Solid-state sensors based on Eu^{3+}-containing supramolecular polymers with luminescence colour switching capability

Electronic Supplementary Information

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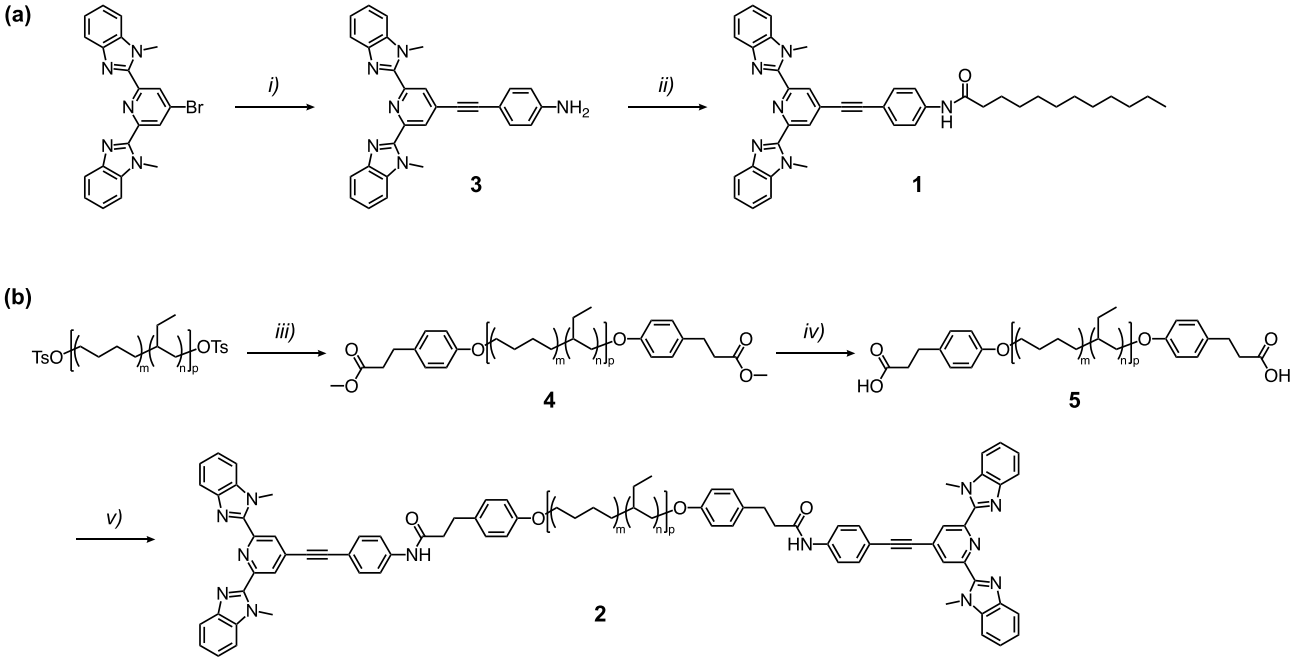


Figure S1: Synthesis of the π-extended low-molecular weight reference ligand **1** and the macromonomer **2** with a poly(ethylene-*co*-butylene) core (with M_n = 4200 g mol^{-1}; m ≈ 0.36, n ≈ 0.64, p ≈55). The preparation of the starting compounds are described elsewhere.[1,2] *Reagents and conditions*: *i*) 4-Ethynylaniline, $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH, THF, 54% ; *ii*) dodecanoic acid, EDCI, DPTS, $CHCl_3$, 78%; *iii*) methyl 3-(4-hydroxyphenyl)propionate, TBAI, K_2CO_3, toluene, 70%; *iv*) NaOH, THF/H_2O 10:1, 45%; *v*) EDCI, DPTS, $CHCl_3$, 54%.

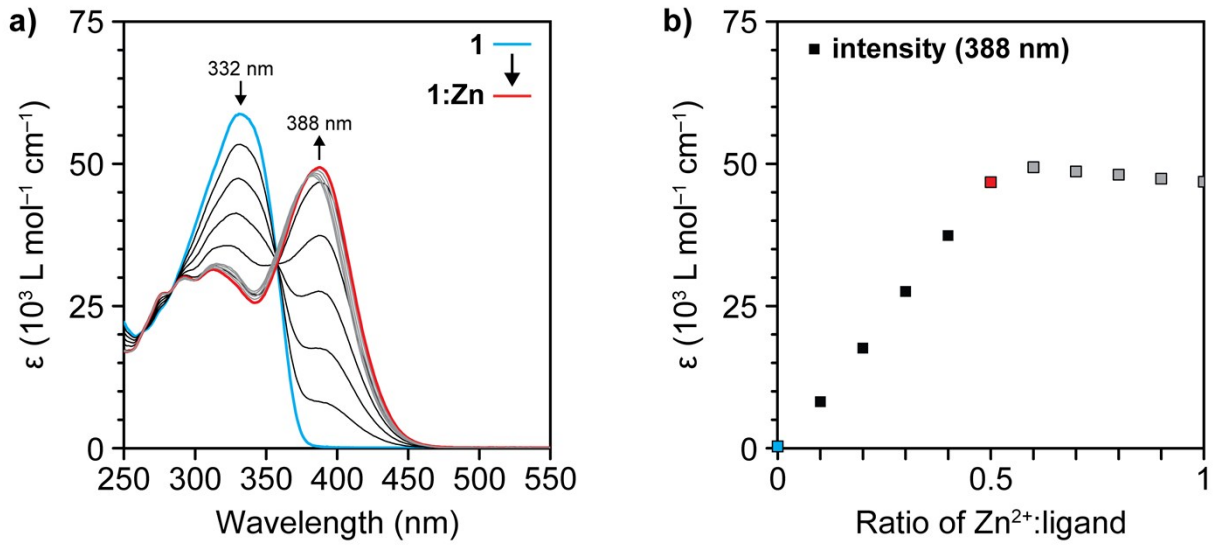
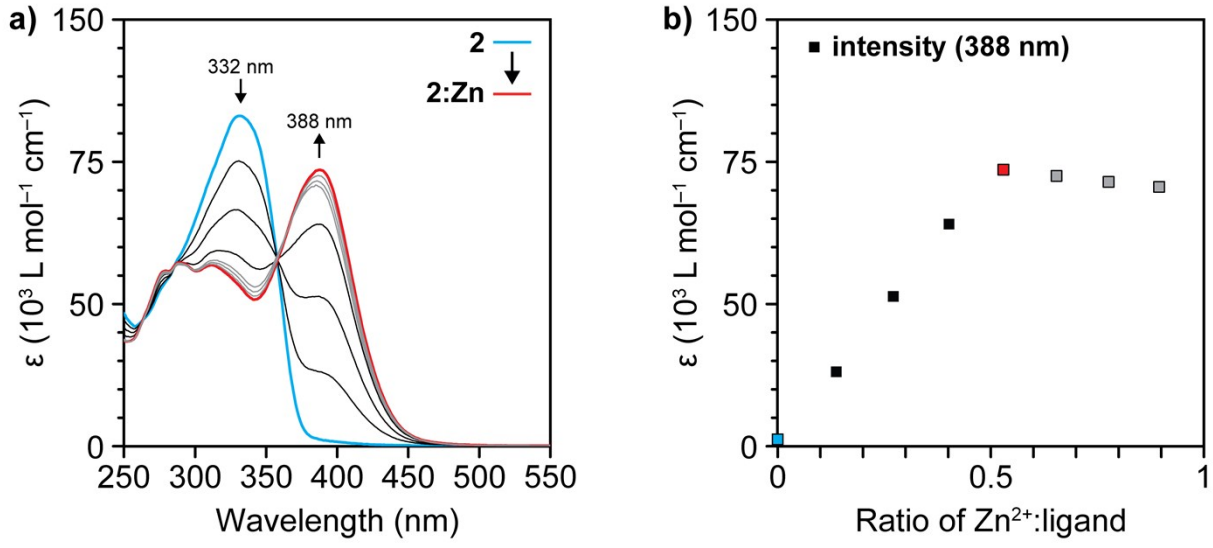


Figure S2: *a)* UV-Vis absorption spectra of solutions of ligand **1** (c = 20 µmol L^{-1} in $CHCl_3$/MeCN 9:1, blue line). Upon titration with aliquots of $Zn(NTf)_2$, the formation of the coordination complexes is observed at a metal-to-ligand ratio of 1:2 (red line). *b*) Absorption intensity of the metal-ligand complex at λ_{max} = 388 nm as a function of the ratio between added $Zn(NTf_2)_2$ and the ligand.



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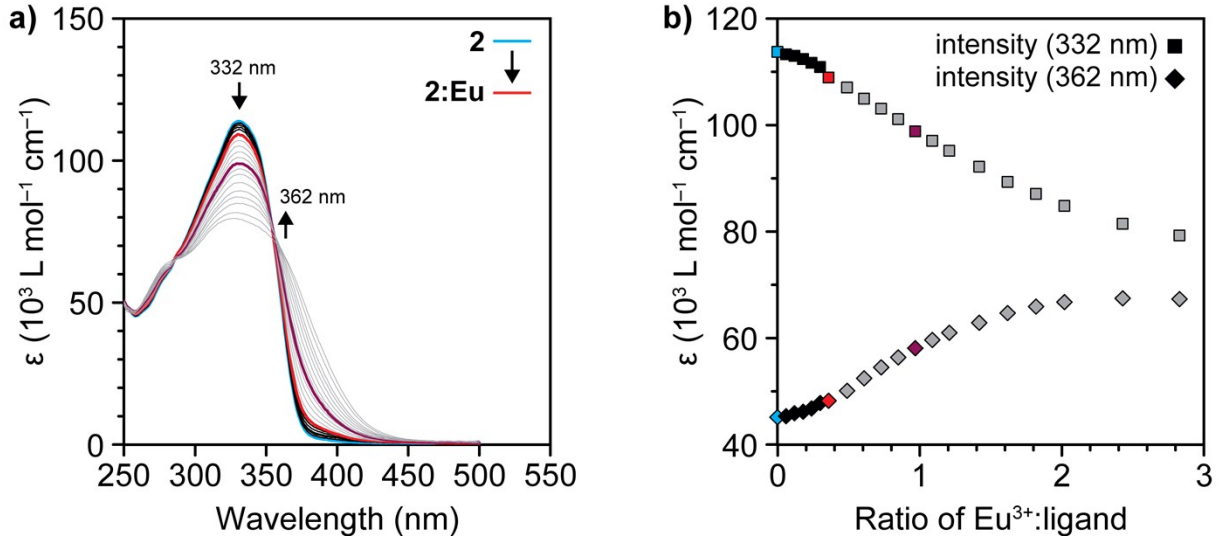
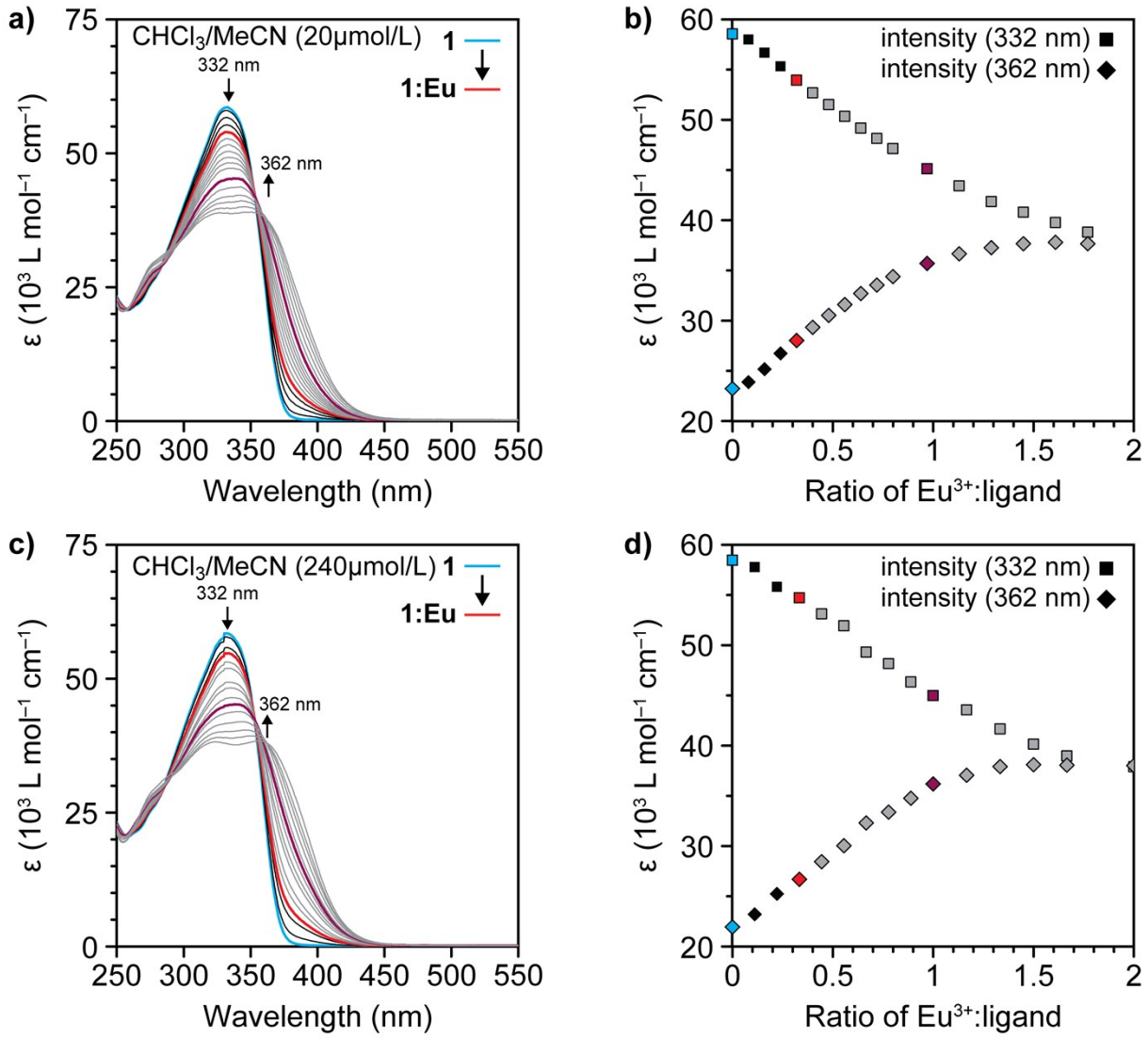


Figure S4: *a)* UV-Vis absorption of solutions of macromonomer **2** (c = 10 µmol L^{-1} in 9:1 $CHCl_3$/MeCN, blue line) Upon titration with aliquots of $Eu(ClO_4)_3$ the formation of the coordination complexes is observed. The spectra obtained at metal-to-ligand ratios of 1:3 and 1:1 are highlighted (red and purple line, respectively). *b)* Absorption intensity of the free ligand (332 nm) and the metal-ligand complex (362 nm) as a function of the ratio between added $Eu(ClO_4)_3$ and the ligand.



