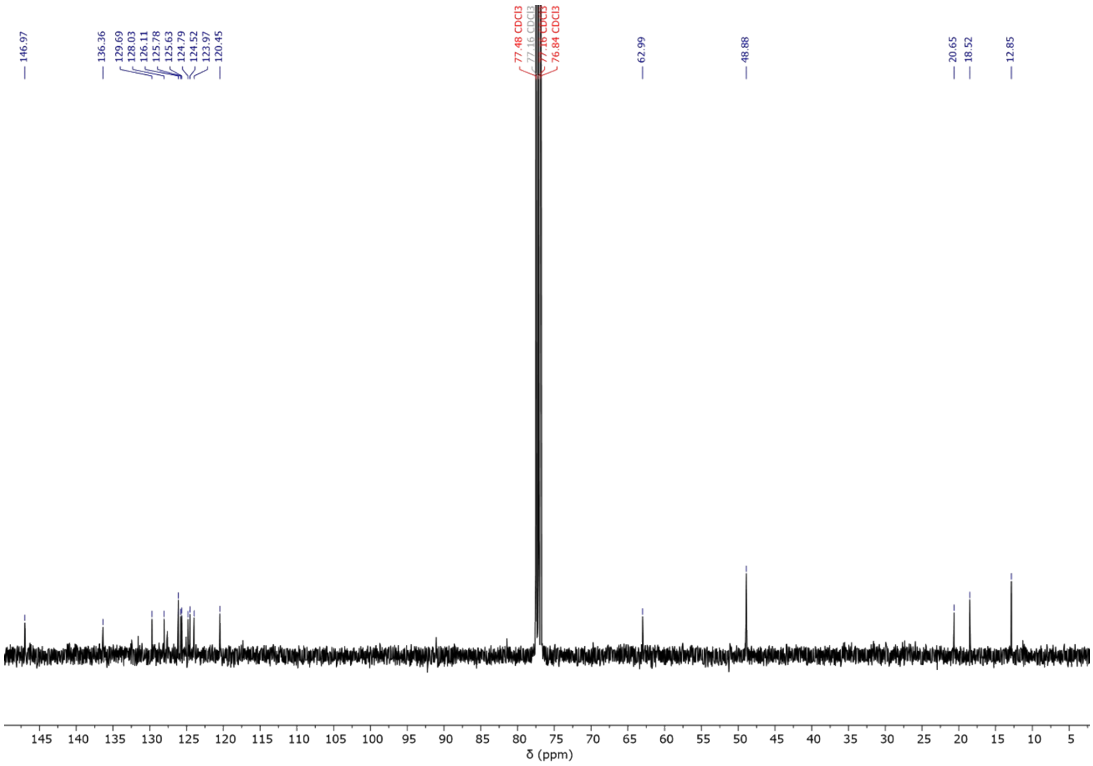
Spectrum S9. HSQC 2D NMR spectrum of DMAPyMA in $CDCL_3$



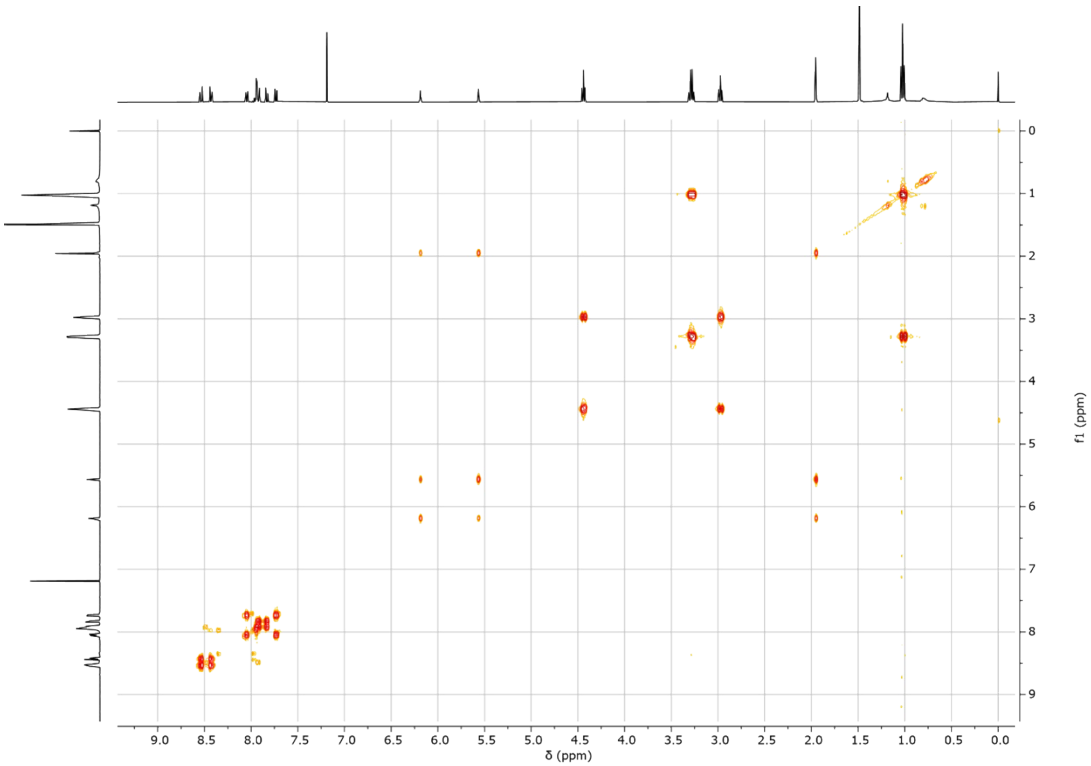
Spectrum S10. HSQC 2D NMR spectrum of DMAPyMA in $CDCL_3$



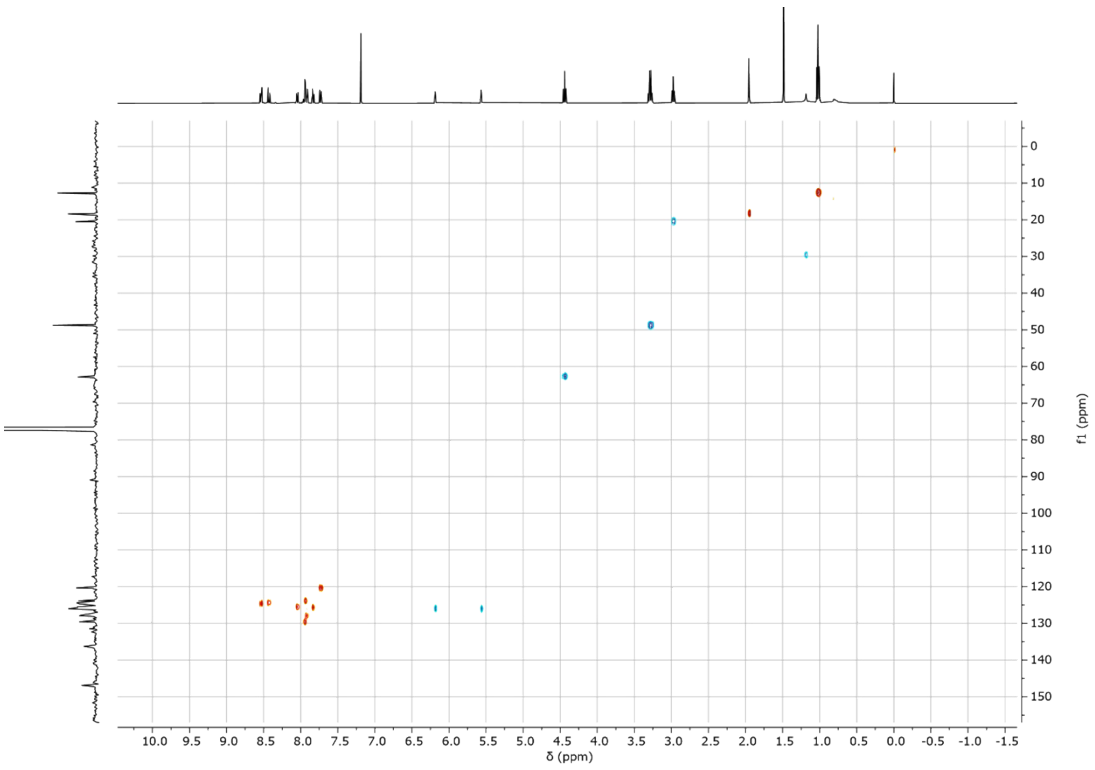
Spectrum S11. ^{1}H NMR spectrum of DEAPyMA in $CDCL_3$



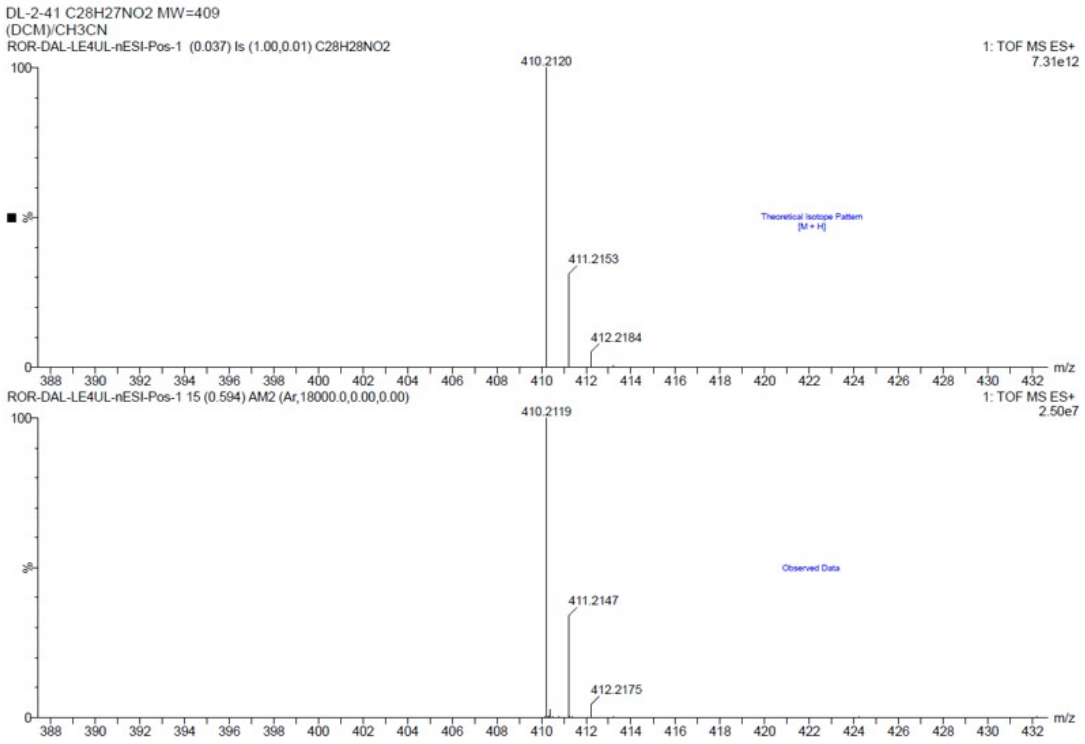
Spectrum S12. ^{13}C NMR spectrum of DEAPyMA in $CDCL_3$



