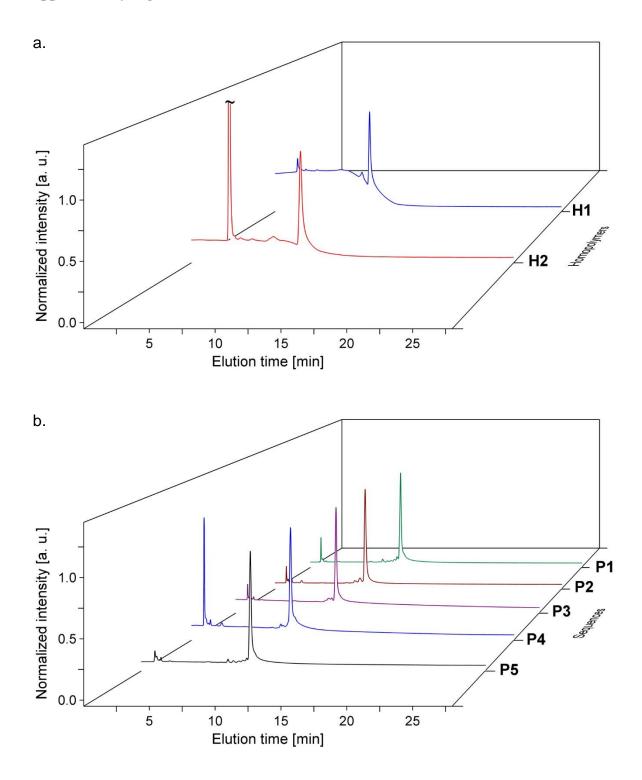
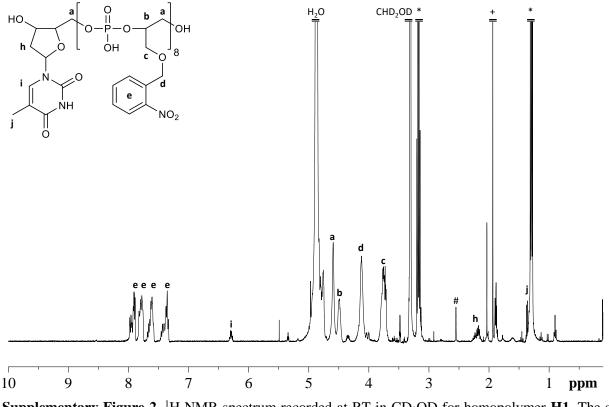
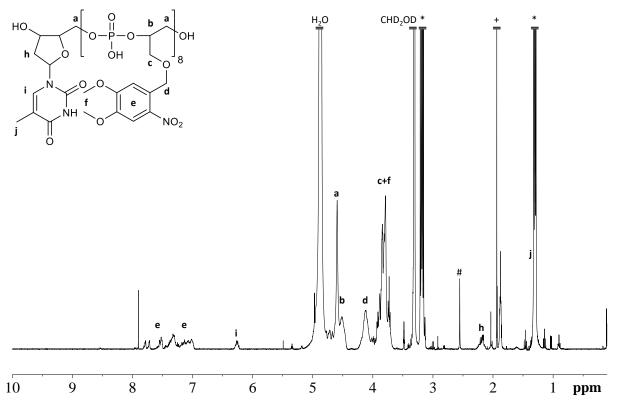
Supplementary Figures.



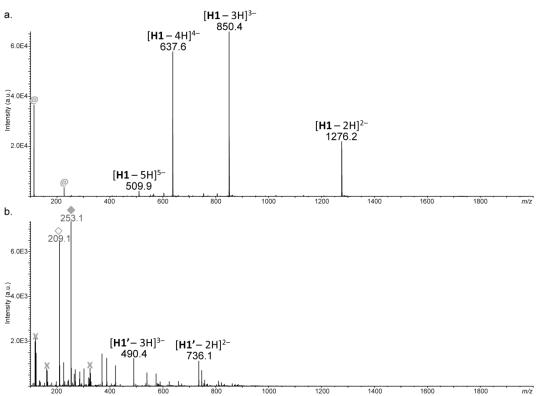
Supplementary Figure 1. IE-HPLC traces measured for (a) homopolymers H1-H2 and (b) copolymers P1-P5. The chromatograms are recorded at $\lambda = 260$ nm. Experimental conditions: phase A: 10 % MeCN 20 % 2M NH₃ in water, phase B: 2.5 M NaCl in water; gradient: 0-3 min 5 % B, 3-23 min 5 % B-30 % B, 23-28 min 30 % B, 28-35 min 30% \rightarrow 5 % B; flow rate: 1 mL·min⁻¹.