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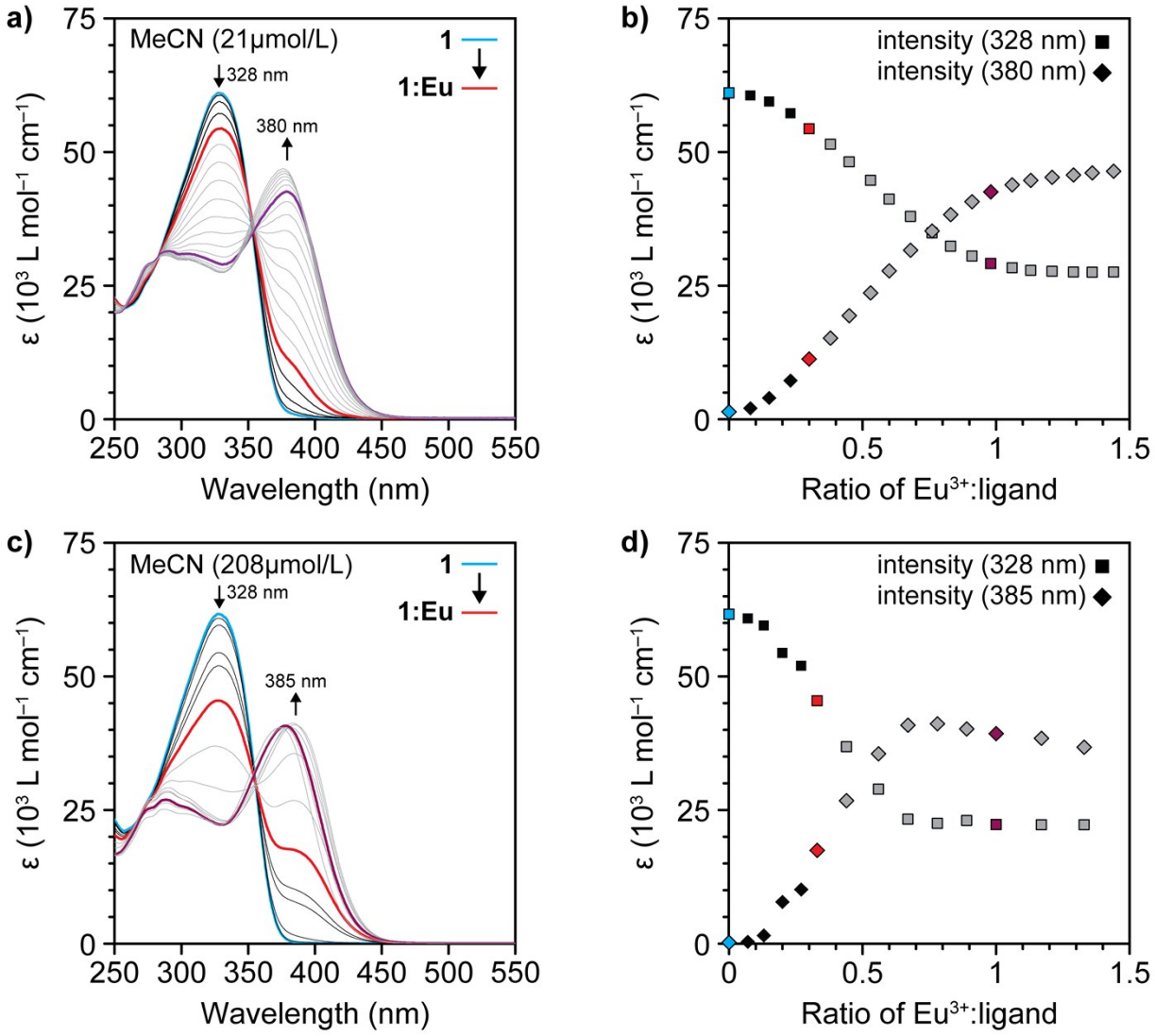

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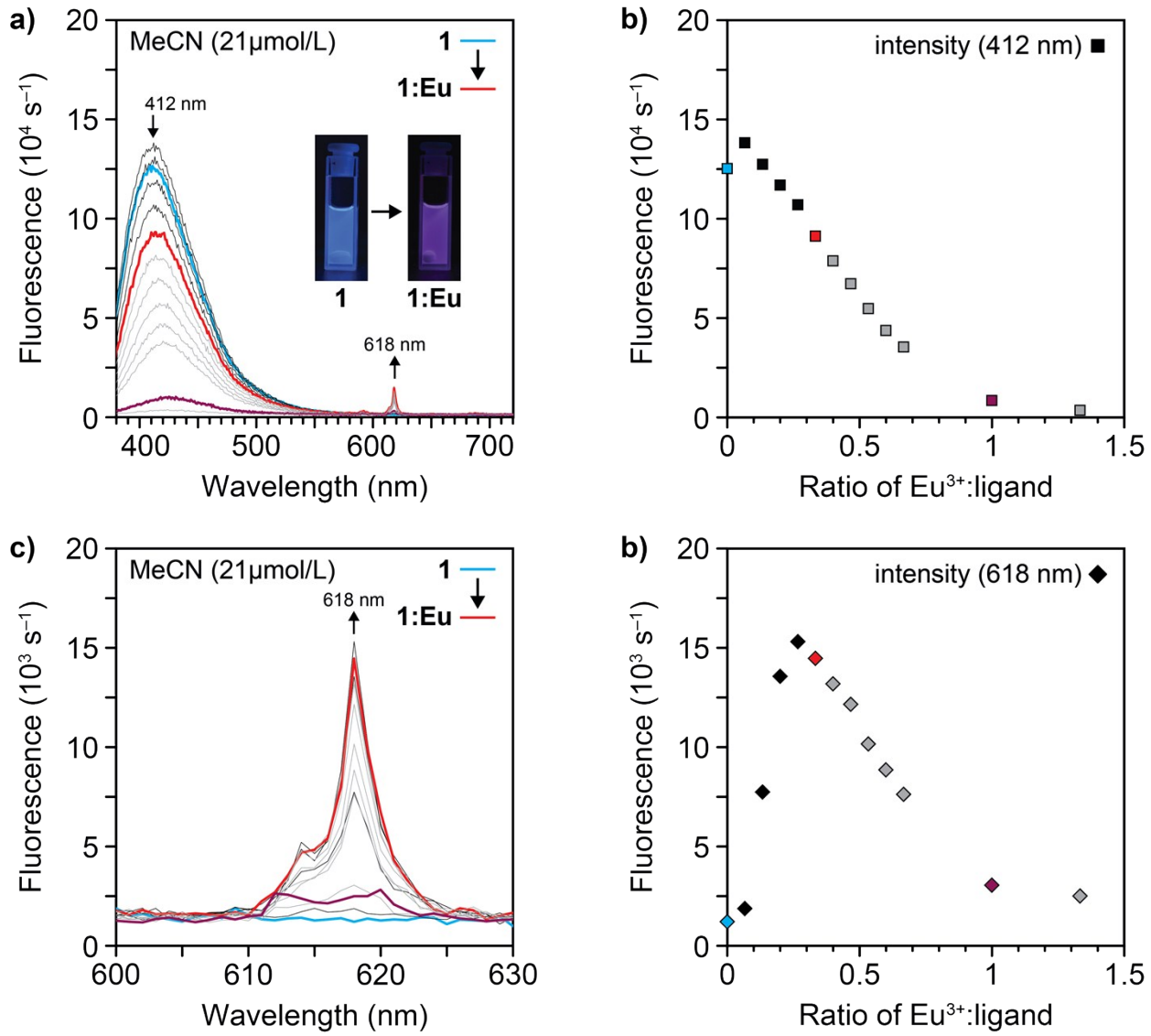

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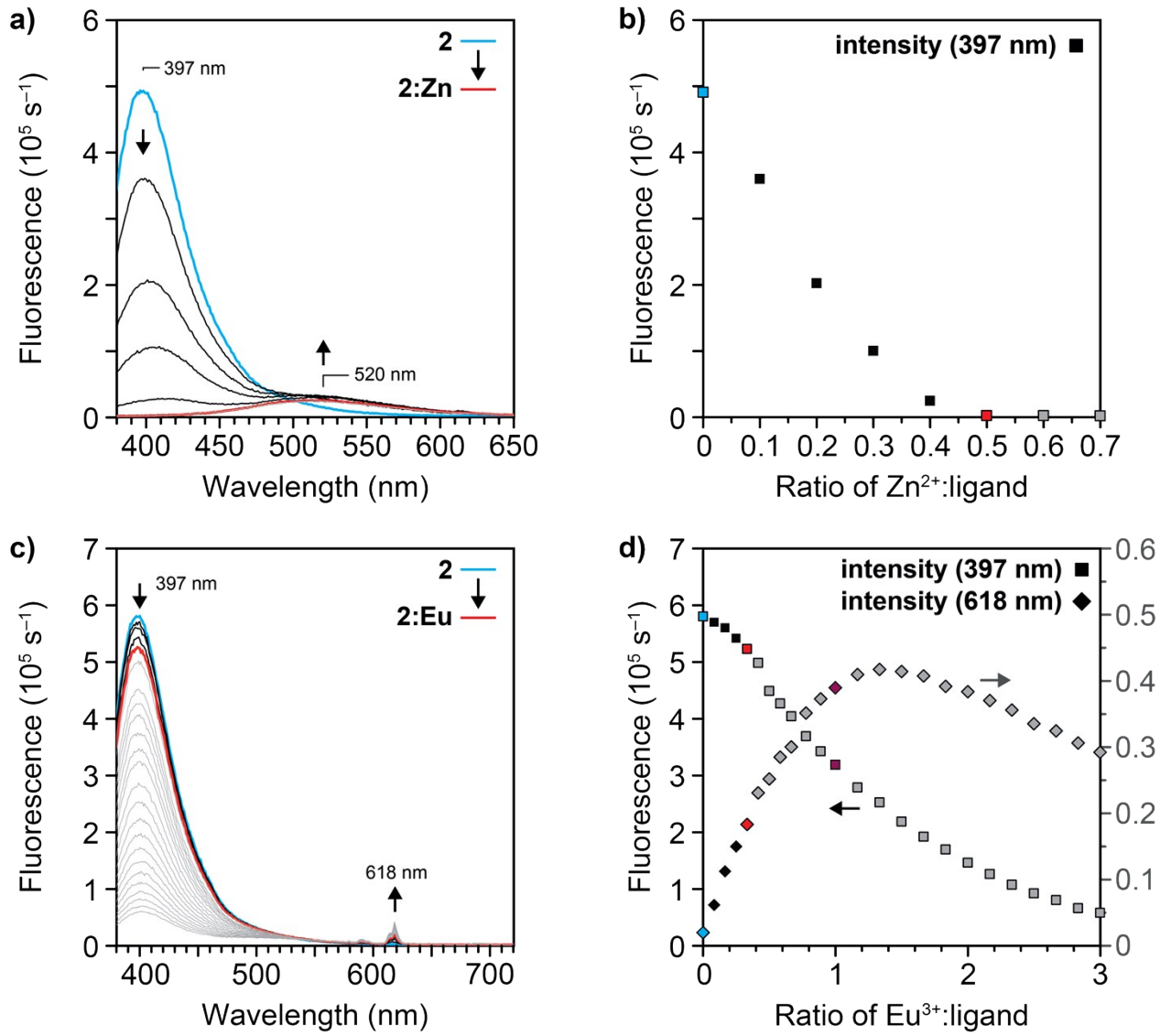

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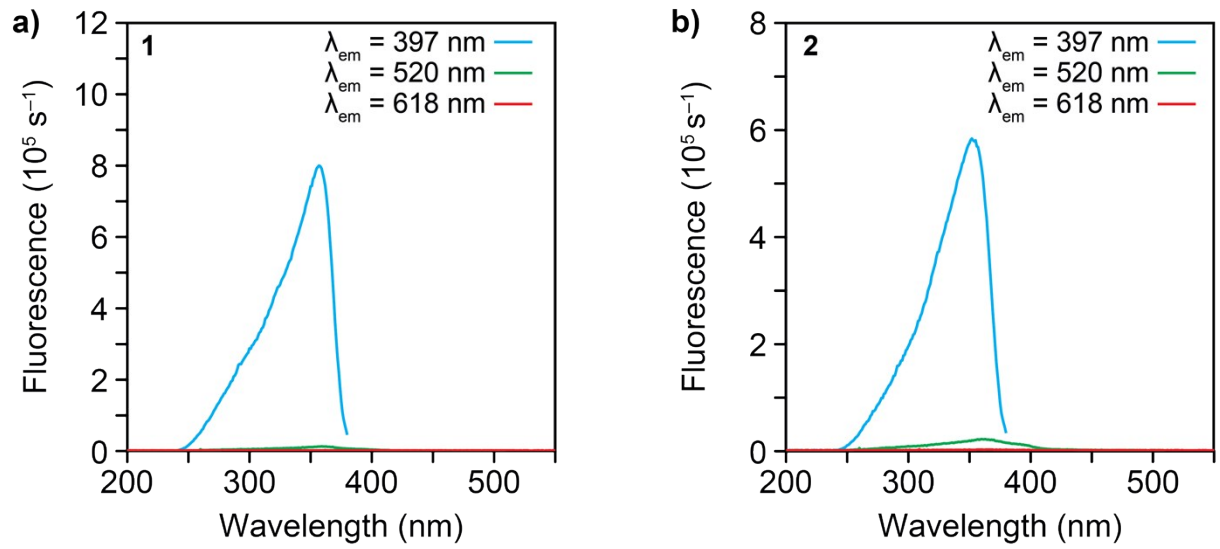