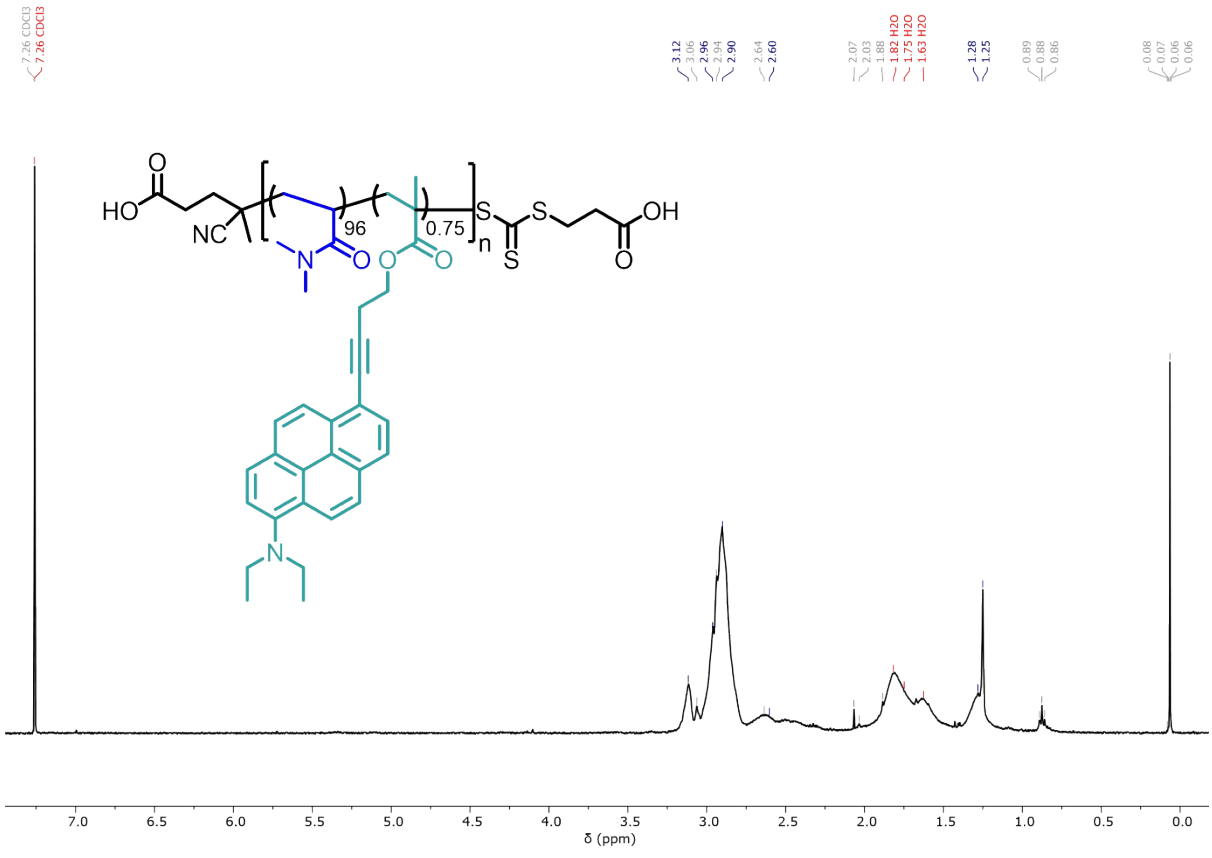
Spectrum S13. COSY 2D NMR spectrum of DEAPyMA in $CDCL_3$



Spectrum S14. HSQC 2D NMR spectrum of DEAPyMA in $CDCL_3$



Spectrum S15. TOF mass spectrum of DEAPyMA in DCM



Spectrum S16. ^{1}H NMR spectrum of P(DMAm-*co*-DEAPyMA) in $CDCL_3$

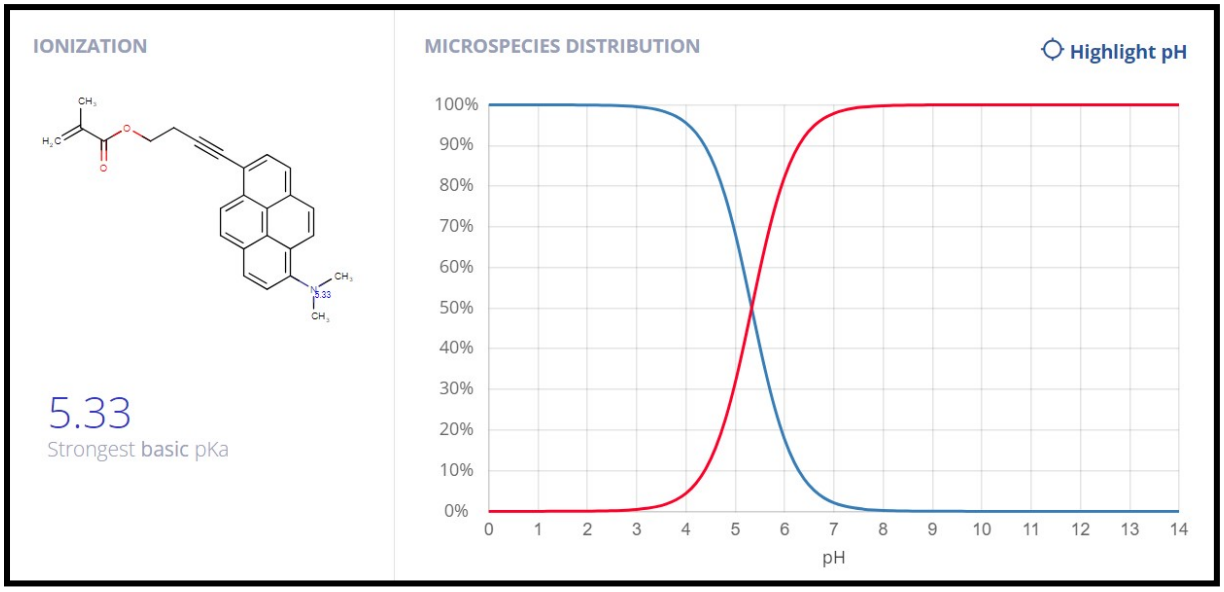


Figure S1. pKa estmation of DMAPyMA. Chemaxon was used for estimating the pKa. Chemaxon (https://www.chemaxon.com).

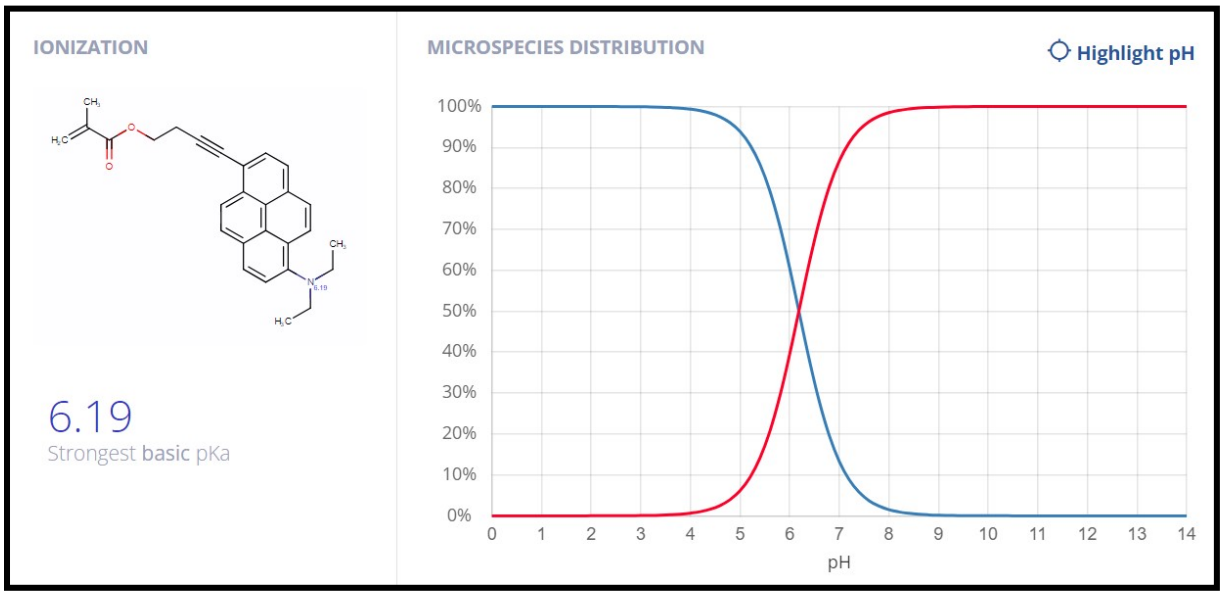


Figure S2. pKa estmation of DEAPyMA. Chemaxon was used for estimating the pKa. Chemaxon (https://www.chemaxon.com).

4. Spectroscopical characterization of monomers and polymers

4.1. PyMA

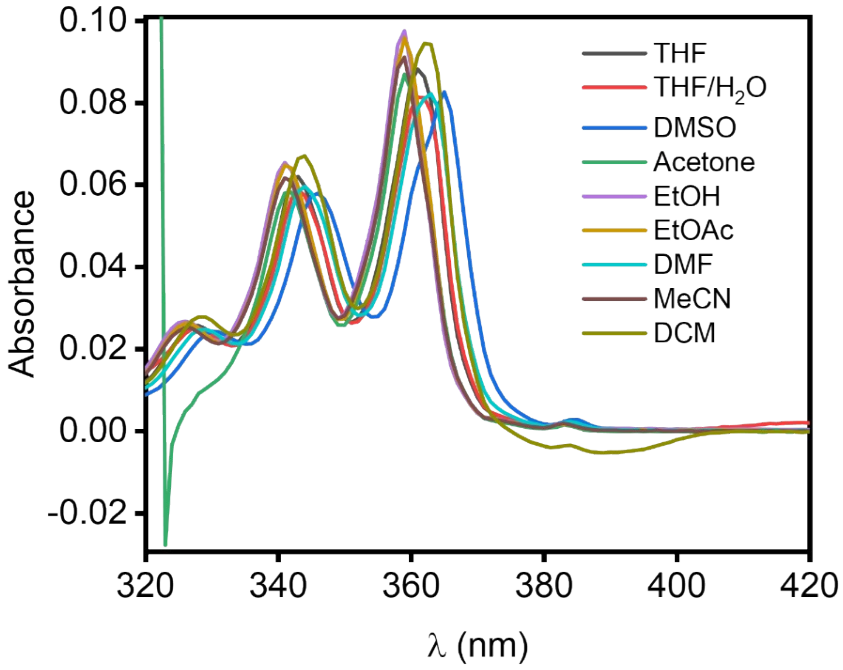


Figure S3. UV-Vis spectrum of PyMA in different solvents at r.t. Concentration of 1.5nM.

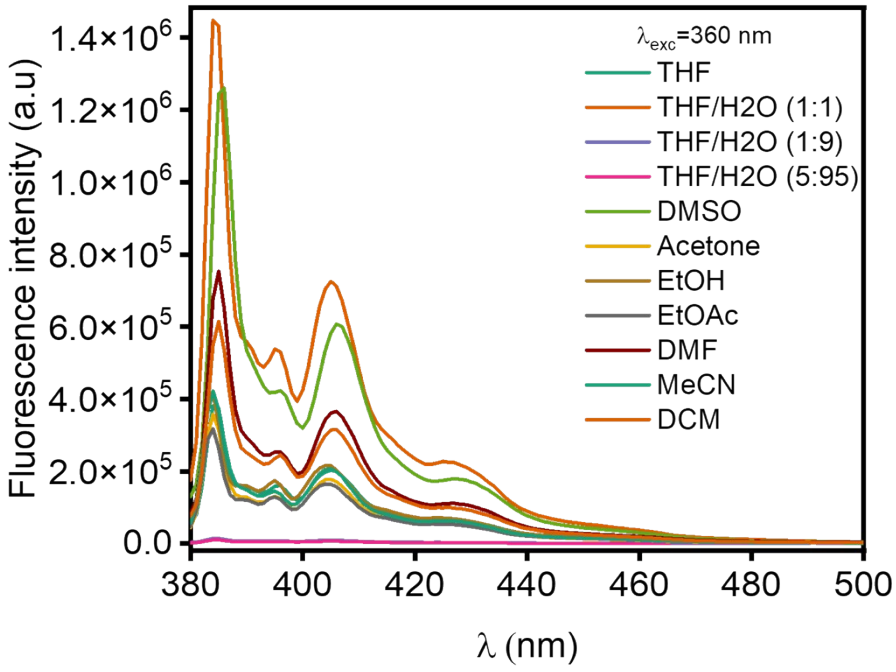


Figure S4. Fluorescence spectrum of PyMA in different solvents. Concentration of 1.5nM. λ_{exc}= 360nm.