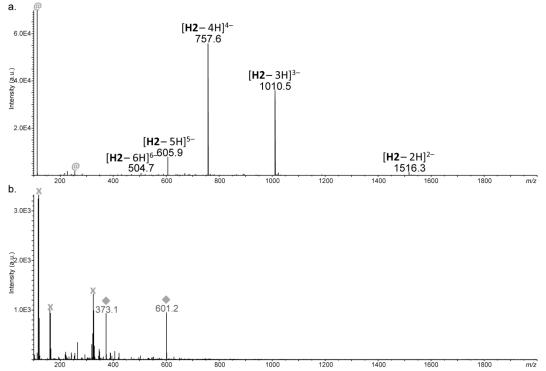
Supplementary Figure 2. ¹H NMR spectrum recorded at RT in CD₃OD for homopolymer **H1**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



Supplementary Figure 3. ¹H NMR spectrum recorded at RT in CD₃OD for homopolymer **H2**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



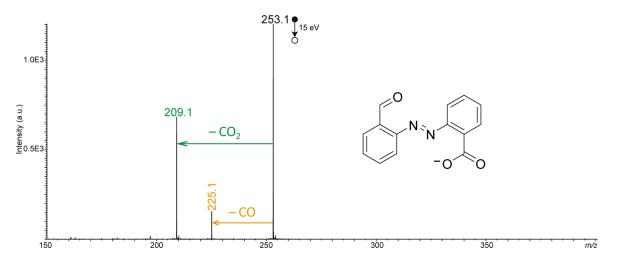
Supplementary Figure 4. ESI HRMS spectra recorded for (**a**) homopolymer **H1** before irradiation and (**b**) the resulting polymer **H1**' after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (*@*), of trichloroacetic acid (x) or photo-deprotection by-products (diamond).



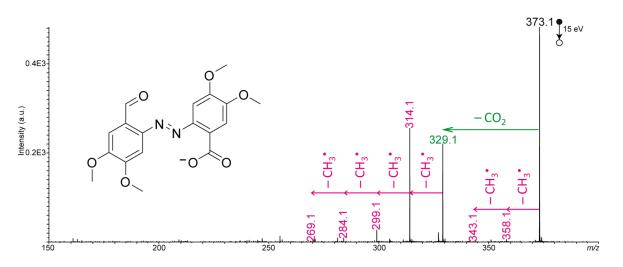
Supplementary Figure 5. ESI HRMS spectra recorded for (**a**) homopolymer **H2** before irradiation and (**b**) the resulting polymer **H2**' after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@), of trichloroacetic acid (x) or photo-deprotection by-products (diamond).

Supplementary discussion.

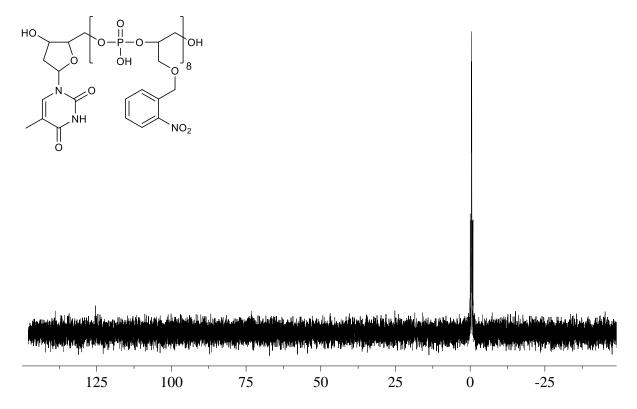
Interpretation of the photo-deprotection by-products detected by ESI HRMS. The peaks indicated by filled grey diamonds in ESI HRMS spectra of photo-exposed samples correspond to photo-deprotection by-products. As indicated in Fig. 1 of the main manuscript, nitrosobenzaldehyde intermediates are usually formed upon *o*-nitrobenzyl and *o*-nitroveratryl photocleavage.¹ However, it has been reported that these intermediates can further photo-dimerize into azobenzene diacid derivatives.^{2,3} In the present photo-deprotection and analytical conditions, the formation of dimers containing carboxylic acid and aldehyde groups was observed,⁴ as evidenced below in Supplementary Figures 6 and 7.



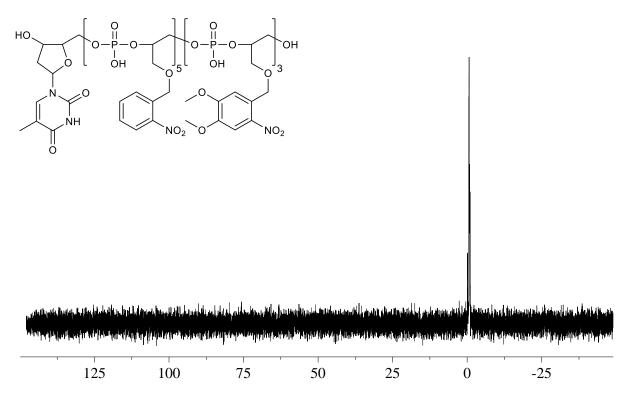
Supplementary Figure 6. MS/MS spectrum recorded for the photo-deprotection by-product observed at m/z 253.1 (C₁₄H₉N₂O₃⁻, m/z_{th} 253.0619, m/z_{exp} 253.0614) after photo-irradiation of homopolymer H1, showing competitive losses of CO and CO₂ consistent with the proposed structure shown in inset. Of note, the m/z 209.1 ion labelled with an empty diamond in Supplementary Figure 4 indicates that the decarboxylation reaction also occurred during ion transfer through the interface of the mass spectrometer.