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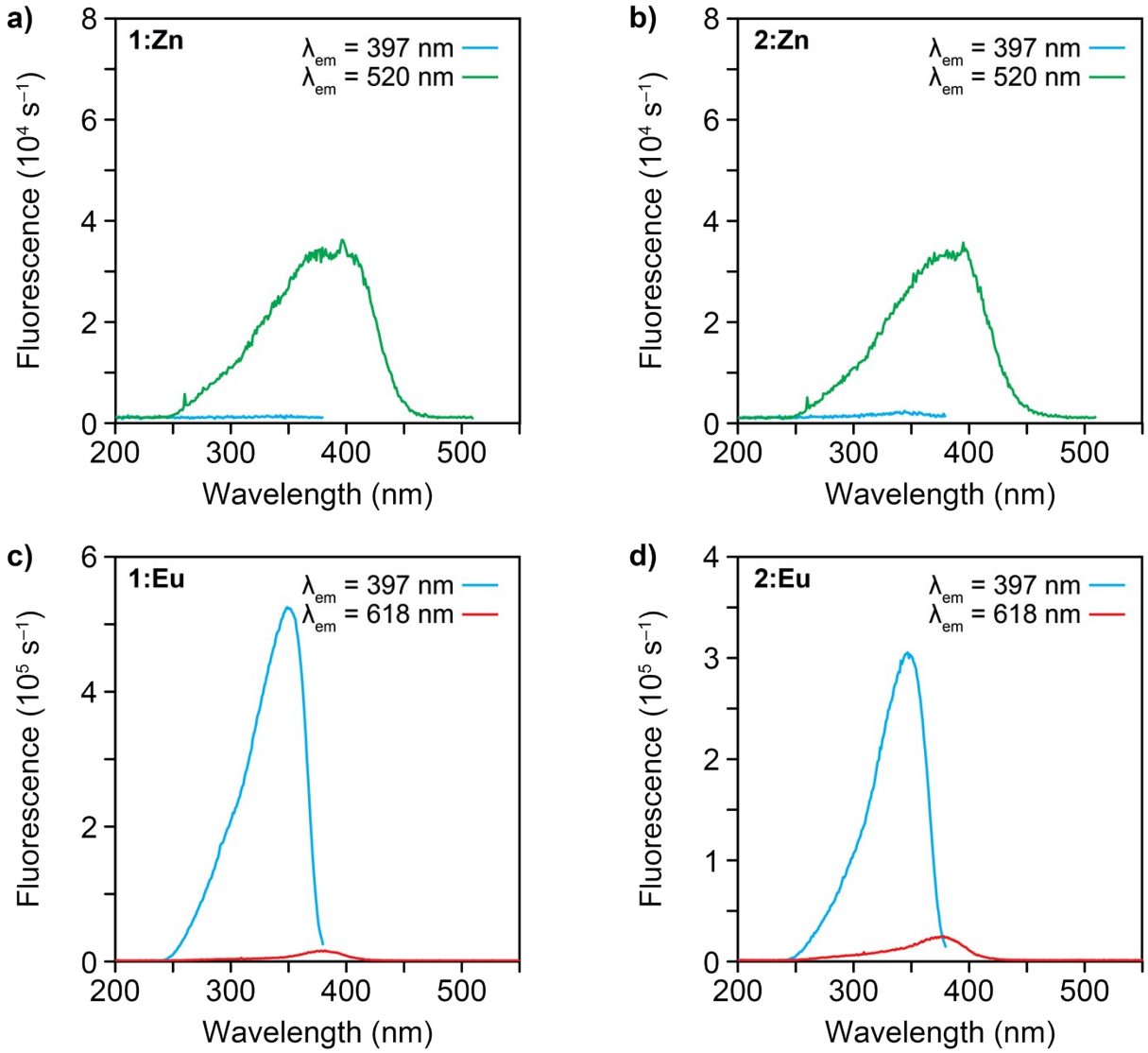

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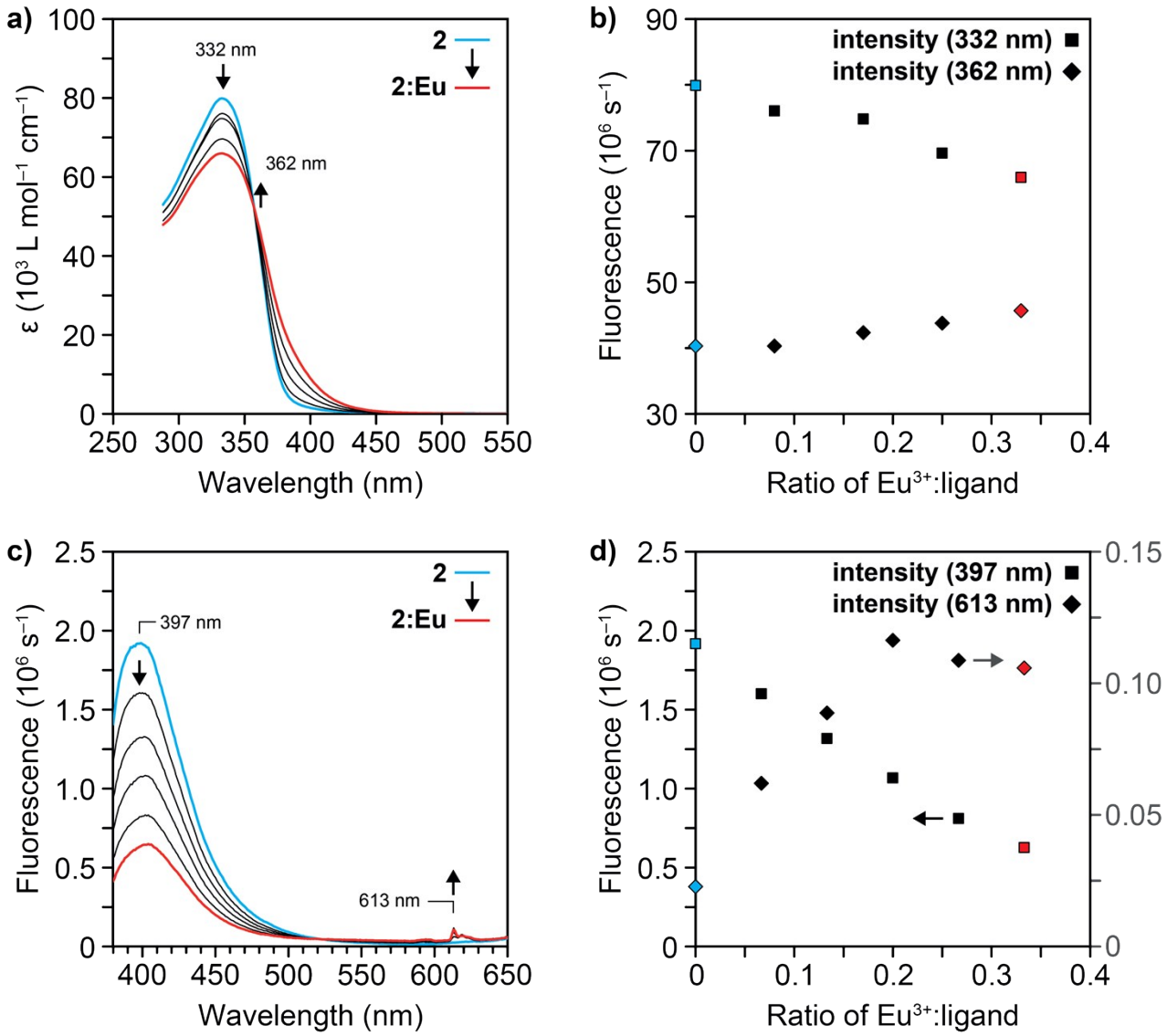
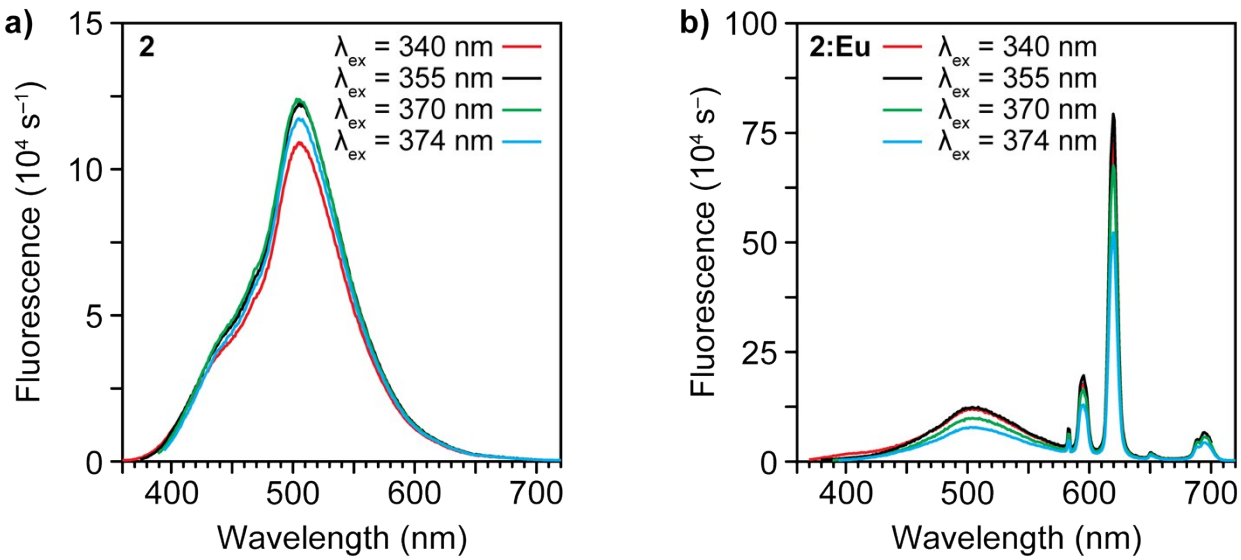


Figure S11: *a)* UV-Vis absorption of solutions of ligand **1** (c = 164 µmol L^{-1} in chlorobenzene/MeCN, blue line). Upon titration with aliquots of $Eu(ClO_4)_3$ the formation of the coordination complexes is observed. The spectrum obtained at metal-to-ligand ratios of 1:3 is highlighted (red line). *b)* Absorption intensity of the free ligand (332 nm) and the metal-ligand complex (362 nm) as a function of the ratio between added $Eu(ClO_4)_3$ and the ligand. *c)* Fluorescence spectra of solutions of macromonomer **2** (*c* = 164 µmol L^{-1} in chlorobenzene/MeCN 9:1, blue line). Upon titration with aliquots of $Eu(ClO_4)_3$, the formation of the coordination complexes is observed. The spectrum obtained at a metal-to-ligand ratio of 1:3 is highlighted (red line). *d)* Emission intensity of the free ligand (397 nm) and the metal-ligand complex (613 nm) as a function of the ratio between added $Eu(ClO_4)_3$ and the ligand.



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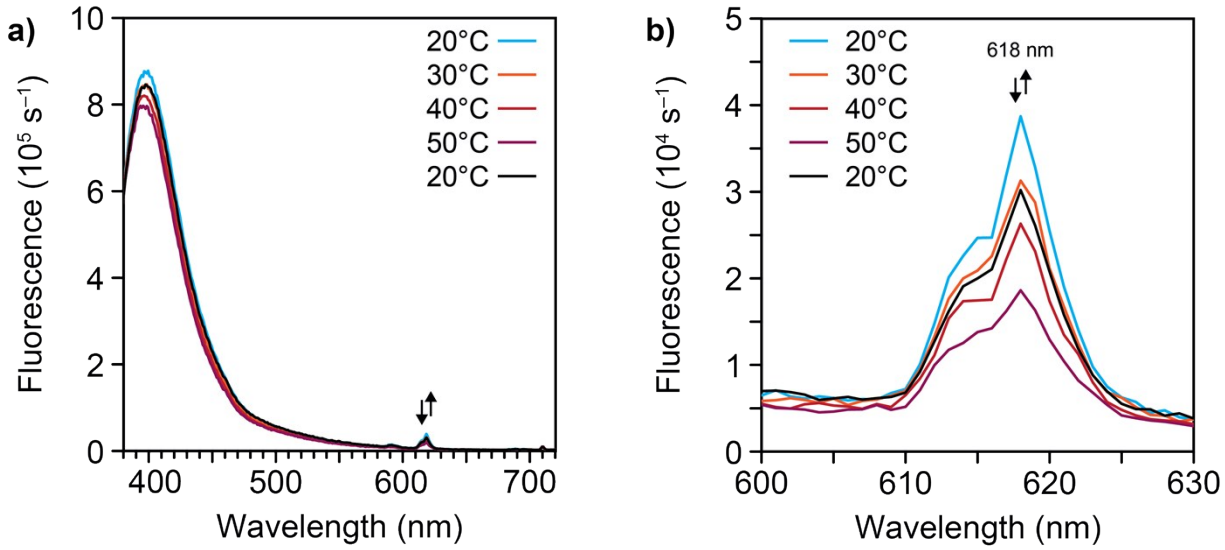