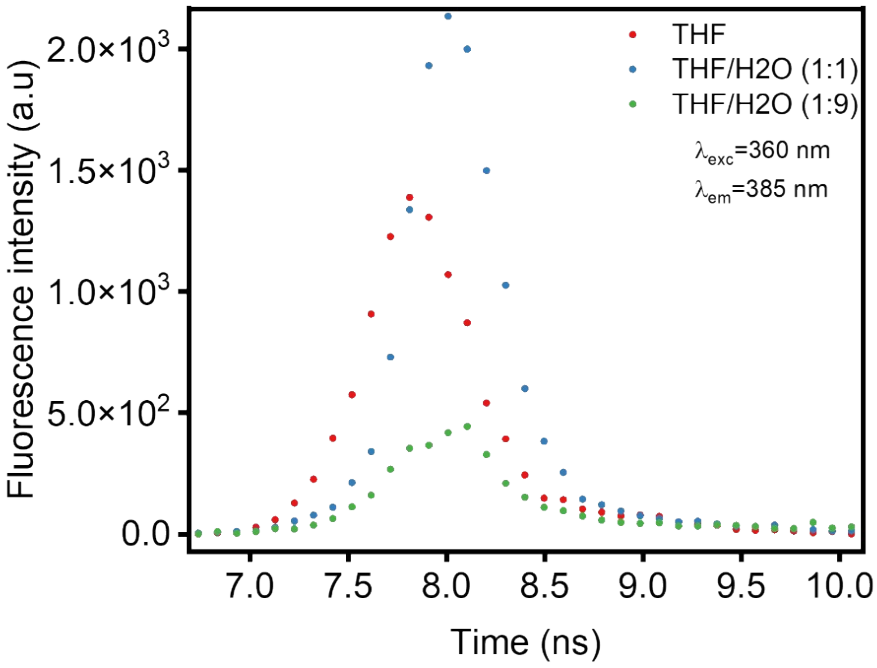


Figure S5. Lifetime spectrum of PyMA in different THF/H_2O mixtures. Concentration of 1.5nM. λ_{exc}= 360 nm. λ_{em}= 385 nm.

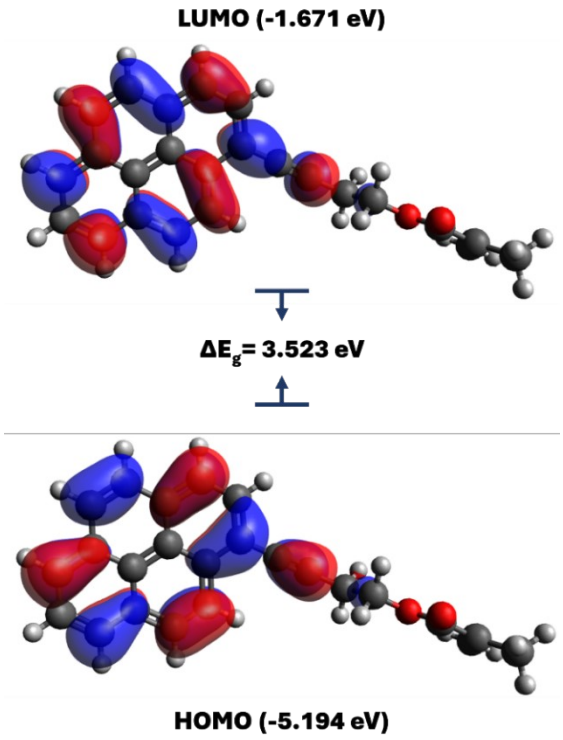


Figure S5. TF-DFT-calculations of PyMA in H_2O.

4.2. PDMAm-co-PyMA

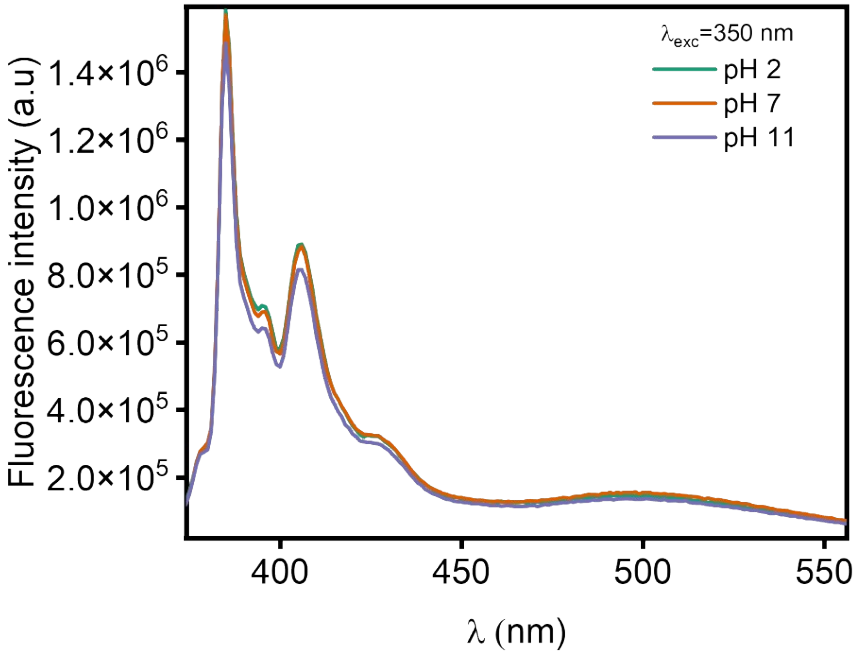


Figure S6. Fluorescence spectrum of PDMAm-co-PyMA at different pHs in aqueous solution. Concentration of 10 ppm. λexc= 350 nm.

4.3. DMAPyMA

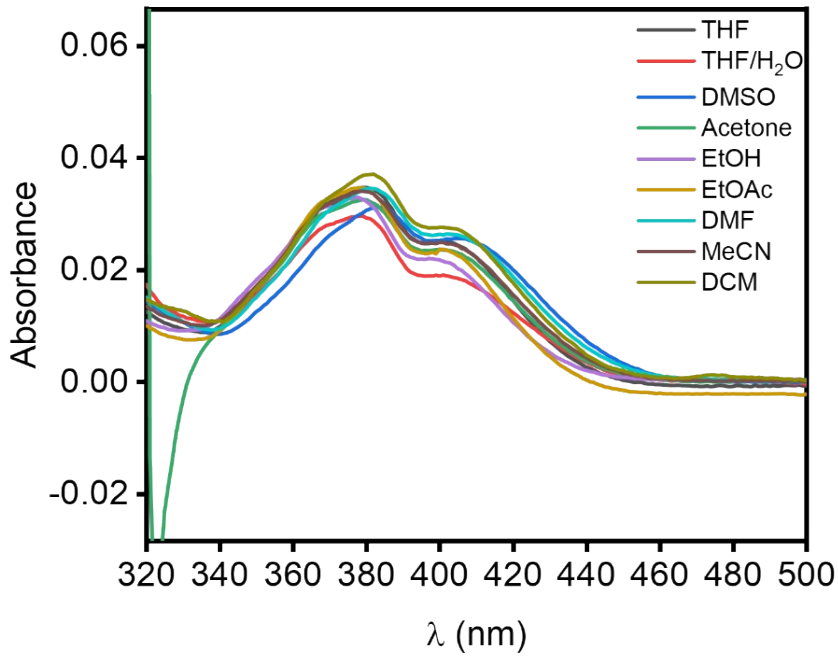


Figure S7. UV-Vis spectrum of DMAPyMA in different solvents at r.t. Concentration of 1.5nM.

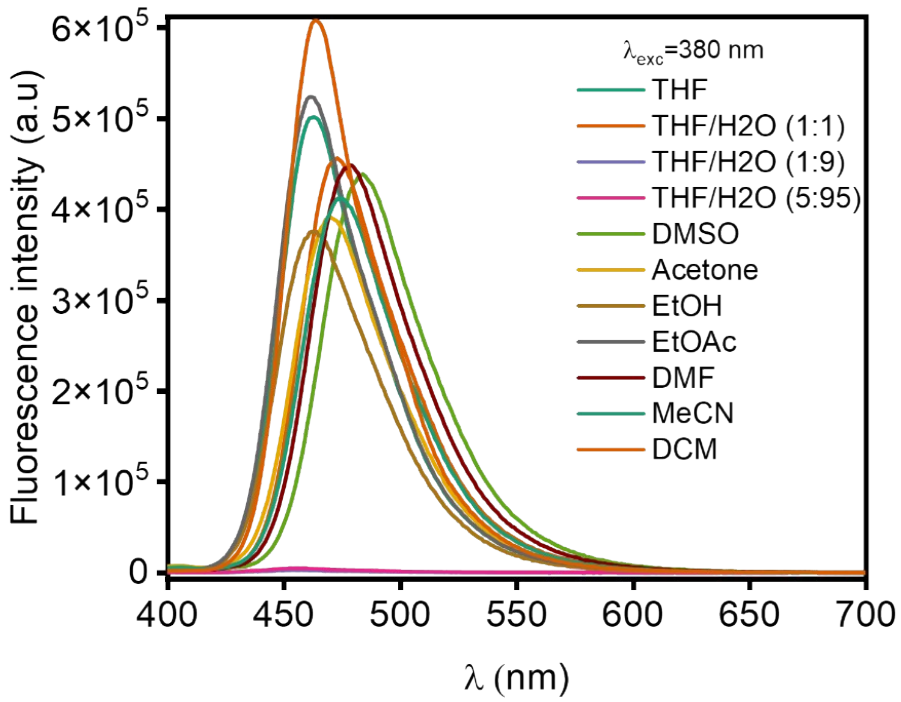


Figure S8. Fluorescence spectrum of DMAPyMA in different solvents. Concentration of 1.5nM. λexc= 380nm.

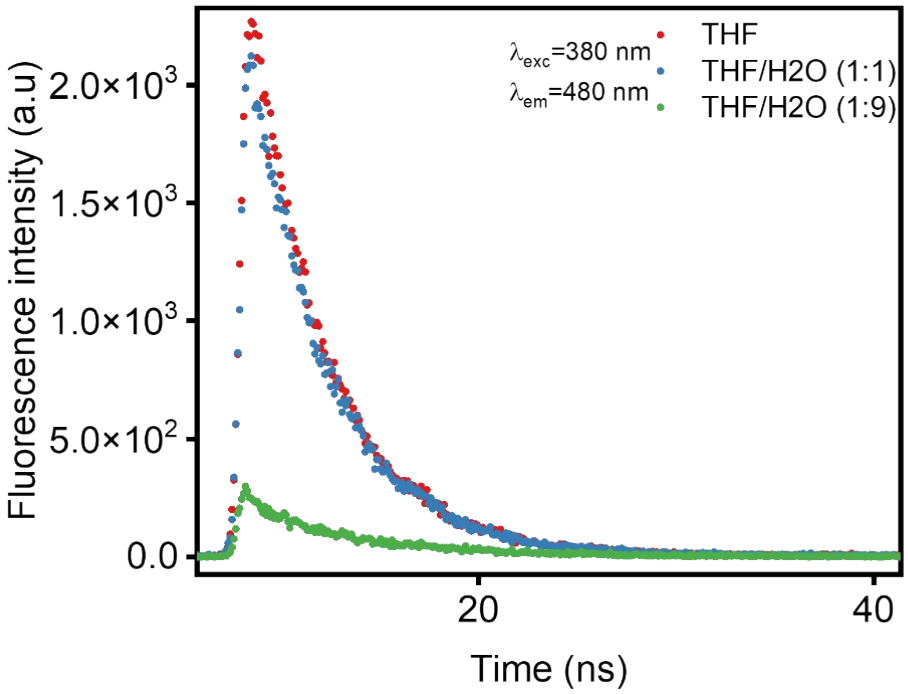


Figure S9. Lifetime spectrum of DMAPyMA in different THF/H_2O mixtures. Concentration of 1.5nM. λexc= 380 nm. λem= 480 nm.