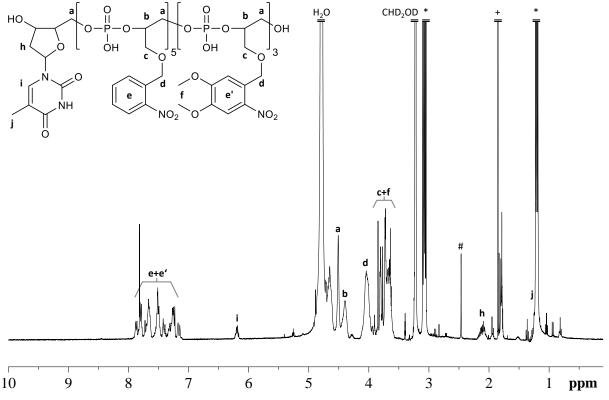
Supplementary Figure 7. MS/MS spectrum recorded for the photo-deprotection by-product observed at m/z 373.1 (C₁₈H₁₇N₂O₇⁻, m/z_{th} 373.1041, m/z_{exp} 373.1022) after photo-irradiation of homopolymer **H2**, showing that the decarboxylation product (m/z 329.1) successively eliminates four methyl radicals, consistent with the four methoxy groups of the precursor ion (see inset structure).



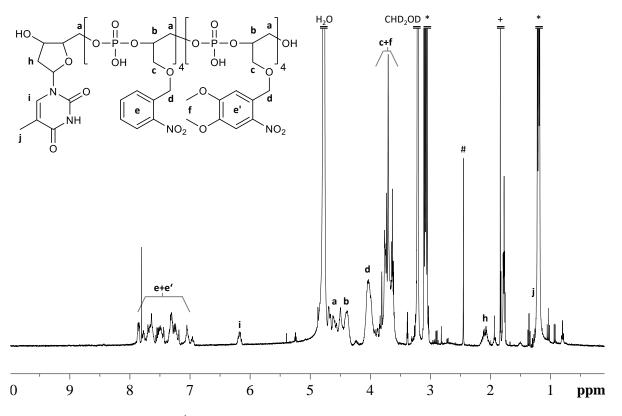
Supplementary Figure 8.³¹P NMR spectrum recorded at RT in CD₃OD for homopolymer **H1**. Comparable spectra were obtained for all other homopolymers studied in this work.



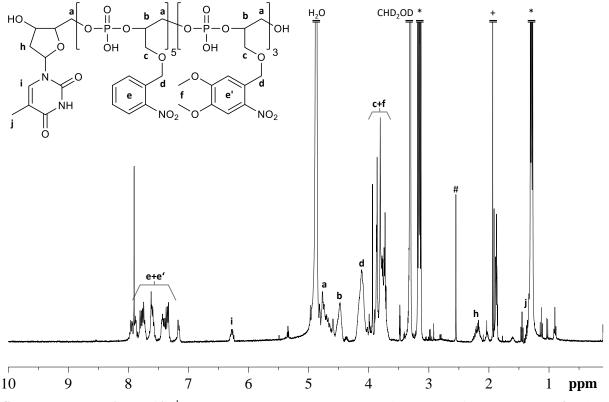
Supplementary Figure 9. ³¹P NMR spectrum recorded at RT in CD₃OD for copolymer **P1**. Comparable spectra were obtained for all other copolymers studied in this work.



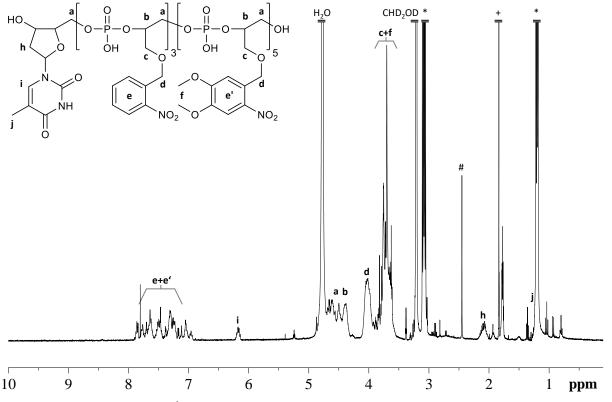
Supplementary Figure 10. ¹H NMR spectrum recorded at RT in CD₃OD for copolymer **P1**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