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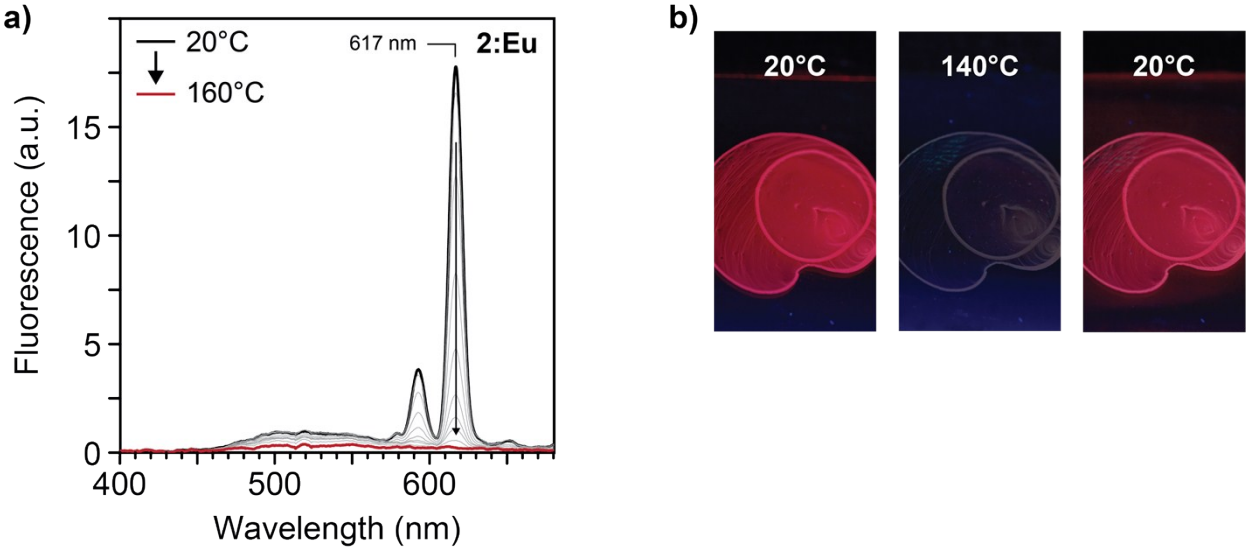

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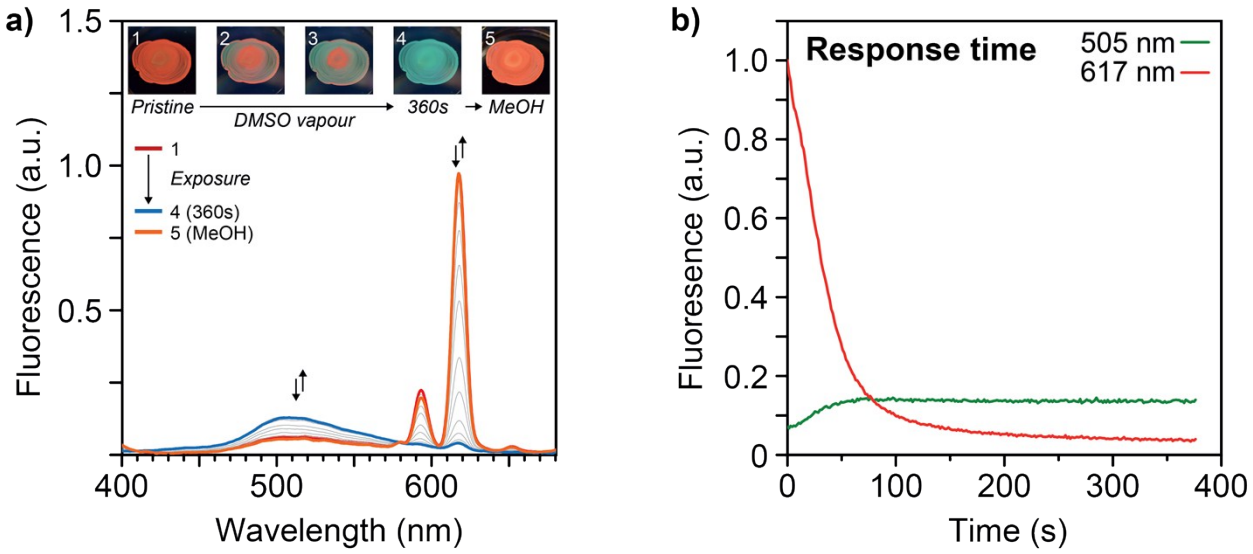

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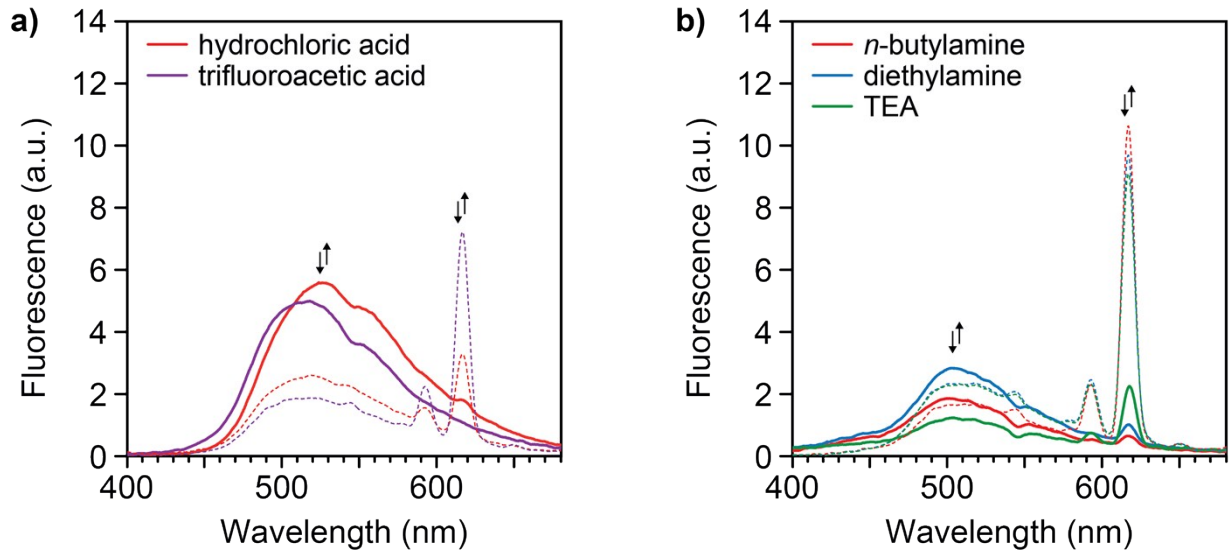

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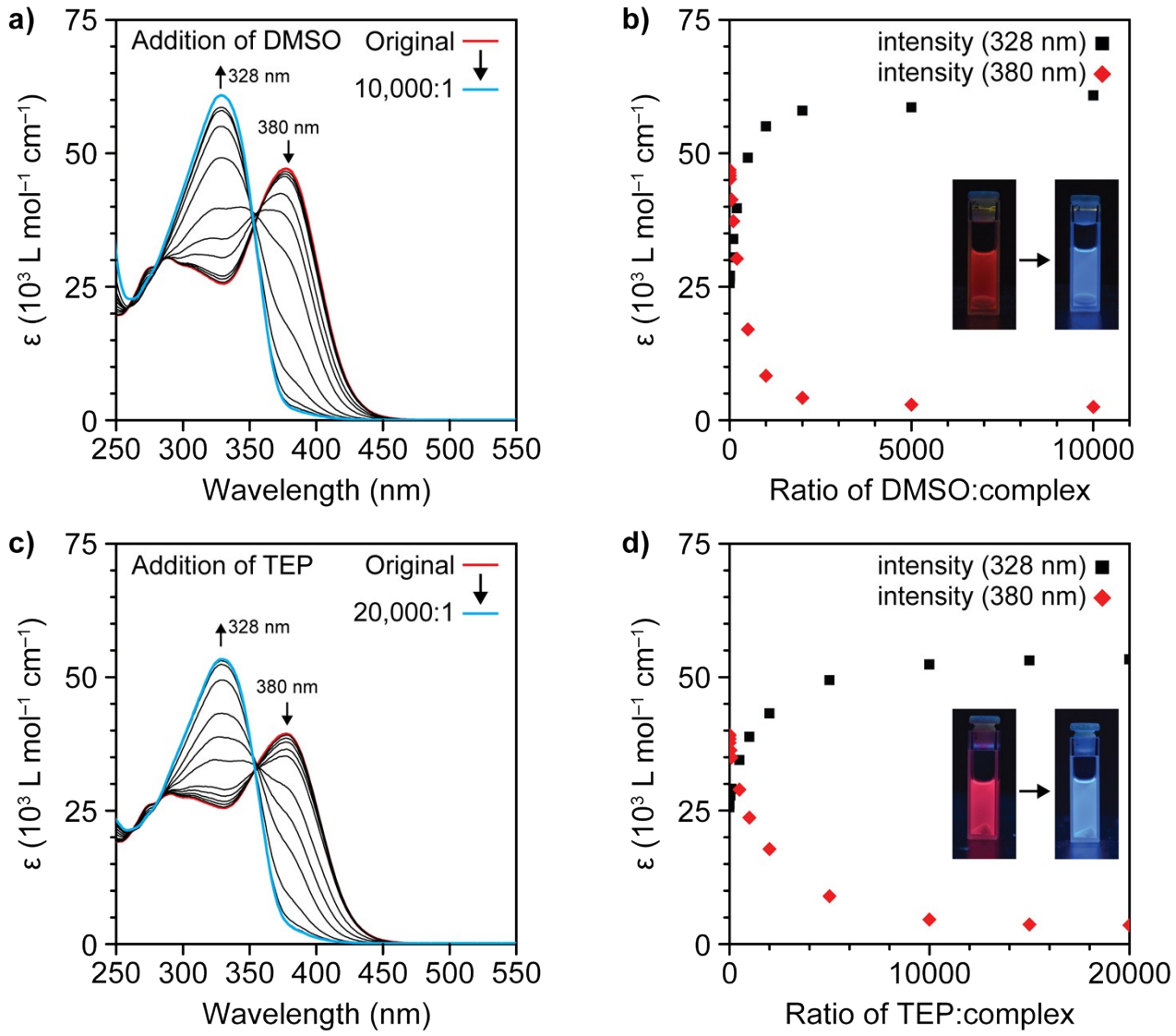
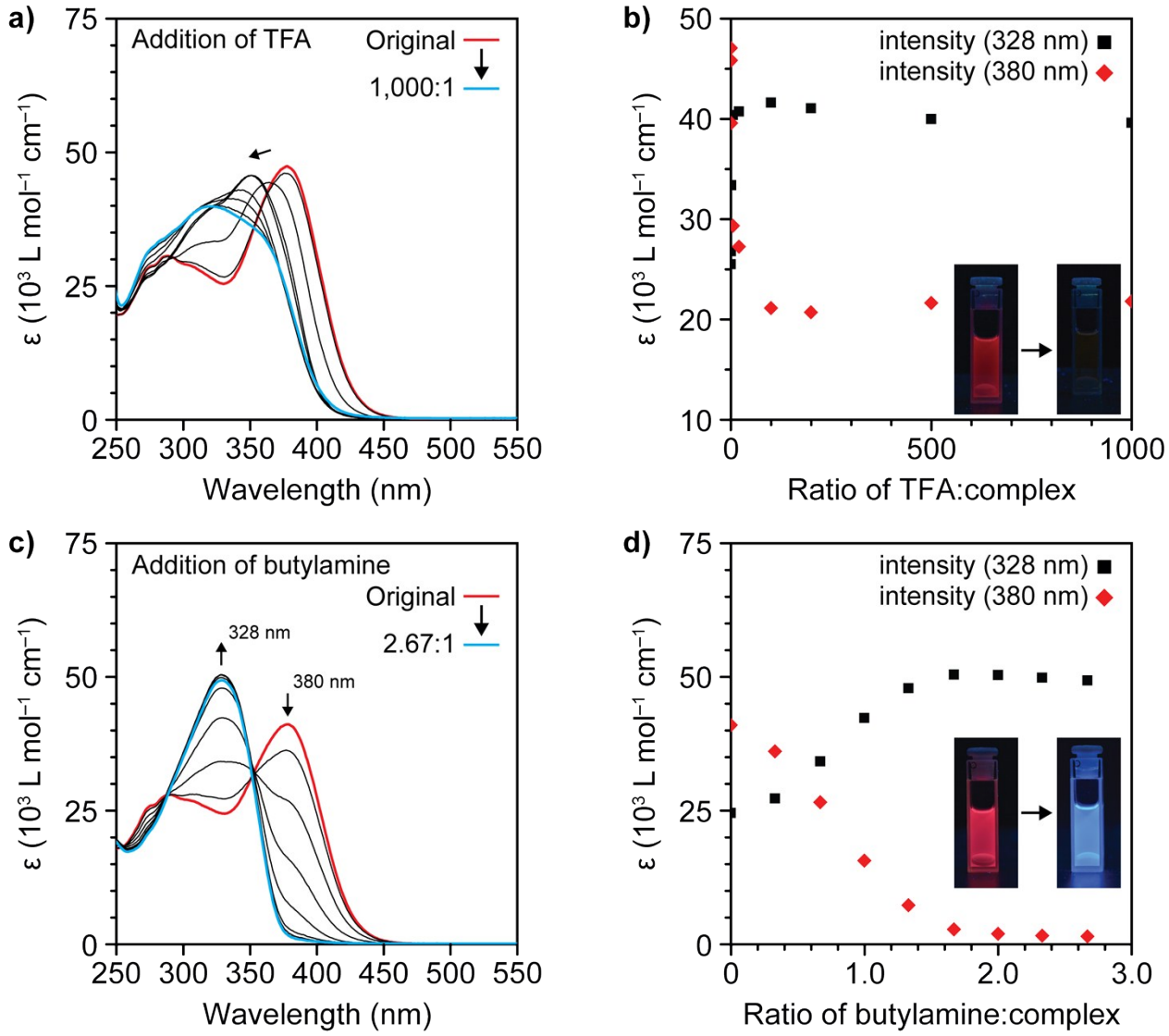


Figure S17: *a)* UV-Vis absorption spectra of a solution (c = 20 µmol L^{-1} in MeCN, red line) of the **1:Eu** coordination complex with a metal-ligand ratio of 1:1, and upon titration with aliquots of DMSO. The spectrum obtained after addition of 10,000 equivalents of DMSO is highlighted (blue line). *b)* Absorption intensity of the free ligand (328 nm) and the metal-ligand complex (380 nm) as a function of the ratio between added DMSO and the complex. The inset shows photographs of the solution at the beginning and end of the titration (taken under illumination with 365 nm UV light). *c)* UV-Vis absorption spectra of a solution (c = 20 µmol L^{-1} in MeCN, red line) of the **1:Eu** coordination complex with a metal-ligand ratio of 1:1, and upon titration with aliquots of triethylphosphate (TEP). The spectrum obtained after addition of 20,000 equivalents of TEP is highlighted (blue line). *d)* Absorption intensity of the free ligand (328 nm) and the metal-ligand complex (380 nm) as a function of the ratio between added TEP and the complex. The inset shows photographs of the solution at the beginning and end of the titration (taken under illumination with 365 nm UV light).