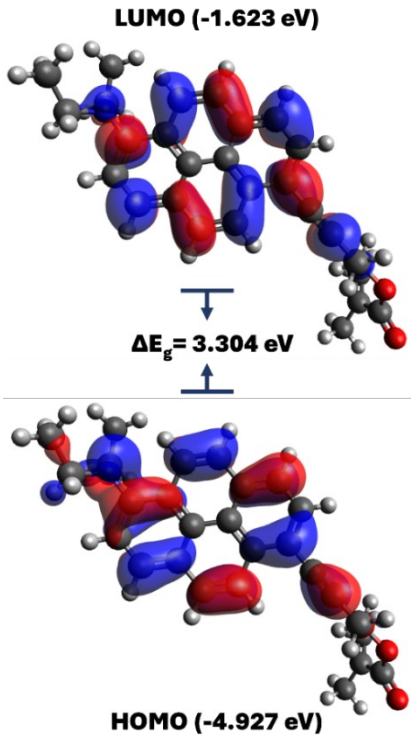


Figure S10. TF-DFT-calculations of DMAPyMA in H_2O.

4.4. PDMAm-co-DMAPyMA

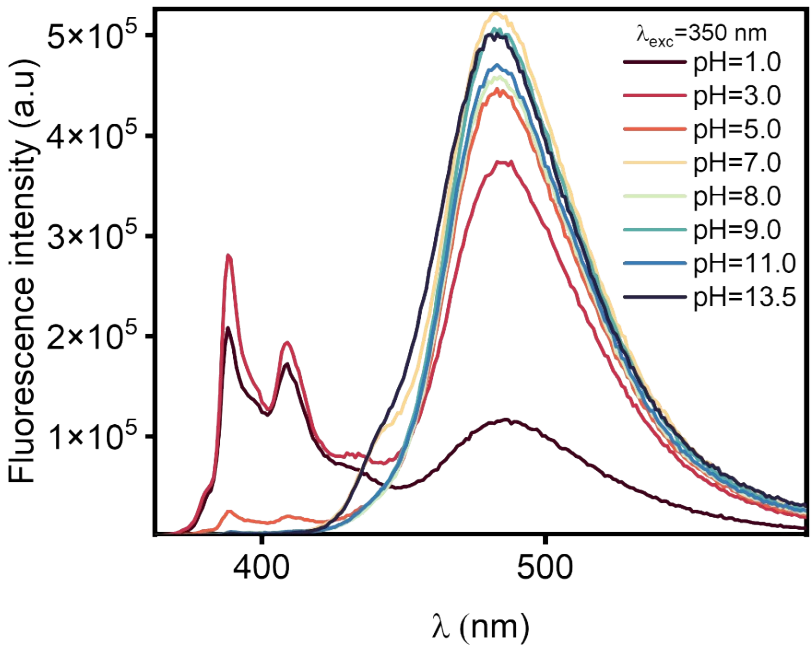


Figure S11. Fluorescence spectrum of PDMAm-*co*-PDMAPyMA at different pHs in aqueous solution. 1 mol% of DMAPyMA. Concentration of 10 ppm. λ_{exc}= 350 nm.

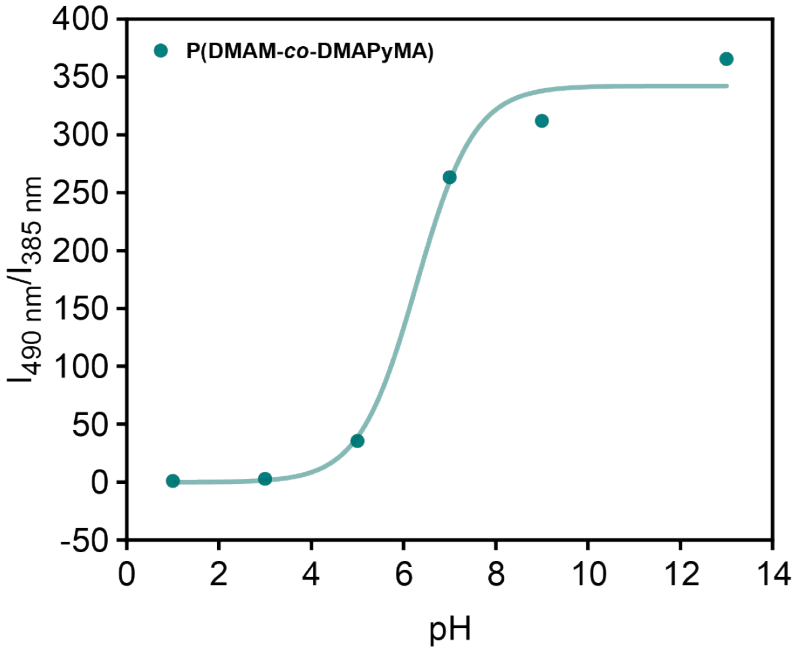


Figure S12. Fluorescence intensity ratio (490 nm/385nm) of PDMAm-*co*-DMAPyMA in aqueous solution at different pHs (1, 3, 4, 7, 9 and 13). Concentration of 0.5 mg/mL

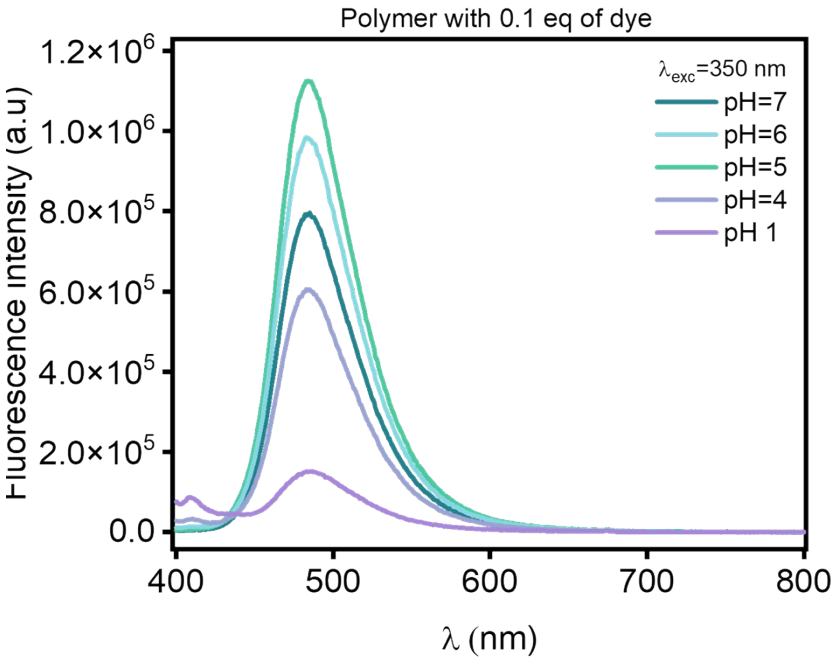


Figure S13. Fluorescence spectrum of PDMAm-*co*-PDMAPyMA at different pHs in aqueous solution. 0.1 mol% of DMAPyMA. Concentration of 10 ppm. λ_{exc}= 350 nm.

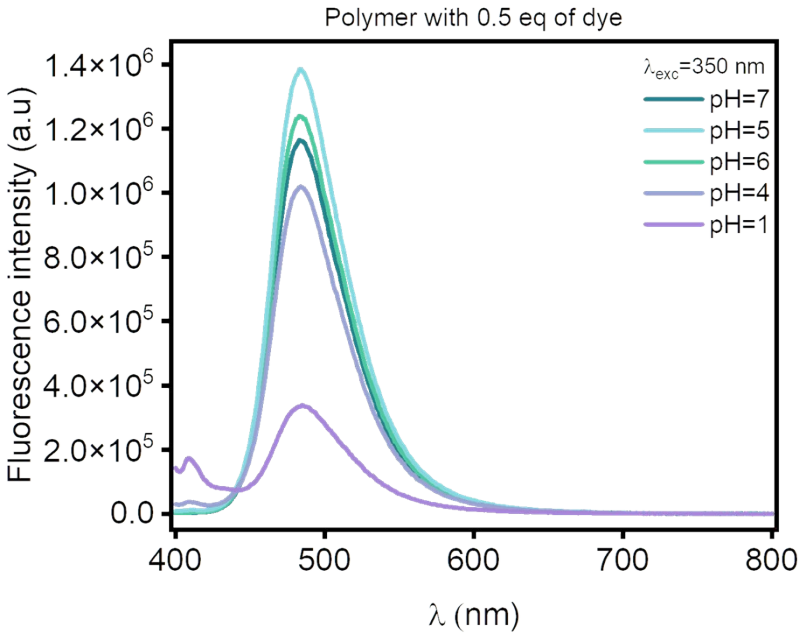


Figure S14. Fluorescence spectrum of PDMAm-*co*-PDMAPyMA at different pHs in aqueous solution. 0.5 mol% of DMAPyMA. Concentration of 10 ppm. λ_{exc}= 350 nm.

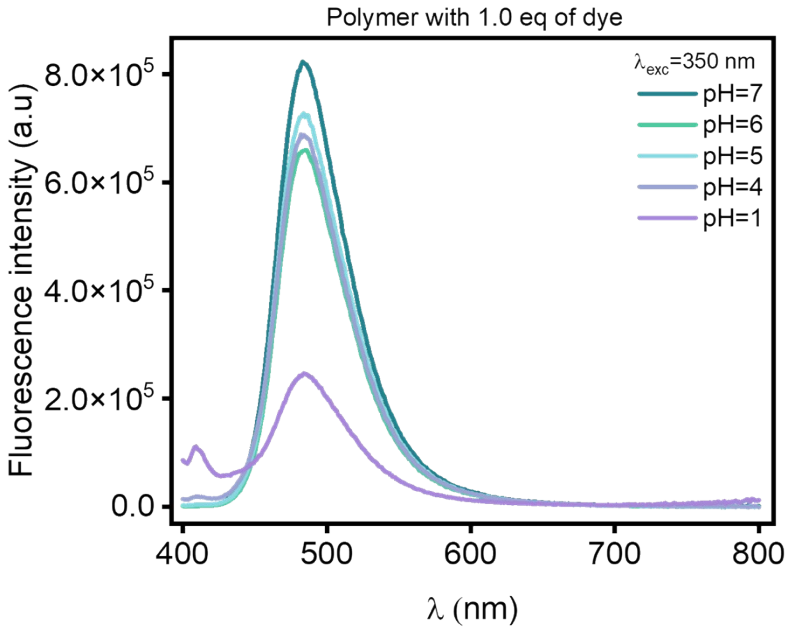


Figure S15. Fluorescence spectrum of PDMAm-*co*-PDMAPyMA at different pHs in aqueous solution. 1 mol% of DMAPyMA. Concentration of 10 ppm. λ_{exc}= 350 nm.

4.5. DEAPyMA

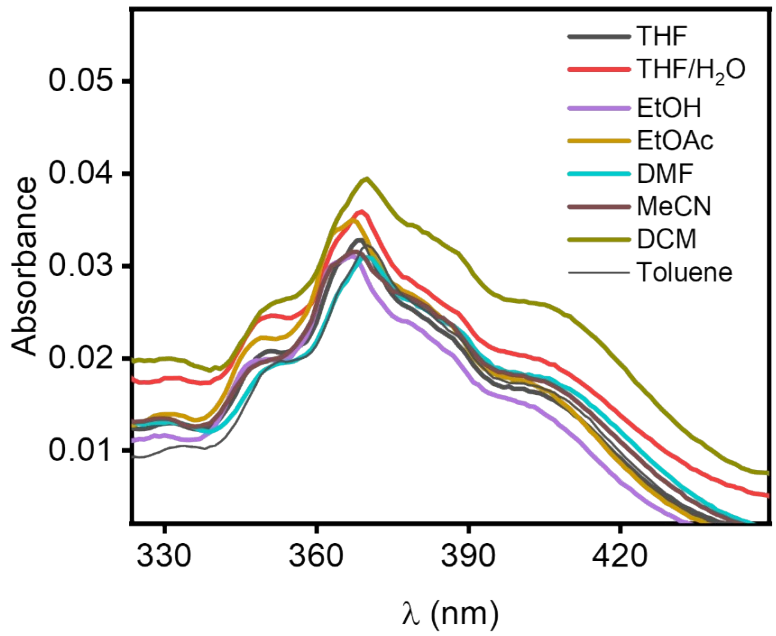


Figure S16. UV-Vis spectrum of DEAPyMA in different solvents at r.t. Concentration of 1.5nM.