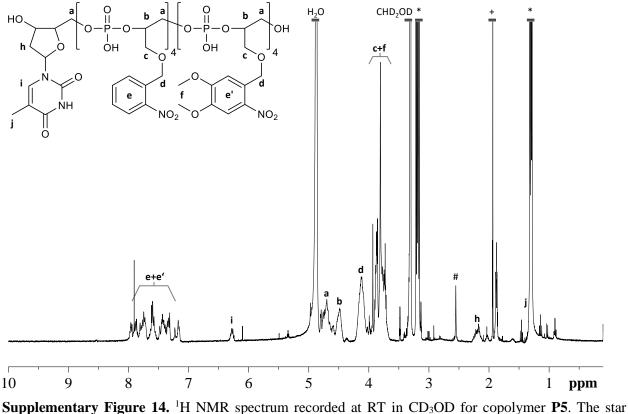
Supplementary Figure 11. ¹H NMR spectrum recorded at RT in CD_3OD for copolymer **P2**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



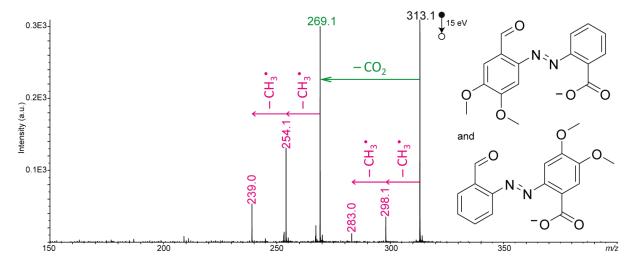
Supplementary Figure 12. ¹H NMR spectrum recorded at RT in CD₃OD for copolymer **P3**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



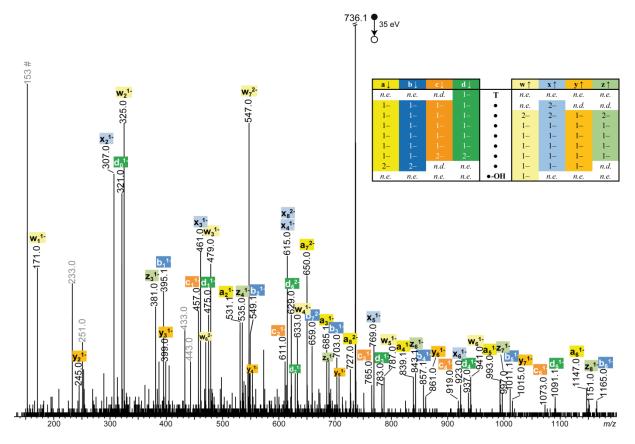
Supplementary Figure 13. ¹H NMR spectrum recorded at RT in CD₃OD for copolymer **P4**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



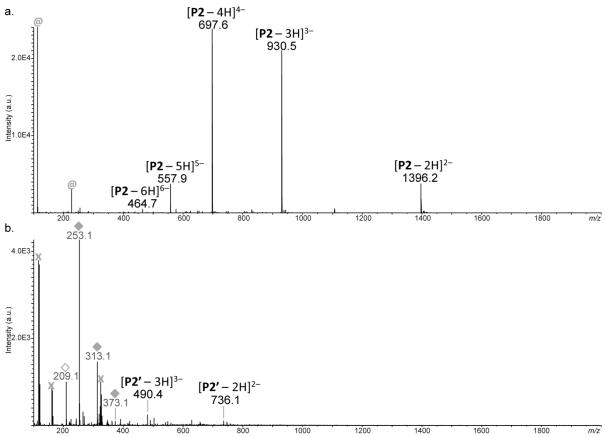
Supplementary Figure 14. ¹H NMR spectrum recorded at RT in CD₃OD for copolymer P5. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



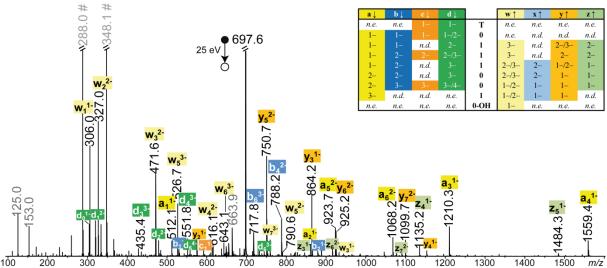
Supplementary Figure 15. MS/MS spectrum recorded for the photo-deprotection by-product observed at m/z 313.1 (C₁₆H₁₃N₂O₅⁻, m/z_{th} 313.0830, m/z_{exp} 313.0835) after photo-irradiation of copolymer **P1**, showing that the decarboxylation product (m/z 269.1) successively eliminates two methyl radicals, consistent with the two methoxy groups in the isomeric precursors (see inset structure).