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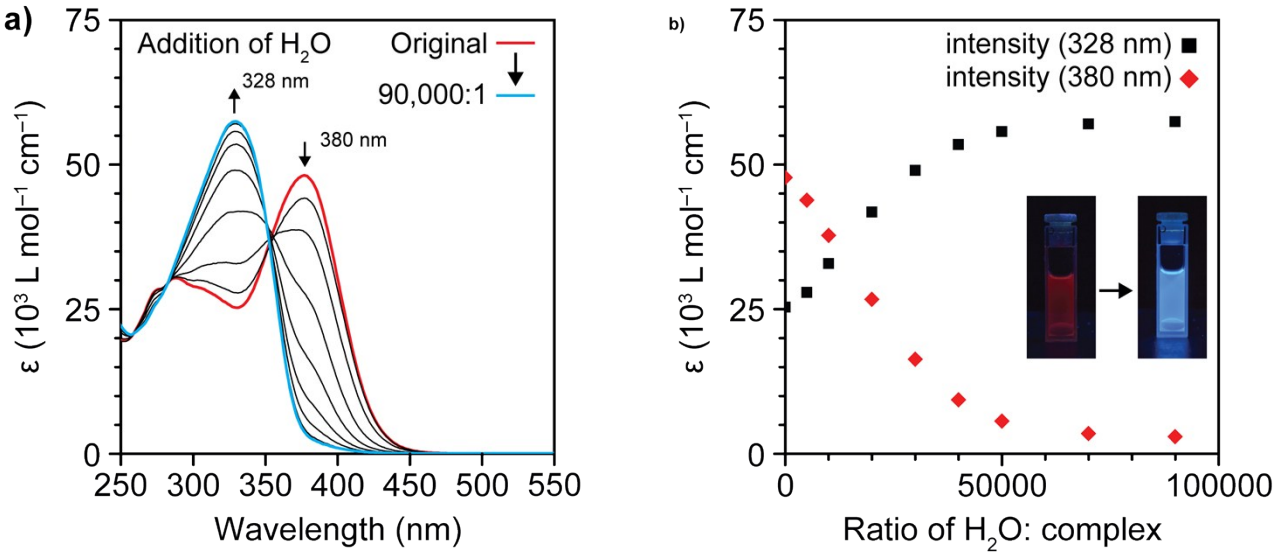


Figure S19: *a)* UV-Vis absorption spectra of a solution (c = 20 µmol L^{-1} in MeCN, red line) of the **1:Eu** coordination complex with a metal-ligand ratio of 1:1, and upon titration with aliquots of water. The spectrum obtained after addition of 90,000 equivalents of water is highlighted (blue line). *b)* Absorption intensity of the free ligand (328 nm) and the metal-ligand complex (380 nm) as a function of the ratio between added water and the complex. The inset shows photographs of the solution at the beginning and end of the titration (taken under illumination with 365 nm UV light).

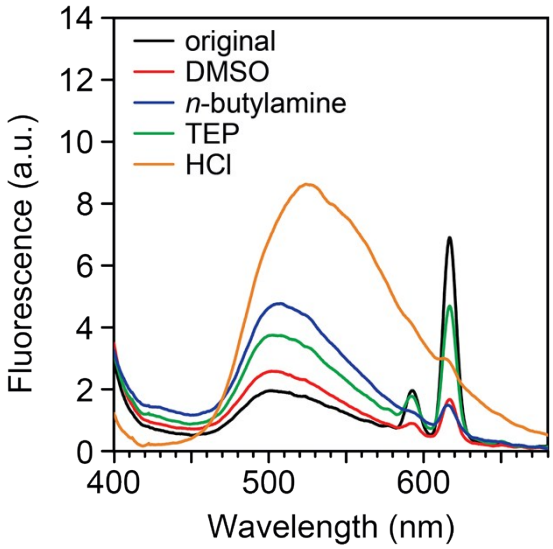


Figure S20: Fluorescence spectra (λ_{ex} = 370 nm) of **2:Eu** coated ethylene vinyl alcohol copolymer substrates before (black line) and after exposure to different analytes.

2. Experimental Details

2.1 Instrumentation

NMR Spectroscopy was carried out at 297.2 K on a Bruker Avance DPX 400 spectrometer at frequencies of 400.19 MHz for ^{1}H nuclei and 100.63 MHz for ^{13}C nuclei. Spectra were calibrated to the residual solvent peak of $CDCl_3$ (7.26 ppm ^{1}H NMR; 77.16 ppm ^{13}C NMR) or DMSO-d_6 (2.50 ppm ^{1}H NMR; 39.52 ppm ^{13}C NMR). Data were treated with MestReNova (12.0.2) software suite and all chemical shifts δ are reported in parts per million (ppm) with coupling constant in Hz (multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal).

High resolution mass spectra (HRMS) were recorded as service measurements at the mass spectrometry facilities of the Institute of Chemistry of the University of Fribourg. Electrospray ionization mass spectrometry (ESI-MS) data were acquired on a Bruker FTMS 4.7T BioAPEX II equipped with a ComiSource 1.0 and operated in the positive ionization mode. Data were processed using Xmass 7.0.8 software. Matrix-assisted laser desorption and ionization (MALDI) mass spectra were recorded on a Bruker ultrafleXtreme, using *trans*-2[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix materials.

Elemental analysis was performed as service measurements at the Molecular and Biomolecular Analysis Service MoBiAS of ETH Zürich on a LECO TruSpec Micro (C, H, N) and LECO 628 O Micro (O).

Solution phase UV-Vis spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer in $CHCl_3$/MeCN (9:1) using quartz cuvettes of 1 cm and 2 mm path length.

Fourier transform infrared (FT-IR) spectra were recorded using dried powder/films on a Perkin Elmer Spectrum 65 spectrometer between 4000–600 cm^{-1} with a resolution of 4 cm^{-1} and 4 scans per sample.

Fluorescence spectra were recorded on a PTI C720 fluorescence spectrometer using right angle excitation, a XeArc lamp for excitation and a PTI 814 photomultiplier detection system, a Jasco V-630 Spectrophotometer equipped with a Jasco ETC-272T Temperature Controller, or a Horiba Fluorolog TCSPC using right angle excitation and 1 cm quartz cuvettes. Fluorescence spectra of solid samples were recorded with an Ocean Optics USB4000-FL spectrometer under excitation at λ_{ex} = 370 nm from an Ocean Optics LS-450 LED light source using an Ocean Optics Shimadzu UV-2401 PC optical fiber in reflection geometry. The drop-cast samples were placed on a substrate and the optical fiber was oriented at an angle of 45° to the surface at a distance of approximately 5 mm and the emission was measured. The data were acquired with Stream basic software and smoothed using the Savitzky-Golay method integrated in the Origin 9.1 software.

Photographs were taken with a Nikon D7100 digital camera equipped with a AF-S DX Zoom-NIKKOR 18-135mm lens (f/3.5-5.6G IF-ED).

2.2 Materials and Methods

UV-Vis titrations. UV-Vis absorption spectra were acquired upon titration of solutions of **1** and **2** (c = 25 μmol L^{-1}) in 9:1 $CHCl_3$:MeCN (v/v) with $Zn(NTf)_2$ (c = 195 μmol L^{-1}) and $Eu(ClO_4)_3$ (c = 160 μmol L^{-1}) in 9:1 $CHCl_3$:MeCN (v/v), unless otherwise indicated. The characteristic absorbance band for the ligand and the formed Zn^{2+}- and Eu^{3+}-complexes were plotted as a function of the metal-to-ligand ratio.

Metallosupramolecular polymerization and film formation. Macromonomer **2** was dissolved in THF and the proper amount $Eu(ClO_4)_3$ solution (3 mmol L^{-1} in THF) was added to ensure a stoichiometric metal-to-ligand ratio of 1:3. The THF was evaporated under a nitrogen stream and the sample was redissolved in chlorobenzene/MeCN. Solid films of the samples were obtained by drop-casting of the chlorobenzene/MeCN solution on glass slides and polymer substrates of DuPont™ Elvax® 420 ethylene-vinyl acetate copolymer resin that were processed into uniform films in a hot-press (120 °C, 1 min, thickness of 0.5 mm).

2.3 Synthetic Procedures and Analytical Data

General Procedures. Unless otherwise noted, all reactions were carried out in dried Schlenk glassware in an inert argon atmosphere. Hydroxyl terminated poly(ethylene-*co*-butylene) of a number-average molecular weight M_n of 3100 g/mol was kindly donated by Cray Valley Company under the trade name Krasol® HLBH-P 3000 and dried *in vacuo* at 50 °C overnight prior to use. Chromatography solvents were purchased as reagent grade and used as received. Spectroscopic grade $CHCl_3$ (Acros) used for titrations was passed through a plug of dry, activated basic alumina (Brockman I) prior to use. Europium perchlorate ($Eu(ClO_4)_3$, 50% aqueous solution) (Strem), zinc bistriflimide ($Zn(NTf_2)_2$) (Strem), DuPont™ Elvax® 420 ethylene-vinyl acetate copolymer resin (18 % by weight vinyl acetate comonomer content; DuPont), chelidamic acid (Intatrade Chemicals GmbH), *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDCI) (TCI Chemicals), copper(I) iodide (Sigma-Aldrich), bis(tri-phenylphosphine)palladium(II) chloride (Sigma-Aldrich), 4-ethynylaniline (Sigma-Aldrich), anhydrous MeCN (Acros), SiliaMetS® TAAcONa metal scavenger (SiliCycle) and all other reagents were commercially obtained and used without further purification.

2,6-Bis(1'-ethylbenzimidazolyl)pyridine (Mebip)[3], 2,6-bis(1'-methyl-benzimidazolyl)-4-bromopyridine (Mebip-Br)[1], 4-(Dimethylamino)pyridinium 4-toluene-sulfonate (DPTS),[4] and telechelic bis(*p*-toluene-

sulfonyl ester)-functionalized poly(ethylene-*co*-butylene)[2] were prepared following previously reported literature procedures.

TLC analyses were performed on TLC plates from Merck (Silica gel 60 F_{254}). UV-light (254 nm) was used for detection. Column chromatography was conducted using a Biotage Isolera One system and Biotage SNAP columns.

***N*-(4-((2,6-Bis(1'-methyl-benzimidazolyl)pyridin-4-yl)ethynyl)phenyl)dodecanamide 1.** 2,6-Bis-(1'-methyl-benzimidazolyl)-4-((4-aminophenyl)ethynyl)pyridine **3** (150 mg, 0.33 mmol), dodecanoic acid (73 mg, 0.36 mmol), EDCI (76 mg, 0.39 mmol), and DPTS (14 mg, 66 µmol) were dissolved in 3 mL anhydrous $CHCl_3$ and stirred for 15 h at room temperature. After dilution with $CHCl_3$ (10 mL) the mixture was washed two times with 1 M NaOH solution (10 mL) and once with saturated NaCl solution (10 mL). The organic phase was dried over Na_2SO_4, and the solvent was removed *in vacuo*. Column chromatography (silica gel; DCM/MeOH 99:1 to 98:2) yielded **1** (165 mg, 78 %) as an off-white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 2H), 7.91-7.85 (m, 2H), 7.63-7.56 (m, 2H), 7.56-7.45 (m, 4H), 7.43-7.33 (m, 6H), 4.27 (s, 6H), 2.39-2.33 (t, J = 7.6 Hz, 2H), 1.78-1.68 (q, J = 7.5 Hz, 2H,), 1.42-1.19 (m, 16H), 0.92-0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.6, 150.0, 149.9, 142.8, 139.3, 137.4, 134.3, 133.2, 127.0, 123.9, 123.2, 120.5, 119.5, 110.1, 86.1, 38.1, 32.7, 32.1, 29.8, 29.6, 29.5, 29.5, 29.4, 25.7, 22.8, 14.8. IR (ATR) ν (cm^{-1}): 3288, 2919, 2852, 2213, 1660, 1592, 1584, 1546, 1520, 1471, 1457, 1440, 1405, 1380, 1326, 1305, 1286, 1248, 1239, 1205, 1178, 1151, 1130, 1102, 1081, 1019, 1003, 992, 963, 929, 892, 833, 765, 740, 719, 696, 593, 577, 543, 531. MS (ESI): calcd. for $C_{41}H_{45}N_6O$ $[M+H]^+$: 637.36494; found 637.36518. EA: calcd. for $C_{41}H_{44}N_6O$: C 77.33%, H 6.96%, N 13.20%, O 2.51%; found: C 77.17%, H 6.92%, N 13.04%, O 2.80%.

Bis(π-extended-Mebip)-functionalized telechelic poly(ethylene-*co*-butylene) 2. Telechelic biscarboxy-functionalized poly(ethylene-*co*-butylene) **5** was dried overnight at 40 °C under vacuum. **3** (140 mg, 0.31 mmol) and **5** (384 mg, 0.13 mmol) were dissolved in 3 mL of anhydrous chloroform, EDCI (60 mg, 0.31 mmol) and DPTS (11 mg, 52 µmol) were added, and the mixture was stirred for 15 h at room temperature. The reaction mixture was diluted with 10 mL of chloroform and extracted twice with 1 M NaOH (5 mL). The combined aqueous phases were extracted once with 5 mL chloroform and the combined organic layers were washed with brine (5 mL) and dried over sodium sulphate. The solvent was removed *in vacuo* and purification by column chromatography (DCM/MeCN 60:40, then DCM/MeOH 97:3) furnished **2** (246 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 4H), 7.96 (m, 4H), 7.57-7.40 (m, 20H), 7.13 (m, 4H), 6.81 (m, 4H), 4.29 (s, 12H), 3.94 (m, 4H), 2.97 (t, J = 6.4 Hz, 4H), 2.66 (t, J = 7.6 Hz, 4H), 2.25-0.92 (m, CH_2 backbone),

0.91-0.63 (m, CH_3 backbone). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.8, 137.3, 133.2, 129.4, 127.0, 124.0, 123.2, 120.4, 119.6, 114.8, 110.1, 39.4–38.0, 36.4–36.1, 34.1–33.3, 31.0–29.7, 27.0–25.8, 11.1–10.2. IR (ATR) ν (cm^{-1}): 2959, 2921, 2852, 2208, 1694, 1588, 1511, 1459, 1407, 1378, 1329, 1243, 1176, 1006, 930, 889, 837, 741, 531, 515. MS (MALDI): calcd. for $C_xH_yN_zO_w$ (m+n=54 $[M+H]^+$): 4230.7; found: 4230.8.