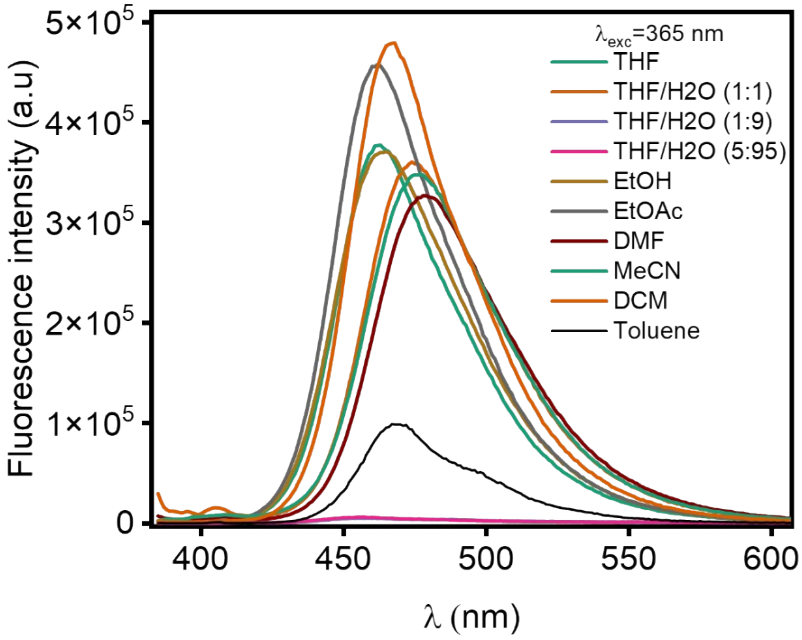


Figure S17. Fluorescence spectrum of DEAPyMA in different solvents. Concentration of 1.5nM. λ_{exc}= 365nm.

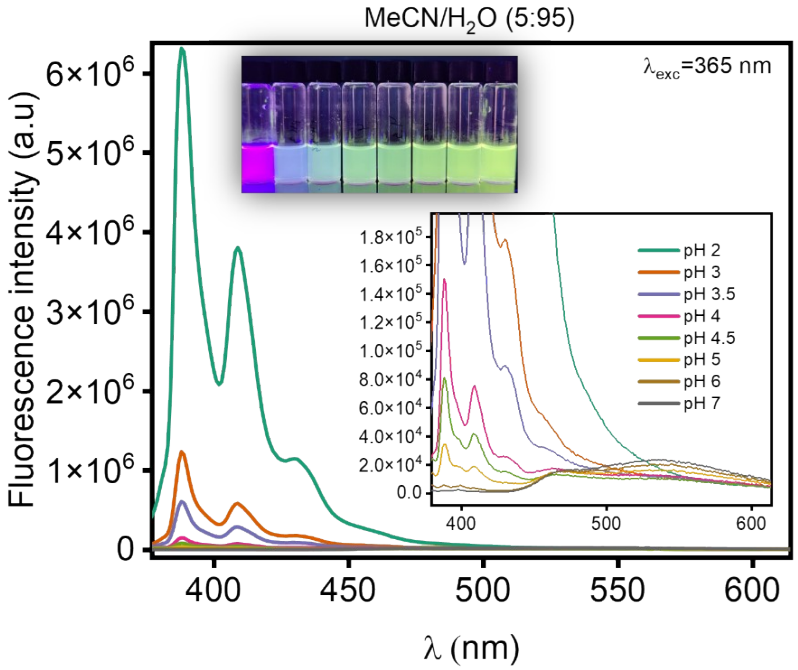


Figure S18. Fluorescence spectrum of DEAPyMA at different pHs in MeCN/H_2O (5:95) mixtures. Concentration of 27 nM. λ_{exc}= 365nm.

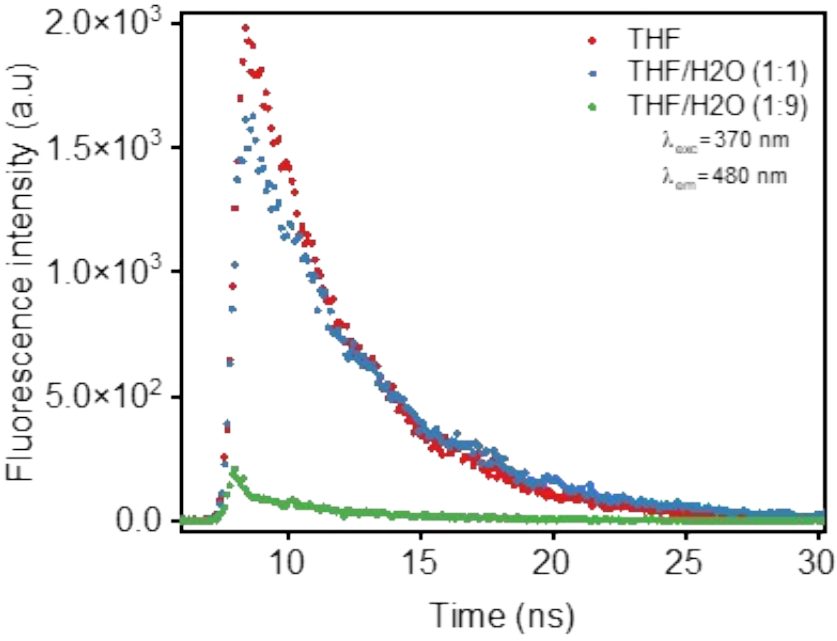


Figure S19. Lifetime spectrum of DEAPyMA in different THF/H_2O mixtures. Concentration of 1.5nM. λ_{exc}= 370 nm. λ_{em}= 480 nm.

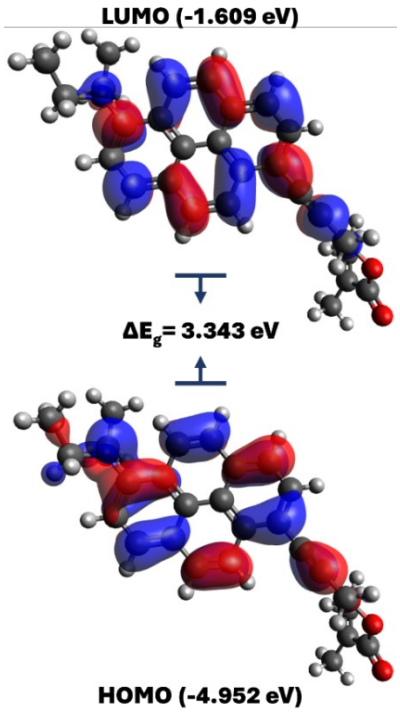


Figure S20. TF-DFT-calculations of DEAPyMA in H_2O.

4.6. P(DMAm-co-DEAPyMA)

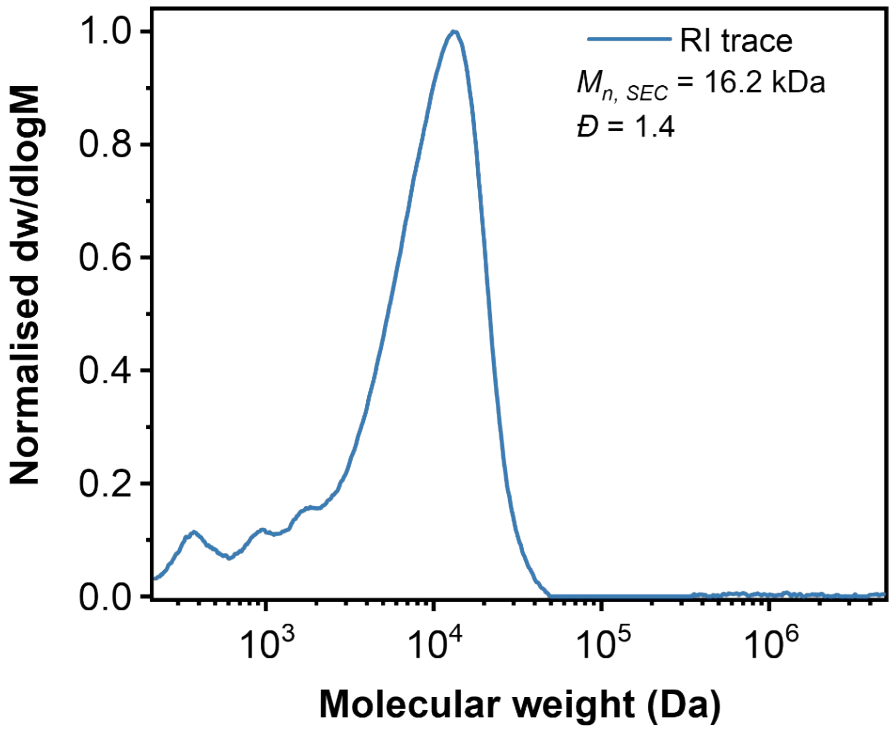


Figure S21. SEC spectrum of P(DMAm-*co*-DEAPyMA) in $CDCL_3$. 1 mg/mL.

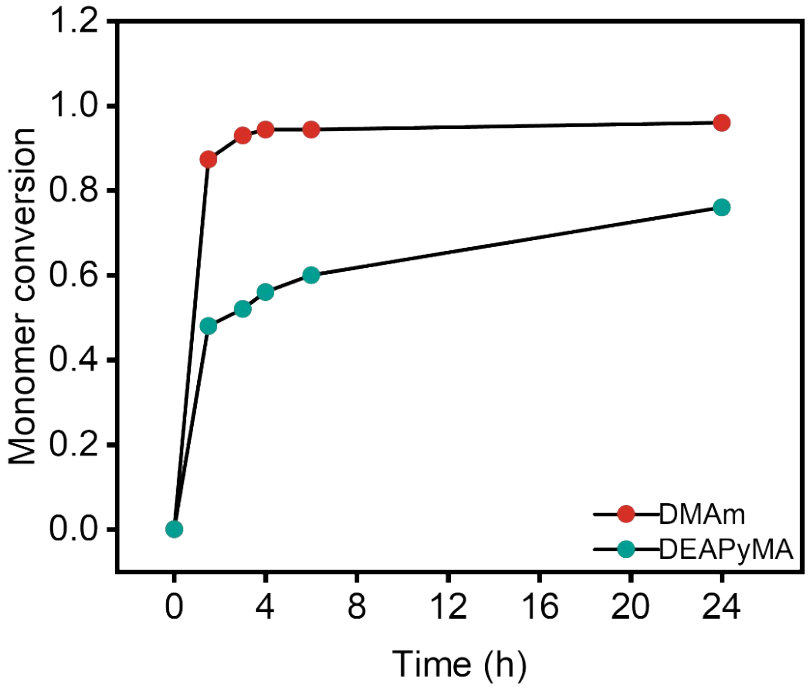


Figure S22. Kinetics of RAFT polymerization of DMAm and DEAPyMA after 24h. 1 mol% of DEAPyMA in polymer.