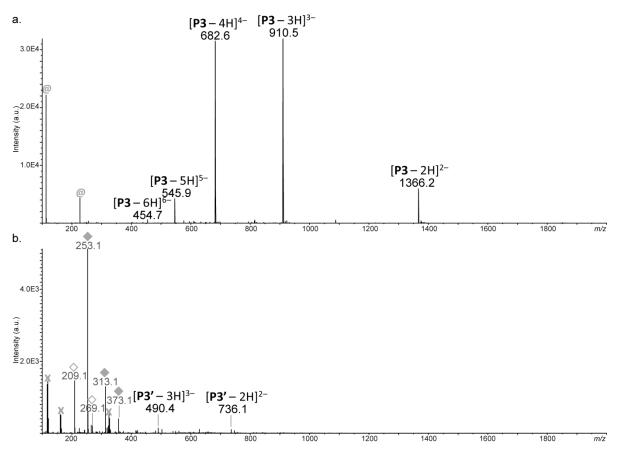
Supplementary Figure 16. MS/MS spectrum recorded for copolymer **P1'** after photo-exposure, using a 35 eV collision energy (laboratory frame) to activate the doubly deprotonated precursor at m/z 736.1. Peaks annotated in grey correspond to secondary fragments, including the deprotonated unit (m/z 153.0) designated by #. The inset table shows that most expected members of the eight fragment series are detected and evidence the monotonic sequence of **P1'**. *n.d.*: not detected. *n.e.*: not expected.



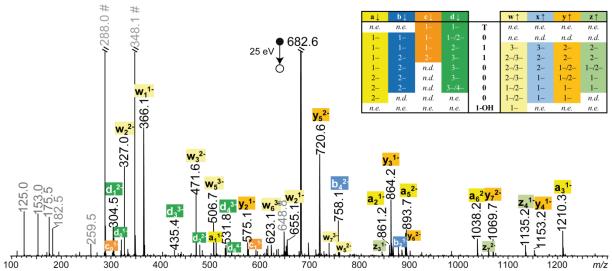
Supplementary Figure 17. ESI HRMS spectra recorded for (**a**) copolymer **P2** before irradiation and (**b**) the resulting polymer **P2'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@), clusters of trichloroacetic acid (x) or photo-deprotection by-products (diamond).



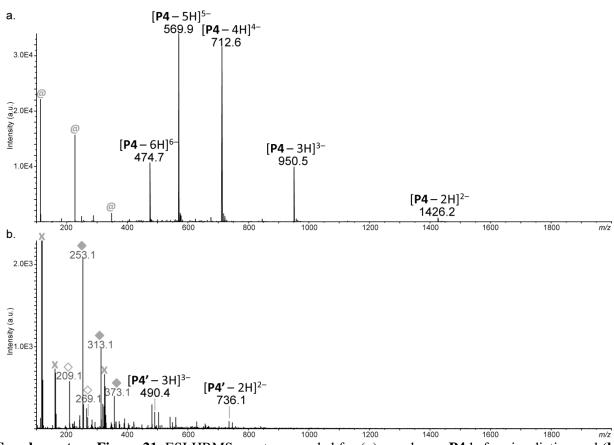
Supplementary Figure 18. MS/MS spectrum recorded for copolymer P2 before irradiation, using a 25 eV collision energy (laboratory frame) to activate the quadruply deprotonated precursor at m/z 697.6. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 288.0 and $[1 - H]^-$ at m/z 348.1, both designated by #. Inset Table: Sequence coverage of P2 (*n.d.*: not detected; *n.e.*: not expected). After photo-exposure, the resulting polymer P2' exhibits the same MS/MS spectrum as P1' in Supplementary Figure 16.



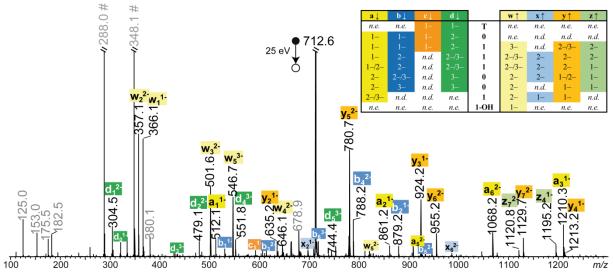
Supplementary Figure 19. ESI HRMS spectra recorded for (**a**) copolymer **P3** before irradiation and (**b**) the resulting polymer **P3'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@), clusters of trichloroacetic acid (x) or photo-deprotection by-products (diamond).



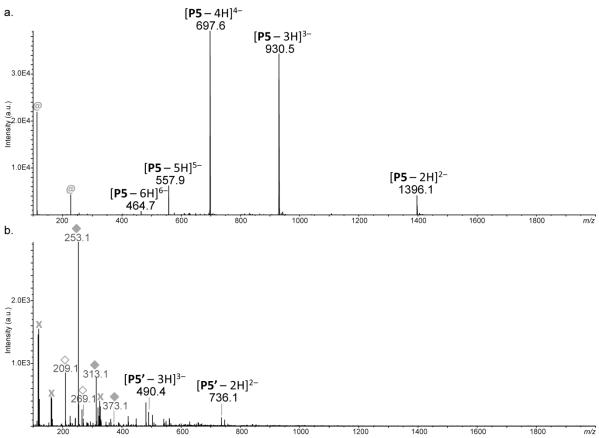
Supplementary Figure 20. MS/MS spectrum recorded for copolymer P3 before irradiation, using a 25 eV collision energy (laboratory frame) to activate the quadruply deprotonated precursor at m/z 682.6. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 288.0 and $[1 - H]^-$ at m/z 348.1, both designated by #. Inset Table: Sequence coverage of P3 (*n.d.*: not detected; *n.e.*: not expected). After photo-exposure, the resulting polymer P3' exhibits the same MS/MS spectrum as P1' in Supplementary Figure 16.