2,6-Bis(1'-methyl-benzimidazolyl)-4-((4-aminophenyl)ethynyl)pyridine 3. Bis(triphenylphosphine)palladium(II) chloride (125 mg, 0.18 mmol), copper(I) iodide (34 mg, 0.18 mmol), and 4-ethynylaniline (546 mg, 4.7 mmol) were dissolved in 25 mL of dry diethylamine and the solution was degassed in three freeze-pump-thaw cycles. In a separate flask, 2,6-bis(1'-methyl-benzimidazolyl)-4-bromopyridine (1.45 g, 3.5 mmol) was dissolved in 30 mL THF, degassed by three freeze-pump-thaw cycles. The two solutions were combined and the resulting mixture was left stirring for 1.5 h at 45 °C before it was poured into 500 mL of deionized water. The precipitate was filtered off, washed with water, and dissolved in DCM/MeOH 50:50 (v/v). After addition of SiliaMetS® TAAcONa metal scavenger the mixture was stirred overnight, the Silicycle was removed by filtration, the solvent was removed *in vacuo*, and recrystallization from DCM yielded **3** (1.14 g, 70 %) as brown solid.

^1H NMR (400 MHz, DMSO-*d6*): δ = 8.35 (s, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H); 7.38 (m, 4H), 7.32 (m, 2H), 6.62 (d, *J* = 8.7 Hz, 2H); 5.82 (s, 2H), 4.27 (s, 6H). ^{13}C NMR (101 MHz, DMSO-*d6*): δ = 150.8, 149.7, 149.2, 142.1, 137.1, 133.6, 133.5, 125.2, 123.4, 122.6, 119.5, 113.6, 110.9, 106.3, 98.4, 84.3, 32.6. IR (ATR) ν (cm^{-1}): 3461, 3325, 3219, 3039, 2935, 2251, 2199, 1635, 1607, 1590, 1543, 1516, 1474, 1455, 1442, 1406, 1385, 1353, 1328, 1300, 1286, 1240, 1174, 1152, 1131, 1112, 1080, 1005, 992, 929, 905, 886, 825, 765, 738, 700, 594, 547. MS (ESI): calcd. for $C_{29}H_{22}N_6$ $[M+H]^+$: 455.19798; found:455.19631.

Telechelic bis(methyl 3-(4-hydroxyphenyl)propanoate)-functionalized poly (ethylene-*co*-butylene) 4. Telechelic bis(*p*-toluenesulfonyl ester)-functionalized poly(ethylene-*co*-butylene)[2] (2 g, 0.6 mmol), methyl 3-(4-hydroxyphenyl)propanoate (0.486 g, 2.6 mmol), tetrabutylammonium iodide (203 mg, 0.5 mmol), and potassium carbonate (0.378 g, 2.7 mmol) were mixed in a 250 mL round-bottomed flask. Toluene (30 mL) was added and the reaction mixture was stirred at 100 °C for 24 h. The reaction was cooled to room temperature and filtered. Toluene was removed under reduced pressure and the brownish crude product was precipitated twice in methanol (150 mL) from a concentrated THF solution. The precipitate was dissolved in hexane (100 mL), washed with saturated NaCl solution (100 mL), dried over $MgSO_4$, and the solvent was removed *in vacuo* to afford **4** (1.32 g, 70%) as a yellowish viscous liquid.

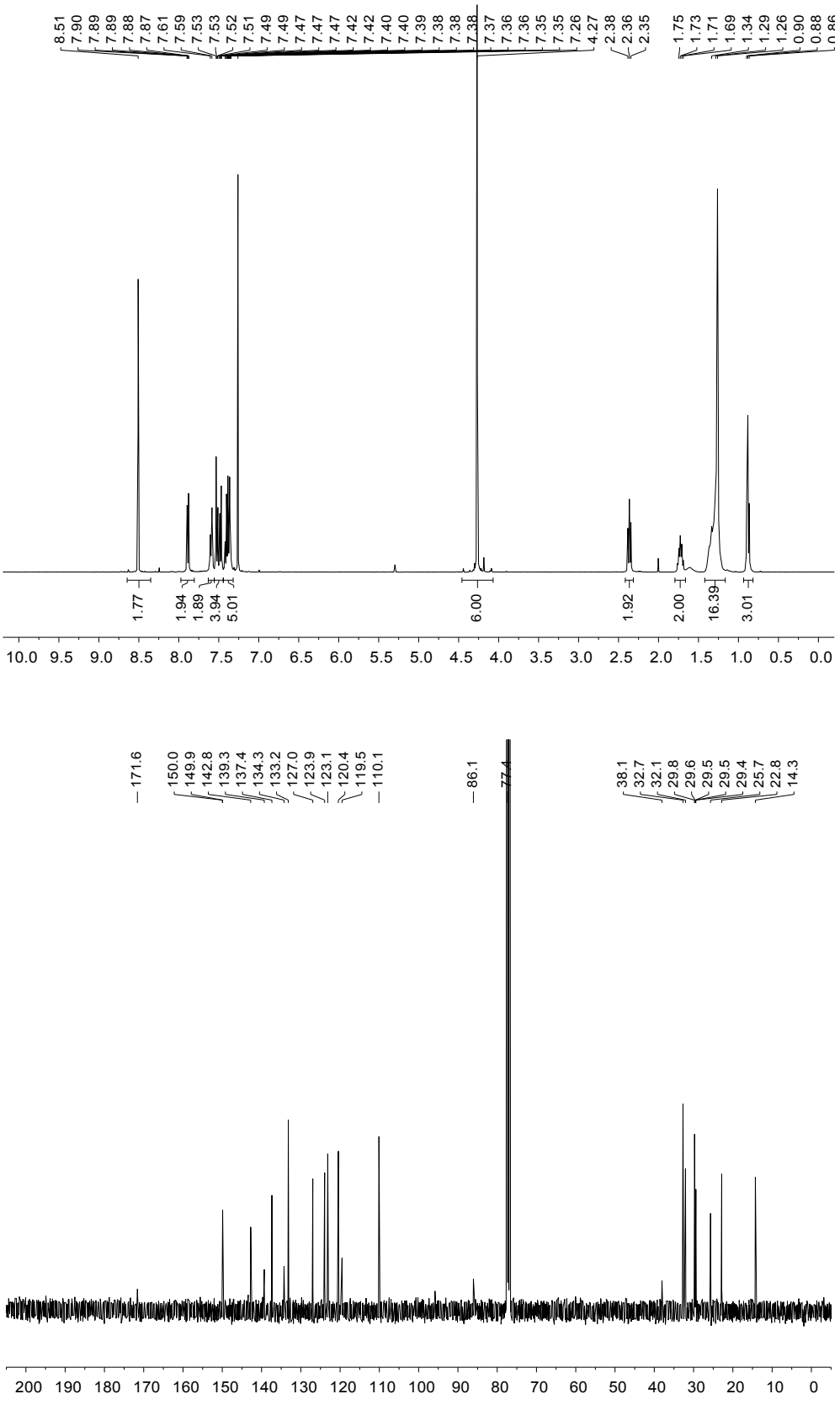
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (d, J = 8.6 Hz, 4H), 6.81 (d, J = 8.4 Hz, 4H), 3.93 (m, 4H), 3.66 (s, 6H), 2.88 (t, J = 7.9 Hz, 4H), 2.59 (t, J = 7.9 Hz, 4H), 2.25-0.92 (m, CH_2 backbone, 0.91-0.63 (m, CH_3 backbone). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.6, 157.8, 132.5, 129.3, 114.7, 66.5, 51.7, 39.4–38.0, 36.4–36.1, 34.1–33.3, 31.0–29.7, 27.0–25.8, 11.1–10.2, 1.2. IR (ATR) ν (cm^{-1}): 2960, 2920, 2852, 1746, 1614, 1583, 1513, 1461, 1379, 1297, 1244, 1174, 1108, 1031, 826, 804, 769, 721. MS (MALDI): calcd. for $C_{236}H_{454}O_6$ (m+n=54 $[M+Na]^+$): 3408.5 found 3408.7.

Telechelic bis(3-(4-hydroxyphenyl)propanoic acid)-functionalized poly(ethylene-*co*-butylene) 5. Poly (ethylene-*co*butylene) **4** (1.85 g, 0.59 mmol) and NaOH (208 mg, 5.2 mmol) were dissolved in a mixture of THF (110 mL) and water (11 mL). The reaction was heated under reflux for 5 h and then cooled to room temperature. HCl (32%) was added dropwise until a pH of 2 was reached. THF was removed *in vacuo* and the residue was dissolved in hexane (100 mL), washed three times with saturated NaCl solution (100 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* to afford **5** as a yellowish viscous liquid (0.86 g, 45% yield).

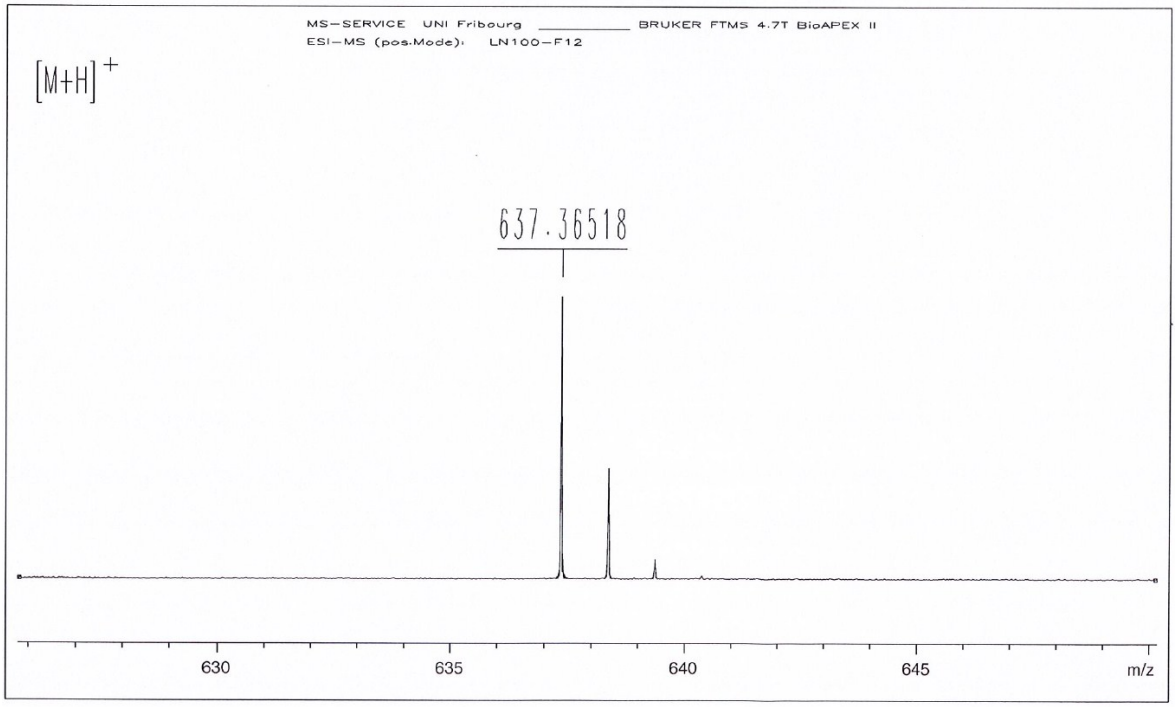
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.4 Hz, 4H), 6.82 (d, J = 8.6 Hz, 4H), 3.95 (m, 4H), 2.90 (t, J = 7.8 Hz, 4H), 2.65 (t, J = 7.7 Hz, 4H), 2.25-0.92 (m, CH_2 backbone, 0.91-0.63 (m, CH_3 backbone). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.9, 132.1, 129.3, 114.7, 68.2, 39.4–38.0, 36.4–36.1, 34.1–33.3, 31.0–29.7, 27.0–25.8, 11.1–10.2, 1.2. IR (ATR) ν (cm^{-1}): 2960, 2920, 2852, 1711, 1614, 1512, 1462, 1379, 1299, 1245, 1177, 1156, 1108, 1030, 935, 860, 826, 768, 721. MS (MALDI): calcd. for $C_{234}H_{449}O_6$ (m+n=54 $[M+K]^+$): 3397.5 found 3397.1.

3. NMR and MS Spectra Appendix

^{1}H and ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **1**.



ESI-MS of **1**.