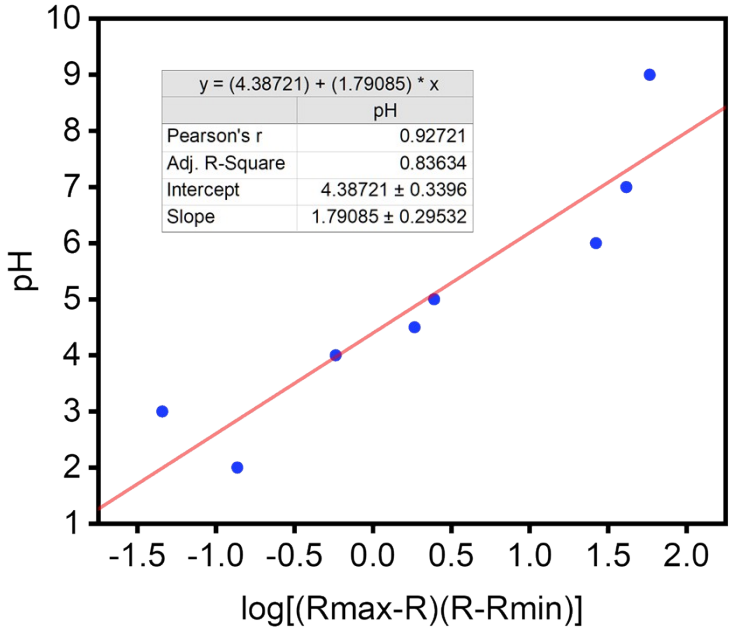


Figure S23. pKa of DEPyMA calculated using the Henderson-Hasselbach-type mass action equation (pH = pKa + c*log[(R−Rmin)/(Rmax−R)] + log(Ia/Ib)) through analyzing fluorescence intensity ratio changes as a function of pH. Where Rmax (or Rmin) is the maximum (or minimum) ratio value, c is the slope and Ia /Ib is the ratio of absorption intensity in acid to the absorption intensity in base at the wavelength chosen for the denominator of R. The pKa value for DEAPyMA was 4.4.

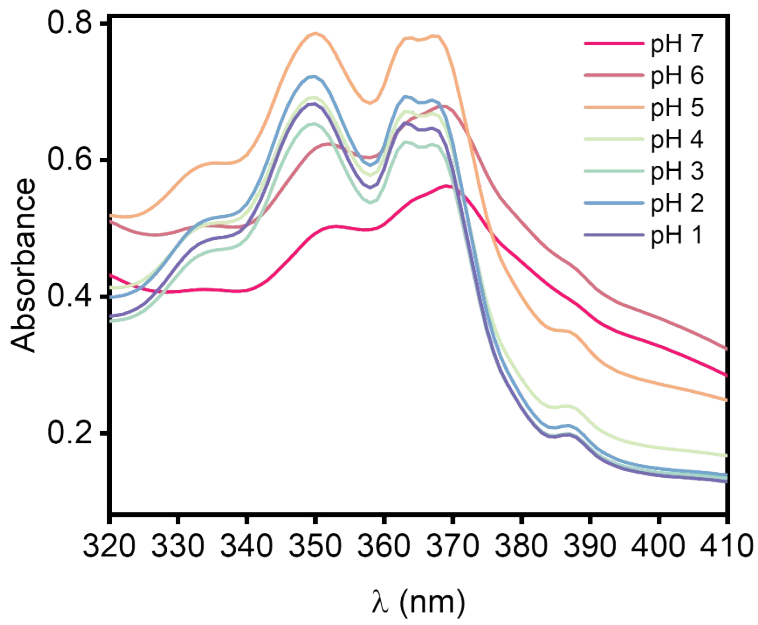


Figure S24. UV-Vis spectrum of PDMAm-*co*-DEAPyMA in aqueous solution at different pHs and at r.t. Concentration of 10 ppm. 1 mol% of DEAPyMA in polymer.

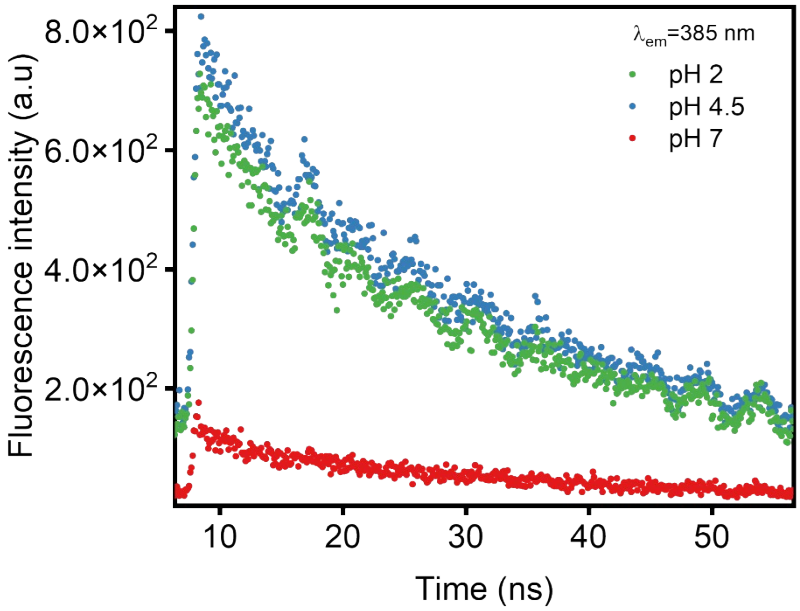


Figure S25. Lifetime spectrum of PDMAm-*co*-DEAPyMA in aqueous solution at different pHs and at r.t. Concentration of 10 ppm. λ_{exc}= 350 nm. λ_{em}= 385 nm. 1 mol% of DEAPyMA in polymer.

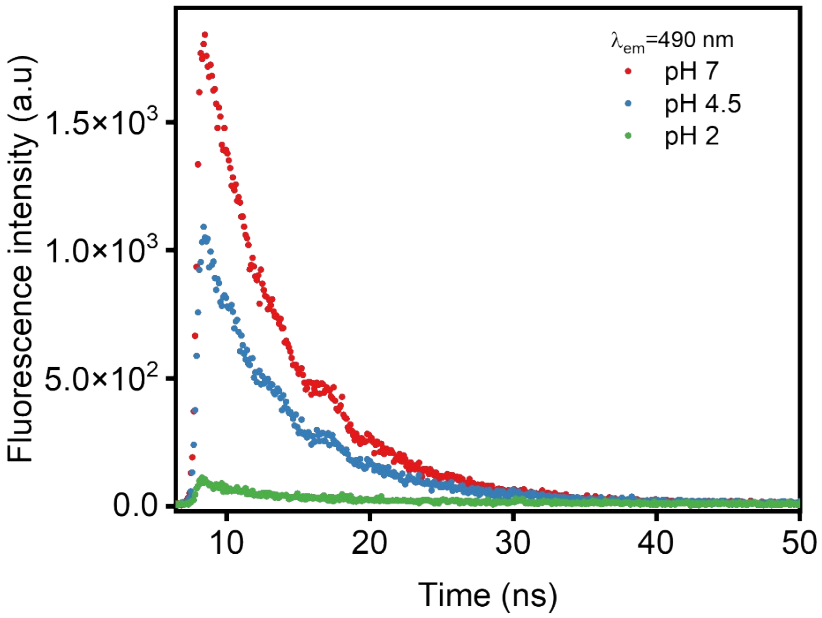


Figure S26. Lifetime spectrum of PDMAm-*co*-DEAPyMA in aqueous solution at different pHs and at r.t. Concentration of 10 ppm. λ_{exc}= 350 nm. λ_{em}= 490 nm. 1 mol% of DEAPyMA in polymer.

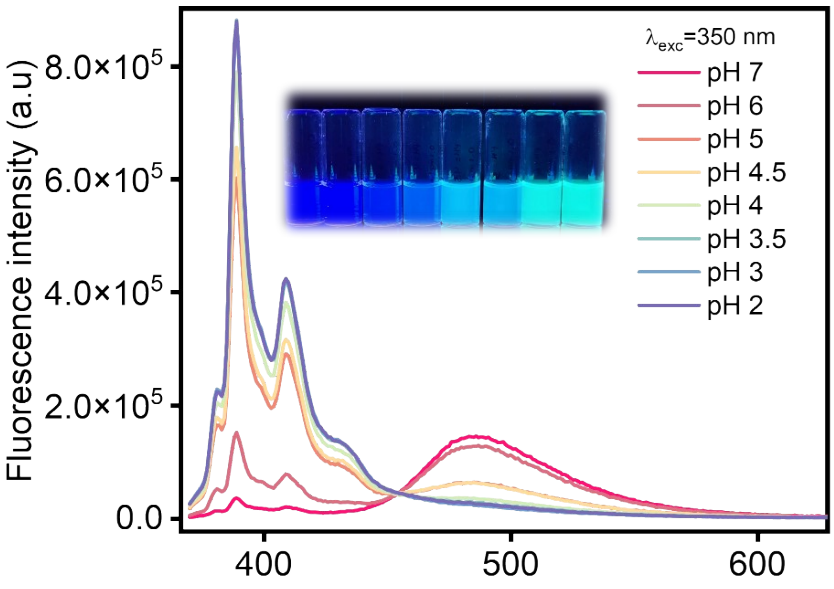


Figure S27. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution at different pHs and at r.t. Concentration of polymer in water = 100 ppm. 1 mol% of DEAPyMA in polymer.

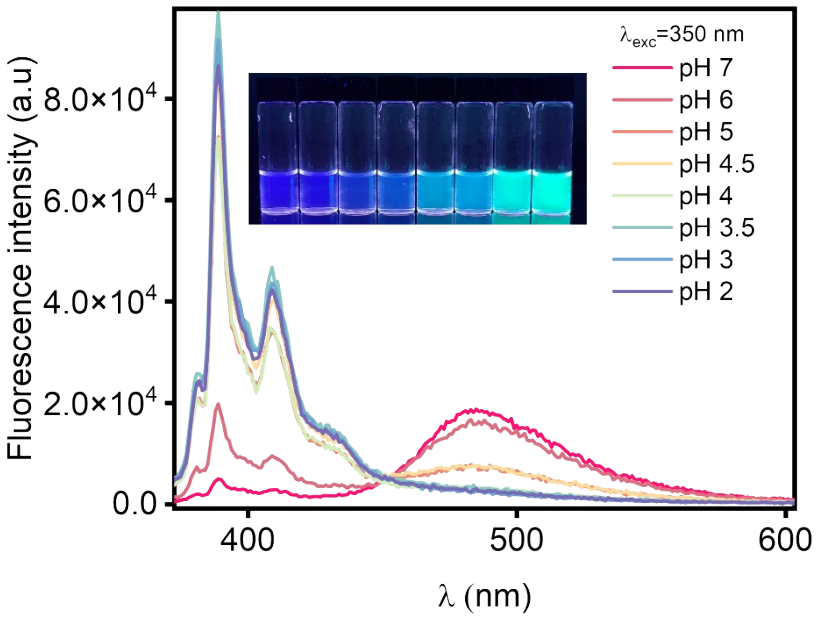


Figure S28. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution at different pHs and at r.t. Concentration of polymer in water = 10 ppm. 1 mol% of DEAPyMA in polymer.

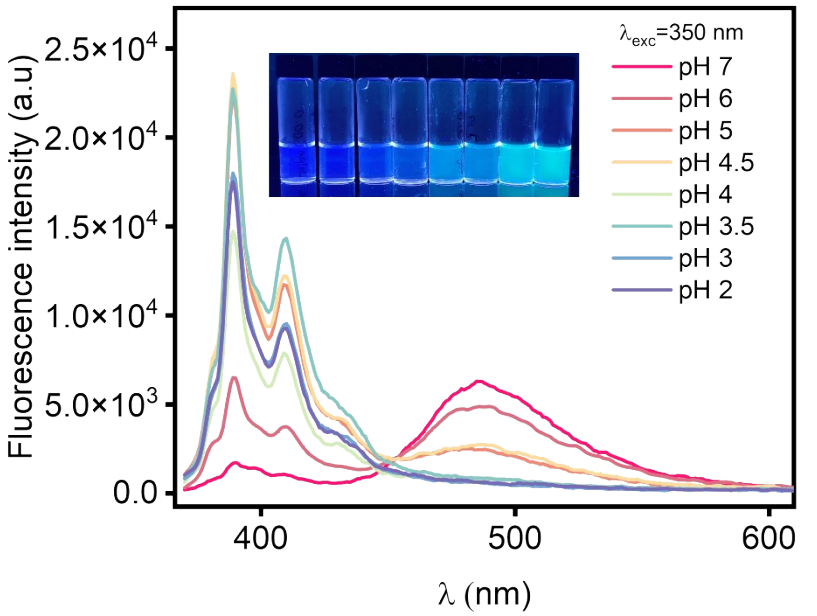


Figure S29. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution at different pHs and at r.t. Concentration of polymer in water = 5 ppm. 1 mol% of DEAPyMA in polymer.