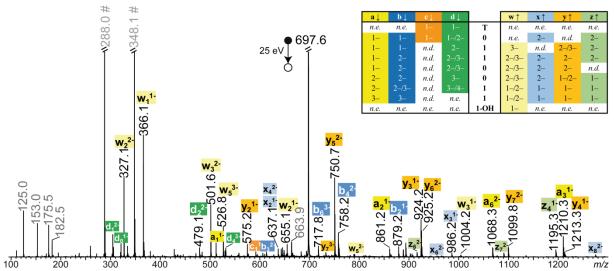
Supplementary Figure 21. ESI HRMS spectra recorded for (**a**) copolymer **P4** before irradiation and (**b**) the resulting polymer **P4'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@), clusters of trichloroacetic acid (x) or photo-deprotection by-products (diamond).



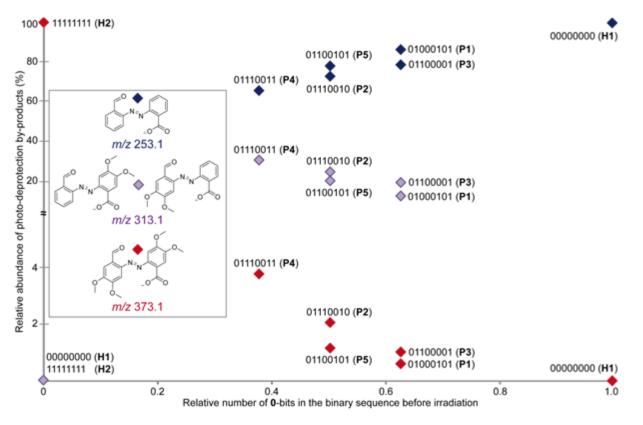
Supplementary Figure 22. MS/MS spectrum recorded for copolymer P4 before irradiation, using a 25 eV collision energy (laboratory frame) to activate the quadruply deprotonated precursor at m/z 712.6. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 288.0 and $[1 - H]^-$ at m/z 348.1, both designated by #. Inset Table: Sequence coverage of P4 (*n.d.*: not detected; *n.e.*: not expected). After photo-exposure, the resulting polymer P4' exhibits the same MS/MS spectrum as P1' in Supplementary Figure 16.



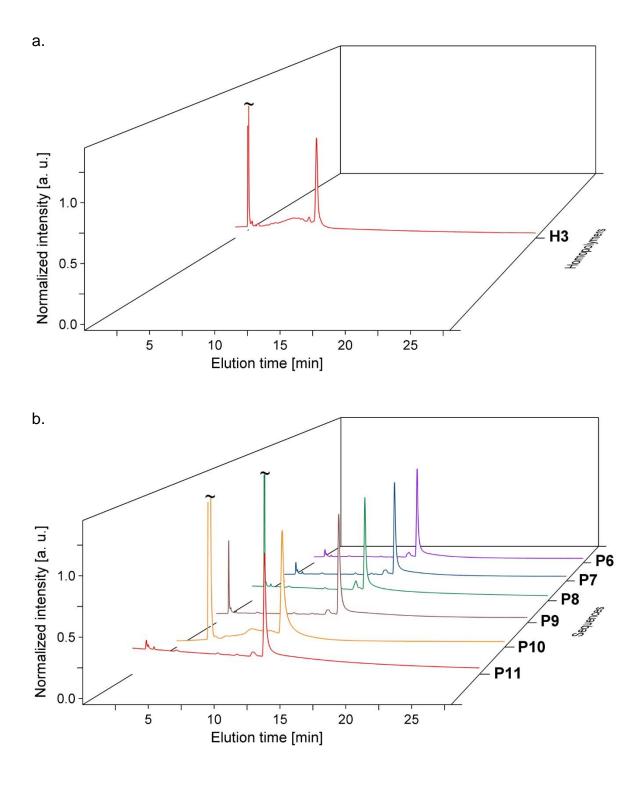
Supplementary Figure 23. ESI HRMS spectra recorded for (**a**) copolymer **P5** before irradiation and (**b**) the resulting polymer **P5'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@), clusters of trichloroacetic acid (x) or photo-deprotection by-products (diamond).