MS—SERVICE UNI Fribourg BRUKER FTMS 4.7T BioAPEX II
ESI—MS (pos.Mode): LN100—F12
[M+H]+
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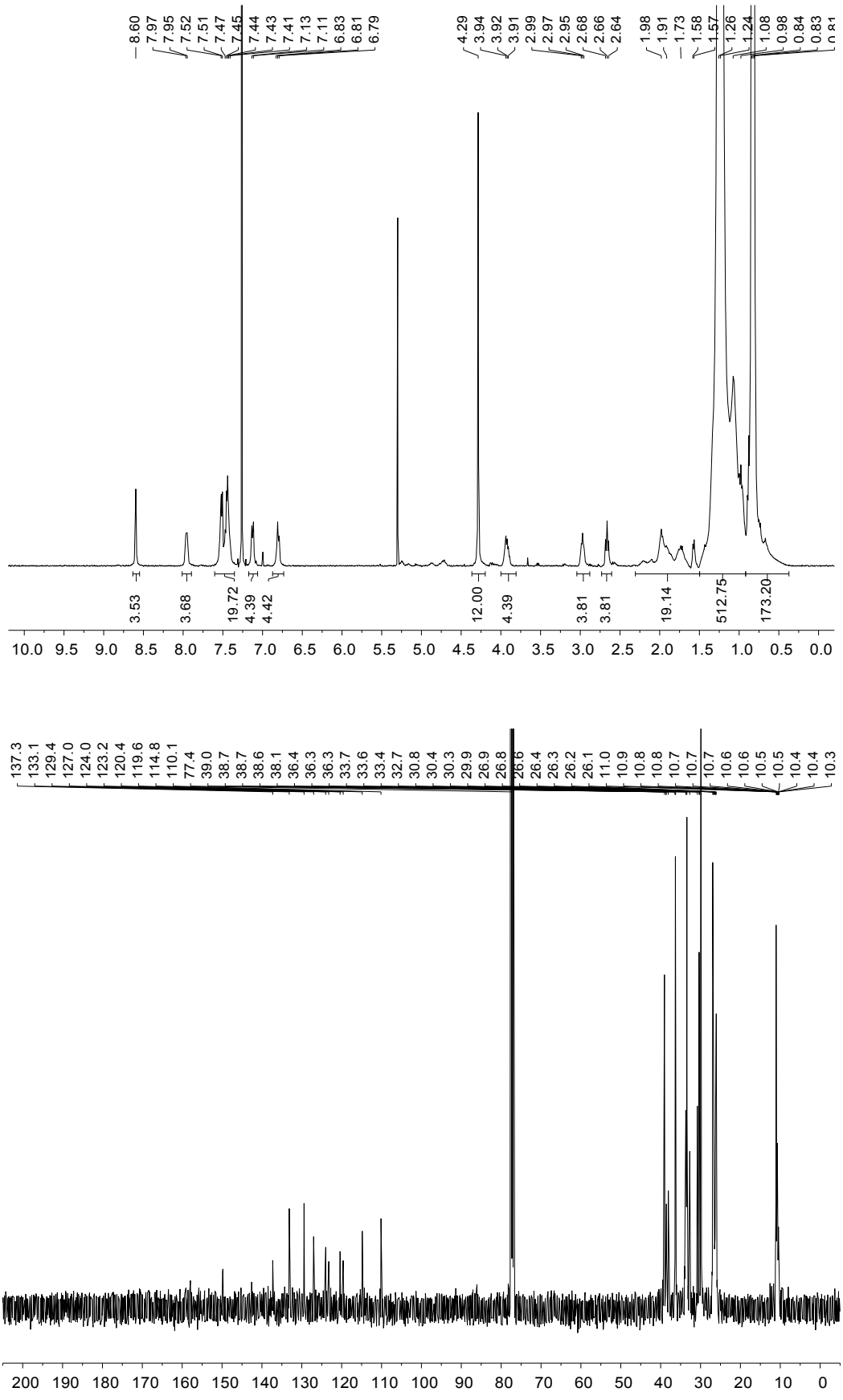
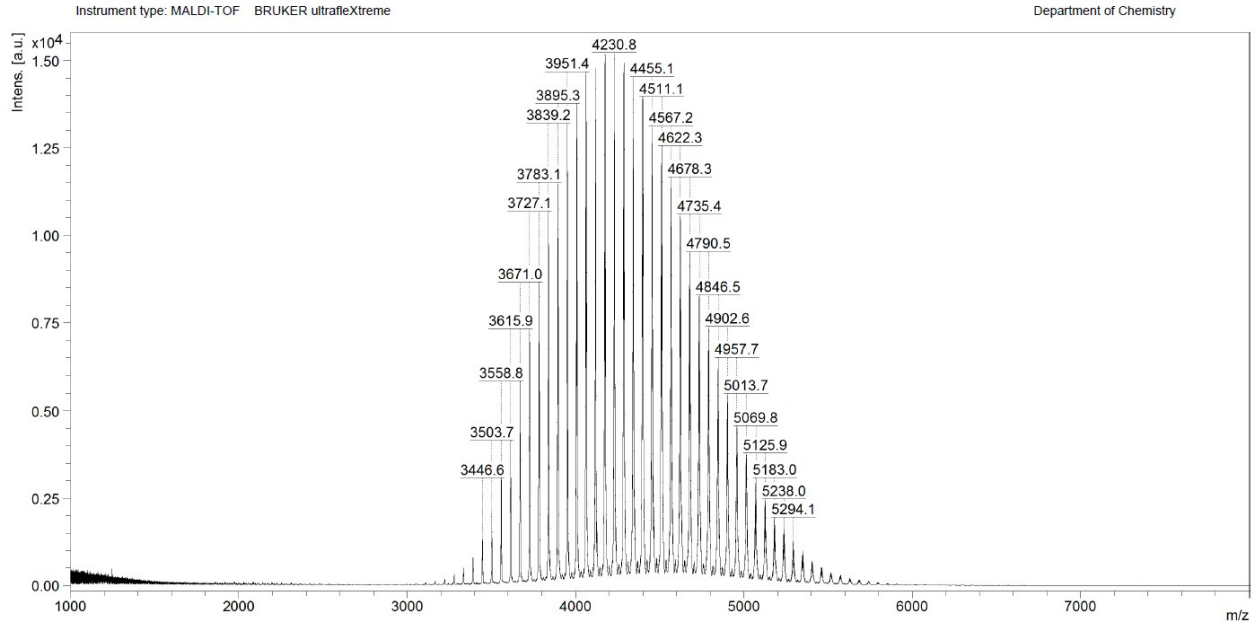
630
635
640
645
m/z

^{1}H and ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **2**.



MALDI of **2**.


Instrument type: MALDI-TOF BRUKER ultrafleXtreme
Department of Chemistry
Intens. [a.u.]
x10^4
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1.00
0.75
0.50
0.25
0.00
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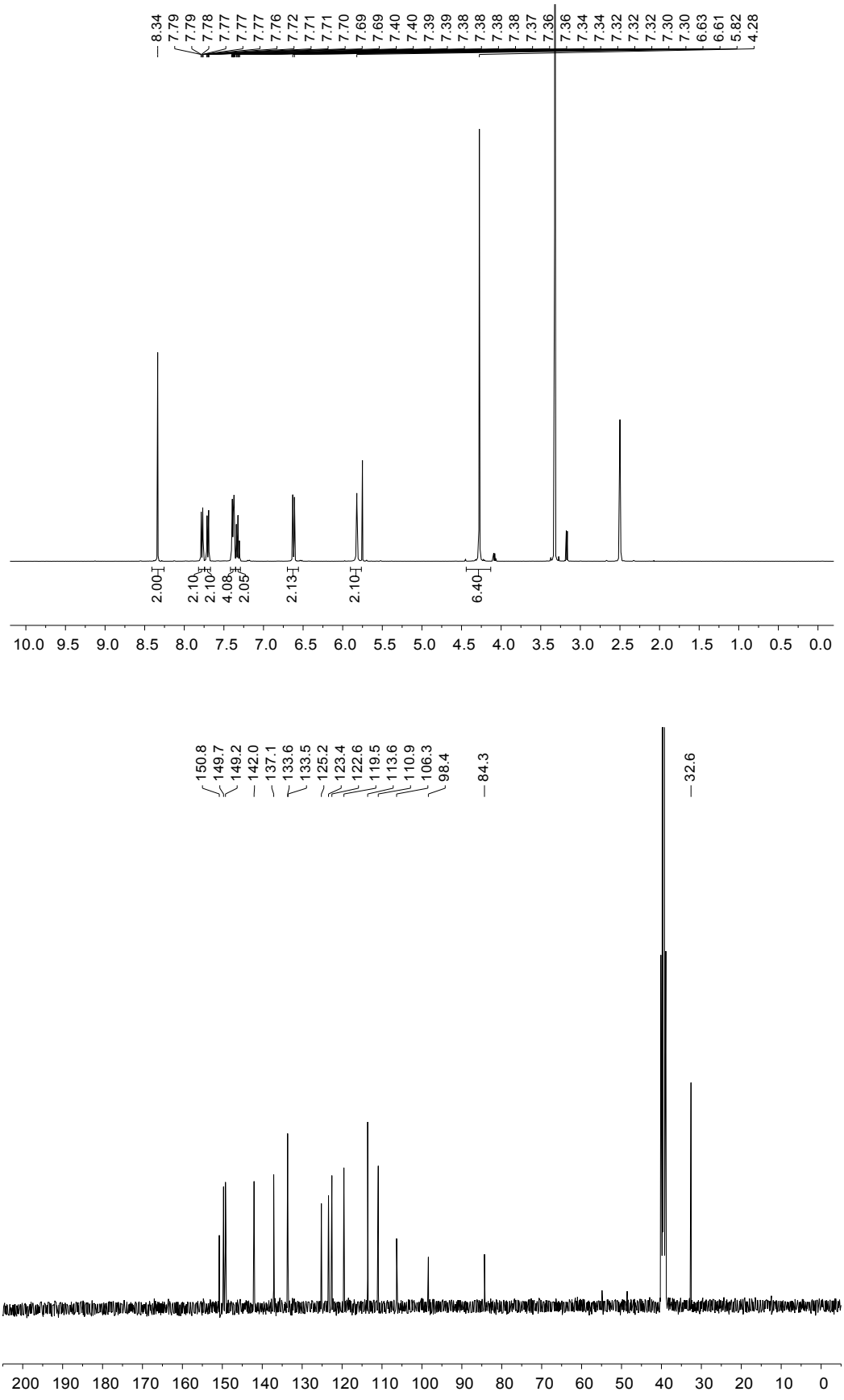
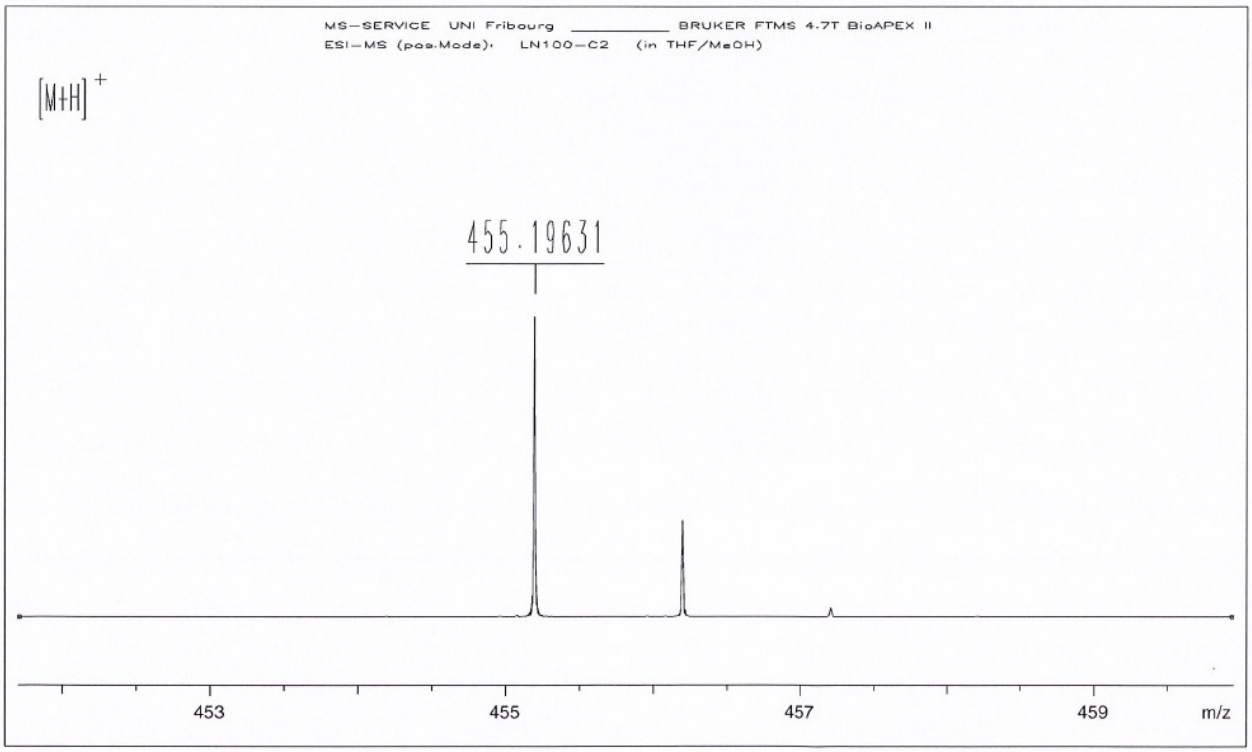
3951.4
4455.1
4511.1
3895.3
3839.2
4567.2
4622.3
3783.1
4678.3
3727.1
4735.4
4790.5
3671.0
4846.5
3615.9
4902.6
4957.7
3558.8
5013.7
5069.8
3503.7
5125.9
3446.6
5183.0
5238.0
5294.1
1000
2000
3000
4000
5000
6000
7000
m/z

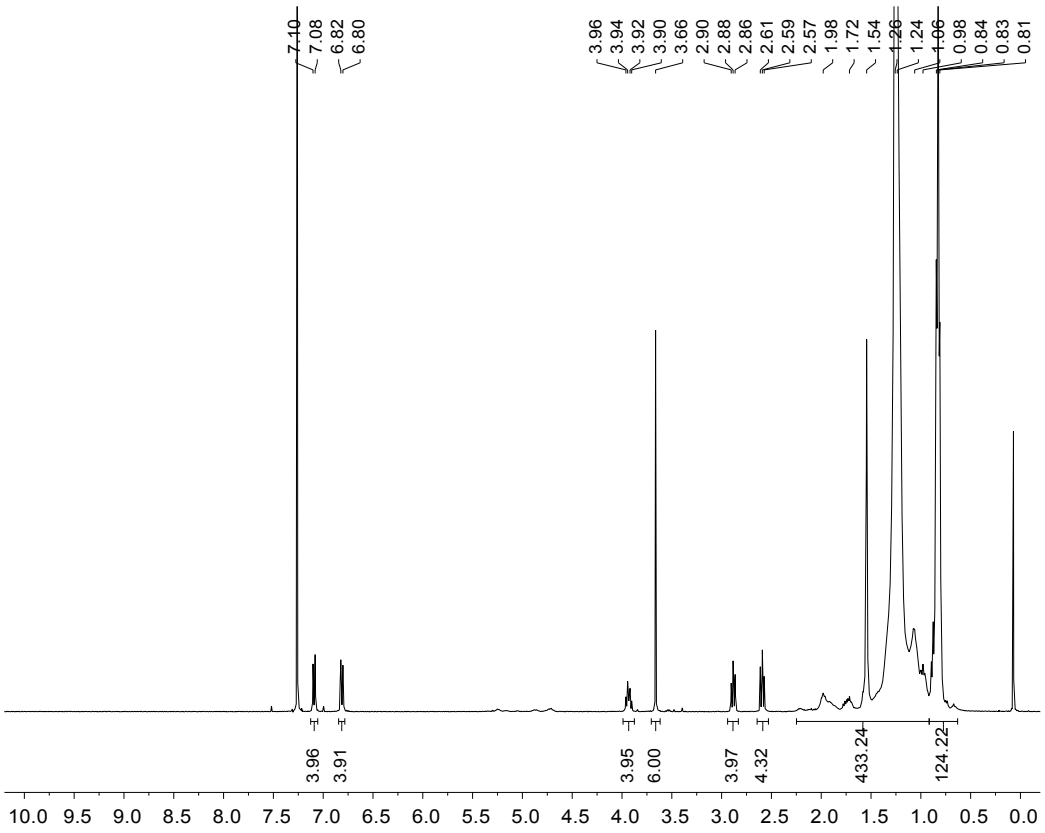
^{1}H and ^{13}C NMR spectrum (DMSO-d_6, 400 MHz) of **3.**