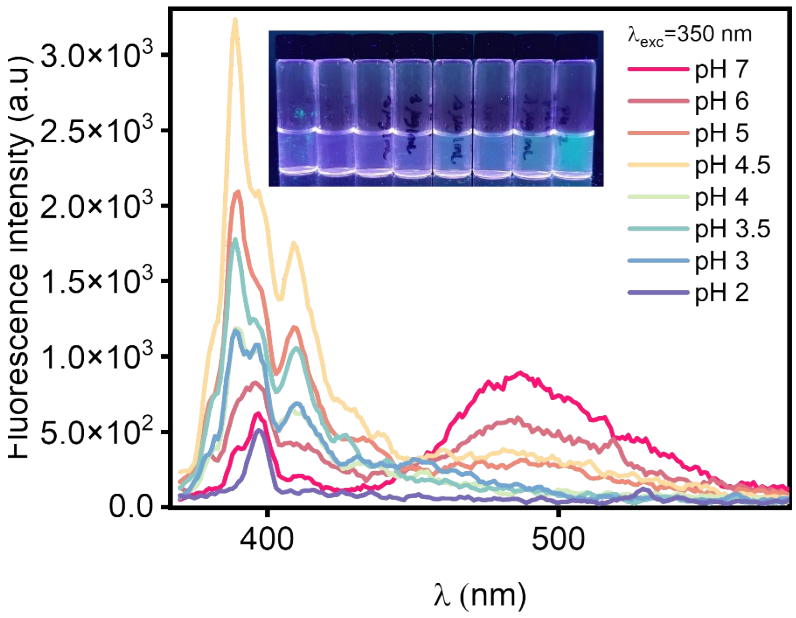


Figure S30. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution at different pHs and at r.t. Concentration of polymer in water = 1 ppm. 1 mol% of DEAPyMA in polymer.

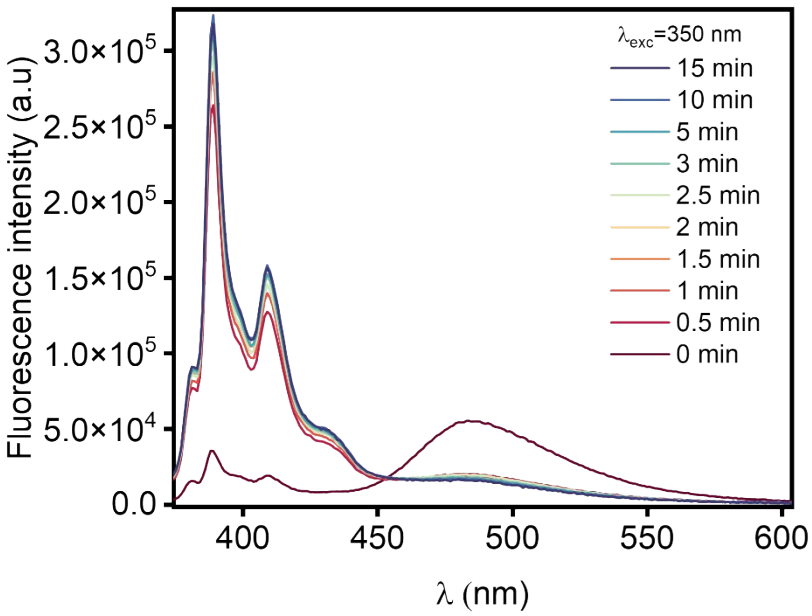


Figure S31. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution after kinetics with CO_2 and at r.t. Concentration of polymer in water = 10 ppm. 1 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 100 cm^3/min

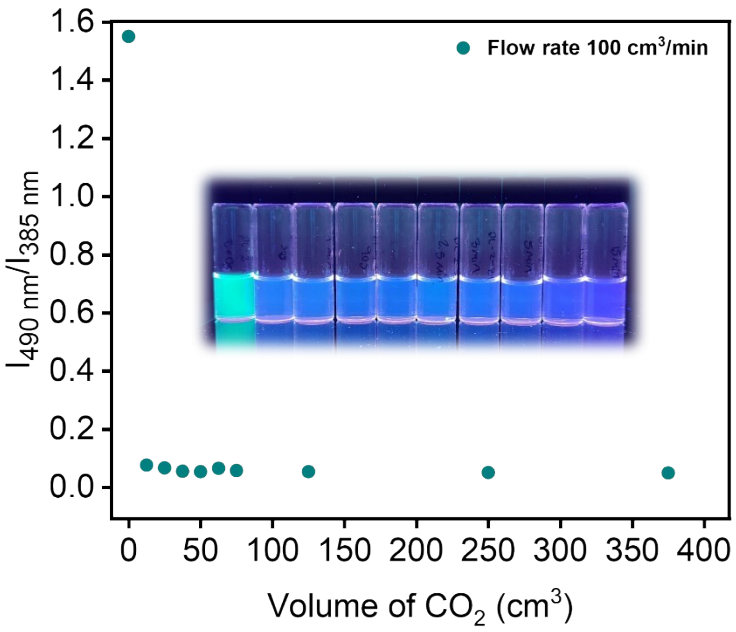


Figure S32. Fluorescence intensity ratio (490 nm/385nm) of PDMAm-*co*-DEAPyMA in aqueous solution after kinetics with CO_2 and at r.t. Concentration of polymer in water = 10 ppm. 1 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 100 cm^3/min

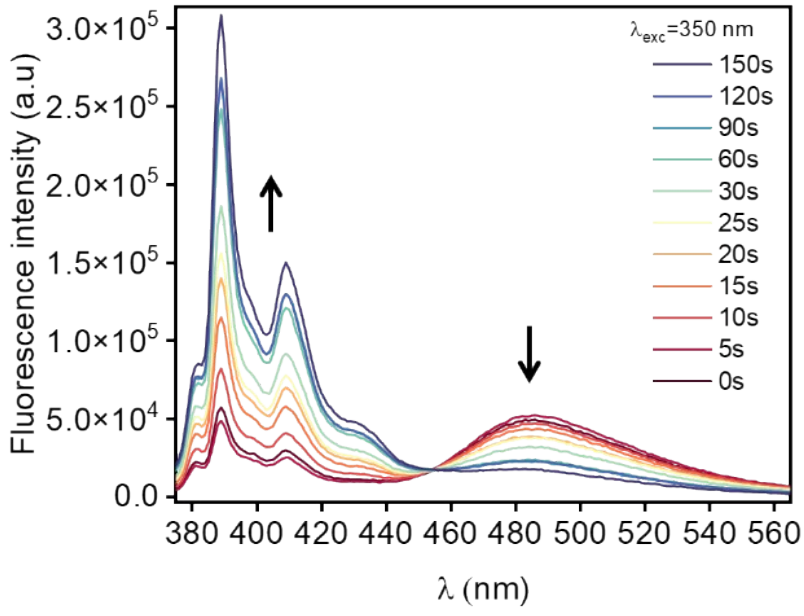


Figure S33. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution after kinetics with CO_2 and at r.t. Concentration of polymer in water = 10 ppm. 1 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 50 cm^3/min

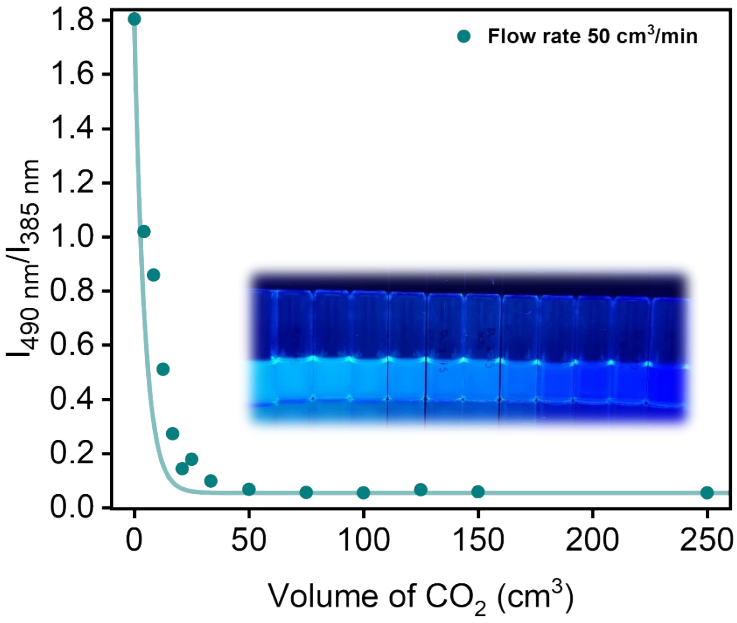


Figure S34. CO_2 and at r.t. Concentration of polymer in water = 10 ppm. 1 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 50 cm^3/min

Figure S35. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution after air exposure kinetics. r.t. Concentration of polymer in water = 10 ppm. 1 mol% of DEAPyMA in polymer.

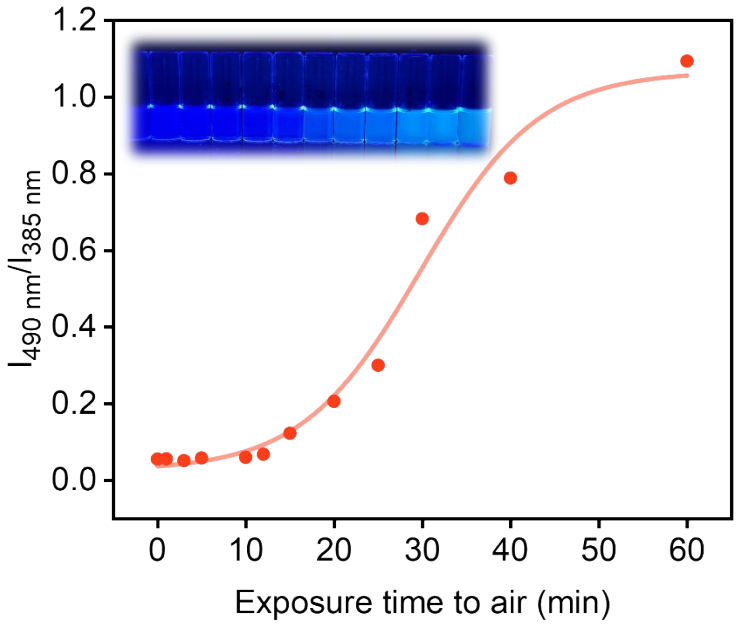


Figure S36. Fluorescence intensity ratio (490 nm/385nm) of PDMAm-*co*-DEAPyMA in aqueous solution after air exposure kinetics. r.t. 1 mol% of DEAPyMA in polymer. Concentration of polymer in water = 10 ppm.

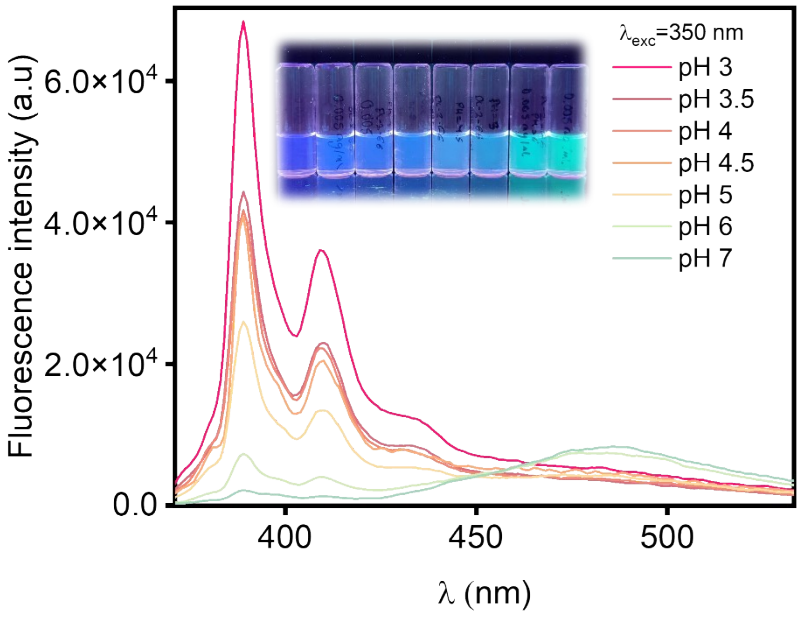


Figure S37. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution at different pHs. r.t. Concentration of polymer in water = 10 ppm. 5 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 50cm^3/min.