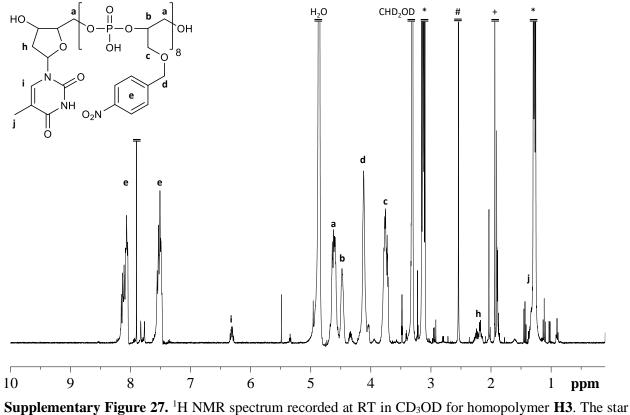
Supplementary Figure 24. MS/MS spectrum recorded for copolymer P5 before irradiation, using a 25 eV collision energy (laboratory frame) to activate the quadruply deprotonated precursor at m/z 697.6. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 288.0 and $[1 - H]^-$ at m/z 348.1, both designated by #. Inset Table: Sequence coverage of P5 (*n.d.*: not detected; *n.e.*: not expected). After photo-exposure, the resulting polymer P5' exhibits the same MS/MS spectrum as P1' in Supplementary Figure 16.



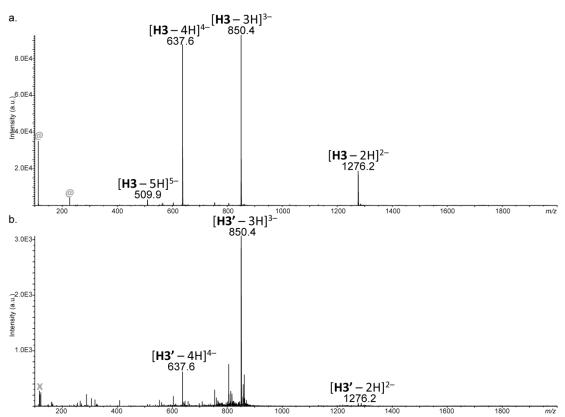
Supplementary Figure 25. Relative abundance of photolysis by-products (structure shown in inset) as a function of 0/1 comonomer composition of the polymer before photo-irradiation. Each data point is annotated by the sequence of the corresponding polymer before irradiation. The relative amount of the homodimer detected at m/z 253.1 increases with the fraction of 0-bits in the original sequence. Similarly, the relative abundance of the homodimer detected at m/z 373.1 increase with the fraction of 1-bits (i.e., decreasing fraction of 0-bits) in the original sequence. Consistent with the decreasing amount of photocleaved veratryl units in the irradiated solution, the relative intensity of the m/z 313.1 signal, assigned to a heterodimer, decreased as the fraction of 0-bits increased in the original sequence.



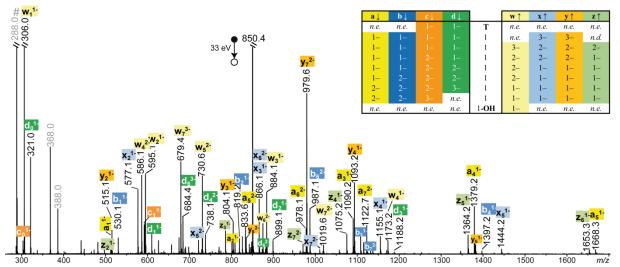
Supplementary Figure 26. HPLC traces measured for (a) homopolymers H3 and (b) copolymers P6-P11. The chromatograms are recorded at $\lambda = 260$ nm. Experimental conditions: phase A: 10 % MeCN 20 % 2M NH₃ in water, phase B: 2.5 M NaCl in water; gradient: 0-3 min 5 % B, 3-23 min 5 % B-30 % B, 23-28 min 30 % B, 28-35 min 30% \rightarrow 5 % B; flow rate: 1 mL·min⁻¹.



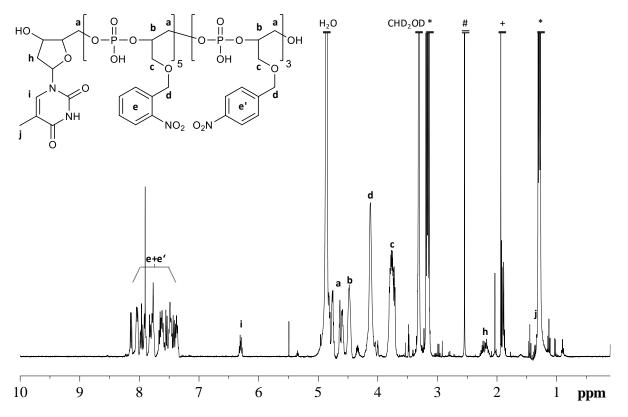
symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



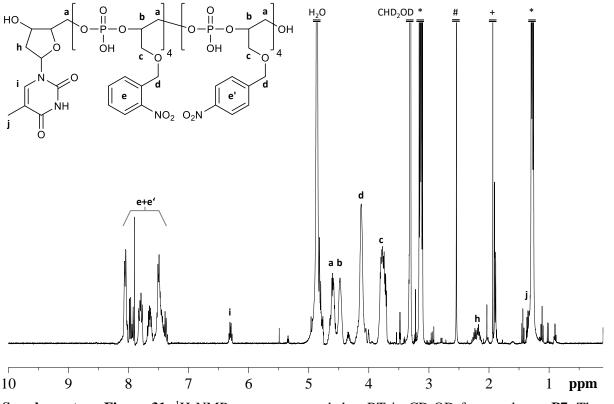
Supplementary Figure 28. ESI HRMS spectra recorded for (**a**) homopolymer **H3** before irradiation and (**b**) the resulting polymer **H3**' after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@) and clusters of trichloroacetic acid (x).