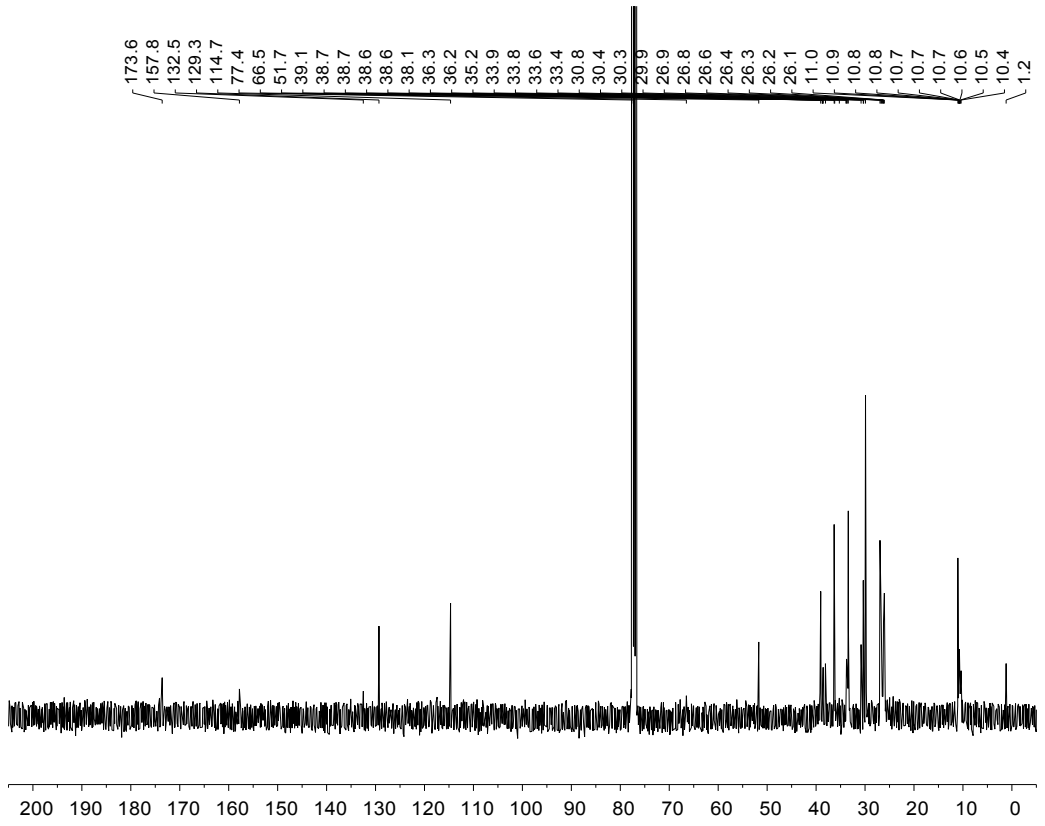


ESI-MS of **3**.

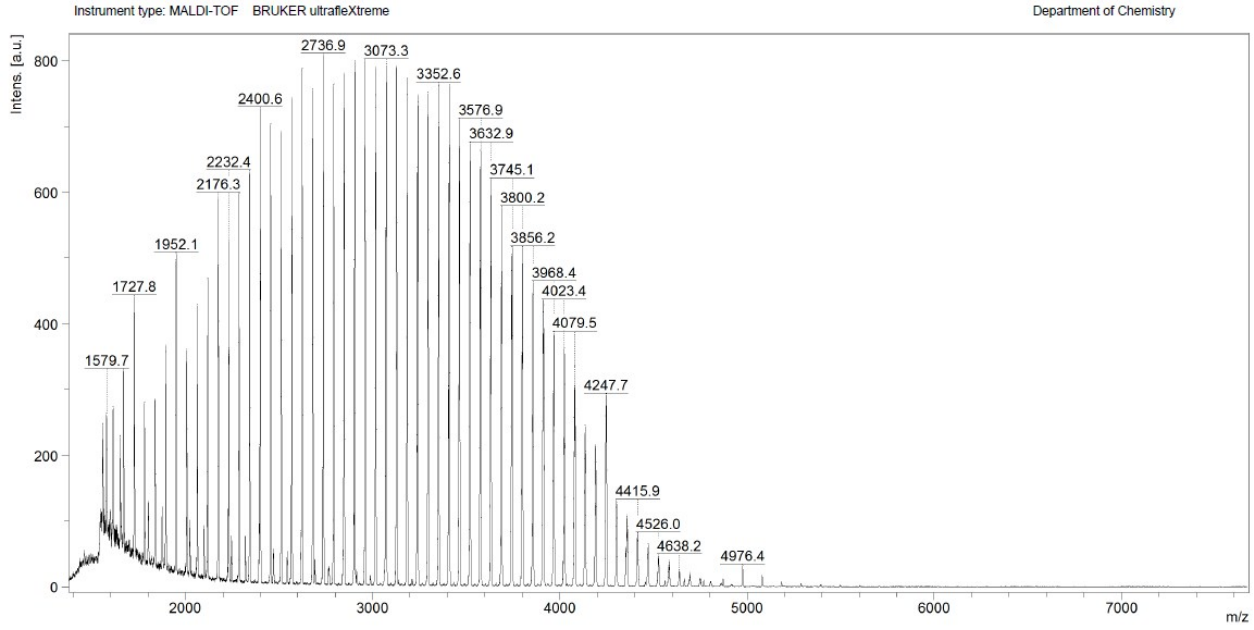

MS—SERVICE UNI Fribourg _____ BRUKER FTMS 4.7T BioAPEX II
ESI—MS (pos.Mode), LN100—C2 (in THF/MeOH)
[M+H]+
455.19631
453
455
457
459
m/z

^{1}H and ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **4.**





MALDI of **4**.


Instrument type: MALDI-TOF BRUKER ultrafleXtreme
Department of Chemistry
Intens. [a.u.]
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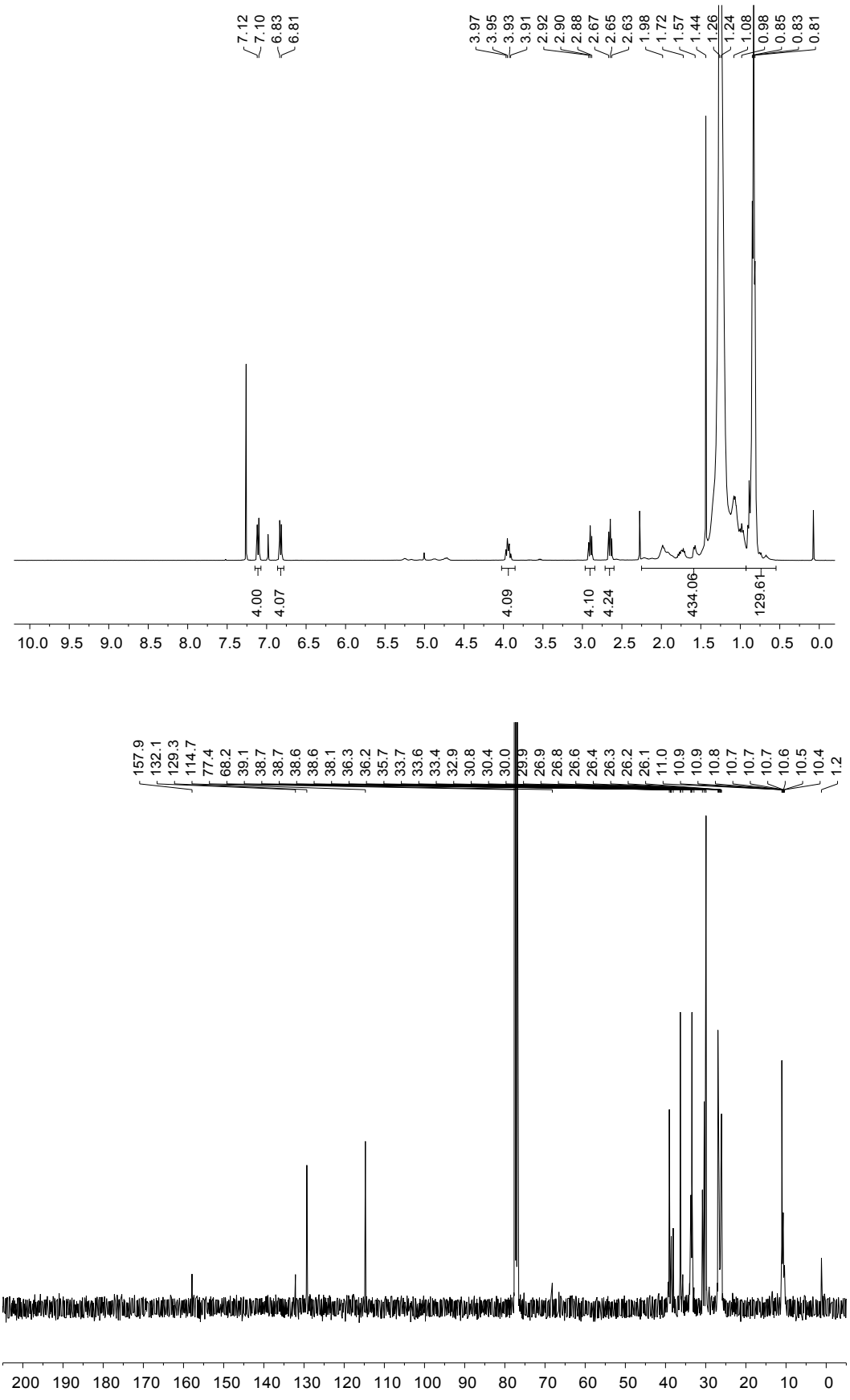
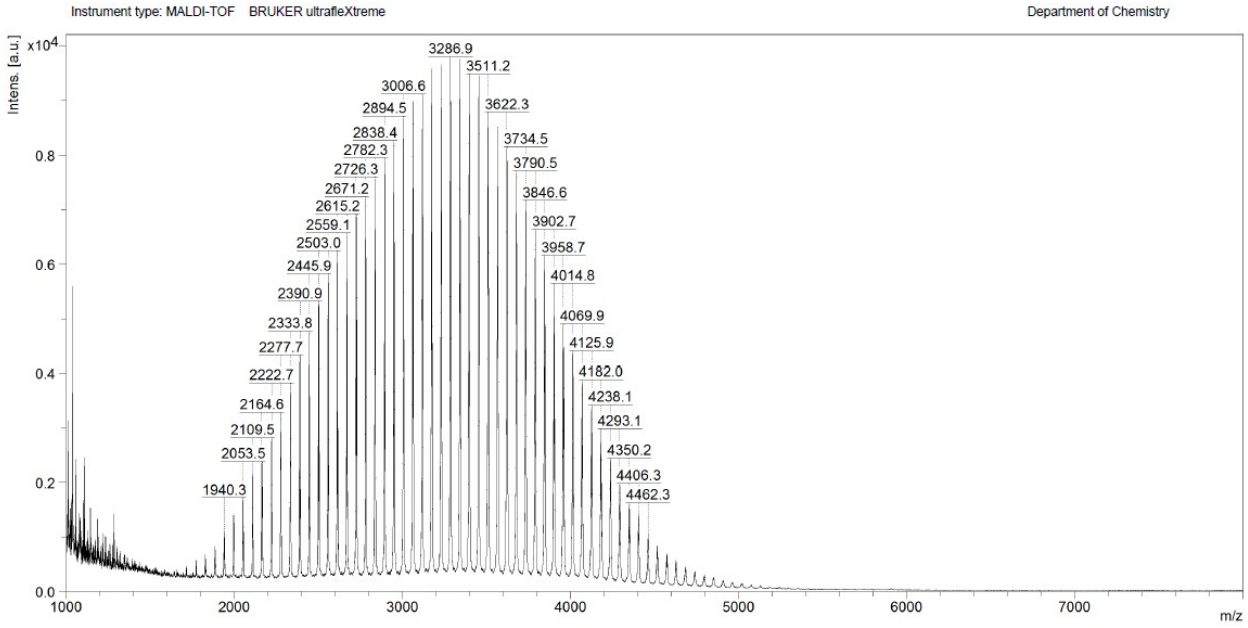
600
400
200
0
2736.9
3073.3
3352.6
2400.6
3576.9
3632.9
2232.4
3745.1
2176.3
3800.2
1952.1
3856.2
3968.4
1727.8
4023.4
4079.5
1579.7
4247.7
4415.9
4526.0
4638.2
4976.4
2000
3000
4000
5000
6000
7000
m/z

^{1}H and ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **5.**



MALDI of **5**.



4. References

1. P. K. Iyer, J. B. Beck, C. Weder and S. J. Rowan, *Chem. Commun.*, 2005, 319-321.
2. L. Montero de Espinosa, S. Balog and C. Weder, *ACS Macro Letters*, 2014, **3**, 540-543.
3. S. J. Rowan and J. B. Beck, *Faraday Discuss.*, 2005, **128**, 43-53.
4. J. S. Moore and S. I. Stupp, *Macromolecules*, 1990, **23**, 65-70.