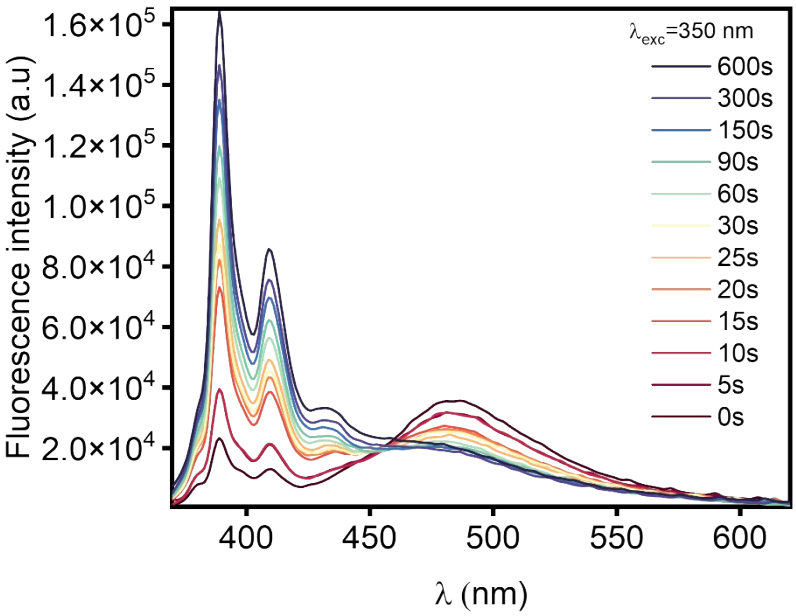


Figure S38. Fluorescence spectrum of PDMAm-*co*-DEAPyMA in aqueous solution after kinetics with CO_2 and at r.t. Concentration of polymer in water = 10 ppm. 5 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 50 cm^3/min.

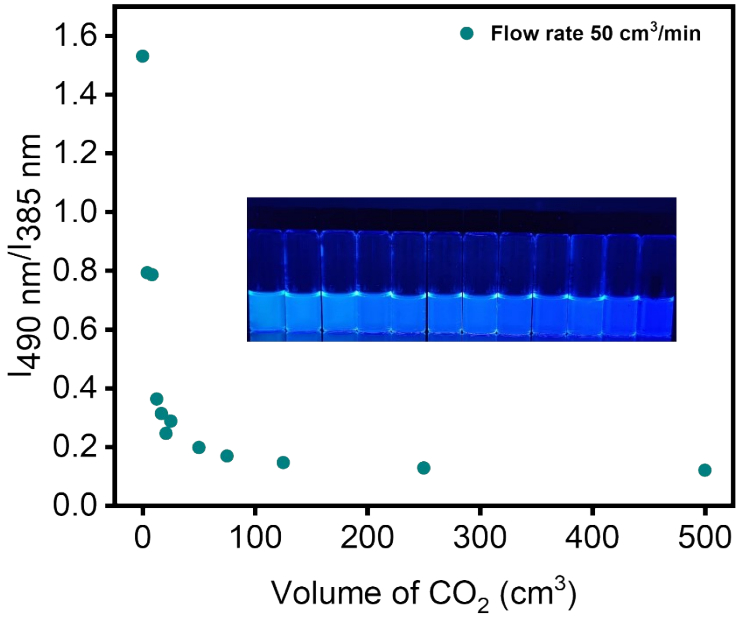


Figure S39. Fluorescence intensity ratio (490 nm/385nm) of PDMAm-*co*-DEAPyMA in aqueous solution after kinetics with CO_2 and at r.t. Concentration of polymer in water = 10 ppm. 5 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 50 cm^3/min.

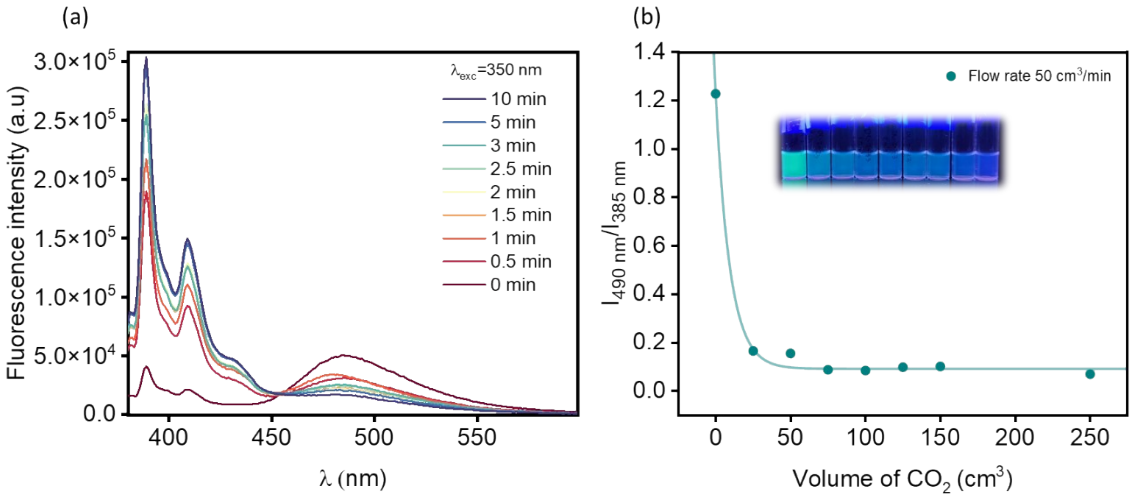


Figure S40. First kinetics of PDMAm-*co*-DEAPyMA in aqueous solution after exposed to CO_2 and at r.t. Concentration of polymer in water = 10 ppm. 5 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 50 cm^3/min. a) Fluorescence spectrum b) Fluorescence intensity ratio (490 nm/385nm) vs CO_2 volume.

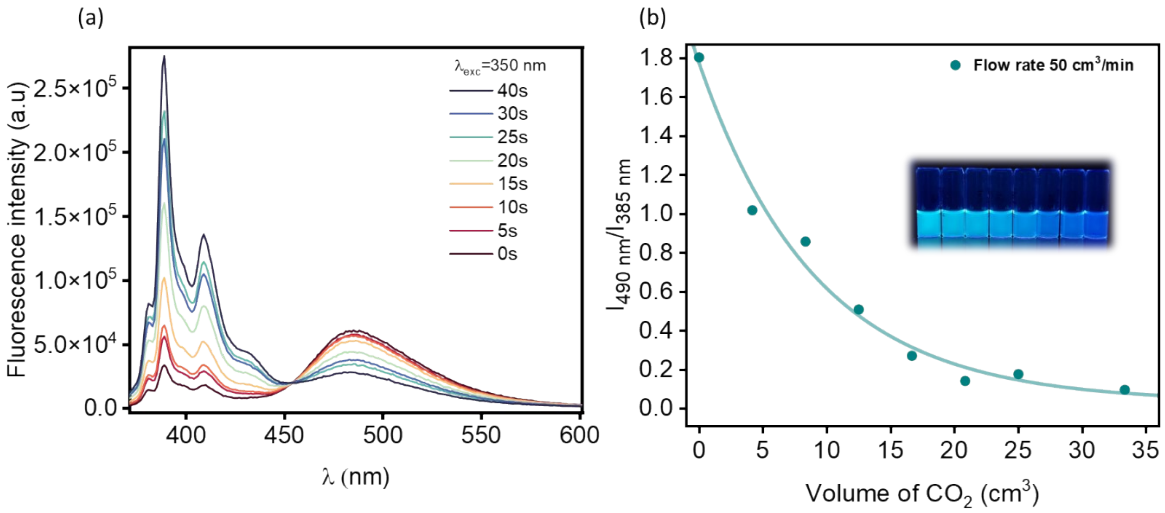


Figure S41. Second kinetics of PDMAm-*co*-DEAPyMA in aqueous solution after exposed to CO_2 and at r.t. Concentration of polymer in water = 10 ppm. 5 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 50 cm^3/min. a) Fluorescence spectrum b) Fluorescence intensity ratio (490 nm/385nm) vs CO_2 volume.

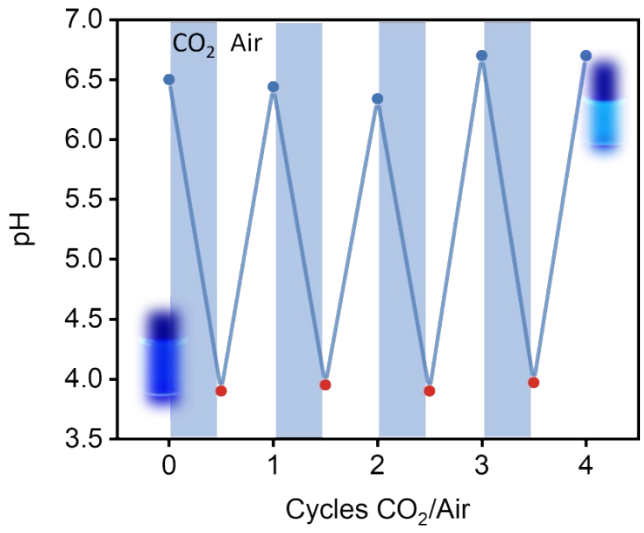


Figure S42. pH variation after each CO_2/Air cyles of PDMAm-*co*-DEAPyMA in aqueous solution after air exposure kinetics. r.t. Concentration of polymer in water = 10 ppm. 1 mol% of DEAPyMA in polymer. Flow rate of CO_2 = 50 cm^3/min.

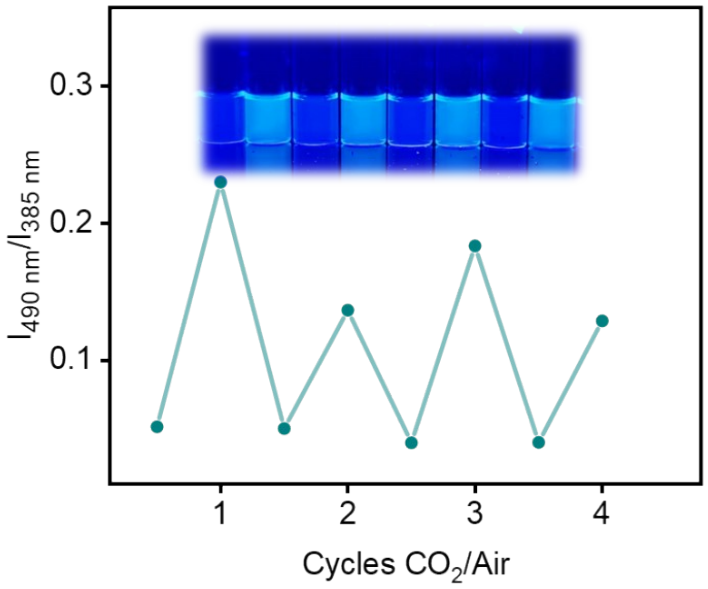


Figure S43. Graphic representing the change in fluorescence intensity ratio I_{490nm}/I_{385nm} of a sample of concentration 0.01 mg/mL, previously exposed to 6 cycles of CO_2/air to test the stability of the sample and stored for one week. Exposed to CO_2 for 5 min and air for 1 h for 4 cycles. Flow rate of CO_2 = 50 cm^3/min.