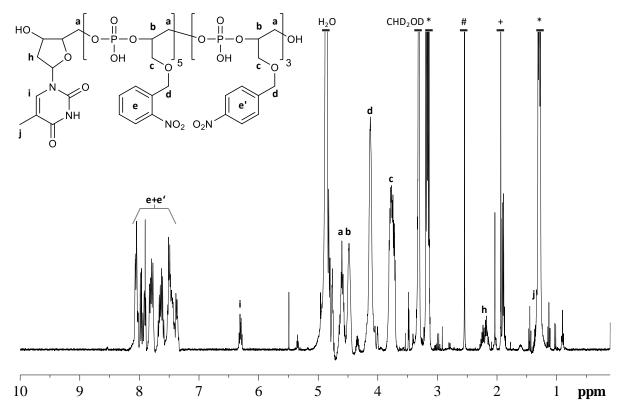
Supplementary Figure 29. MS/MS spectrum recorded for homopolymer H3 before photo-exposure, using a 33 eV collision energy (laboratory frame) to activate the triply deprotonated precursor at m/z 850.4. Peaks annotated in grey correspond to secondary fragments, including the deprotonated unit (m/z 288.0) designated by #. The inset table shows that most expected members of the eight fragment series are detected and evidence the monotonic sequence of H3. *n.d.*: not detected. *n.e.*: not expected.



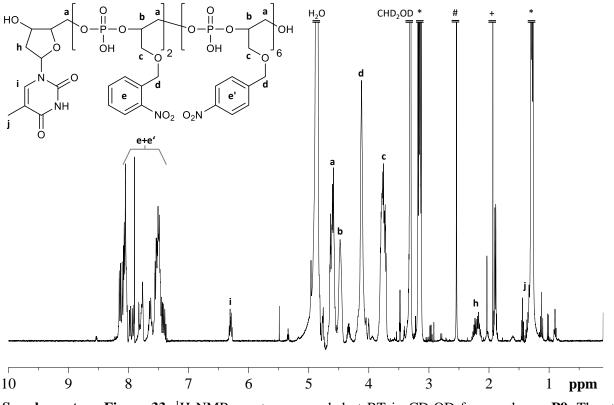
Supplementary Figure 30. ¹H NMR spectrum recorded at RT in CD_3OD for copolymer **P6**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



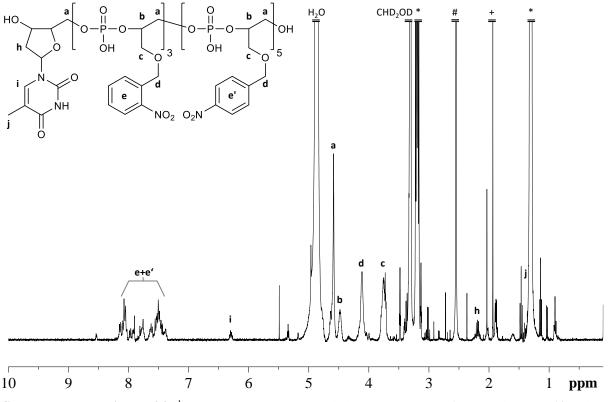
Supplementary Figure 31. ¹H NMR spectrum recorded at RT in CD₃OD for copolymer **P7**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



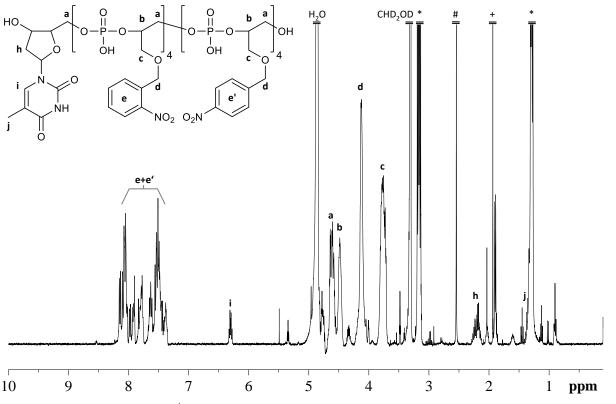
Supplementary Figure 32. ¹H NMR spectrum recorded at RT in CD_3OD for copolymer **P8**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



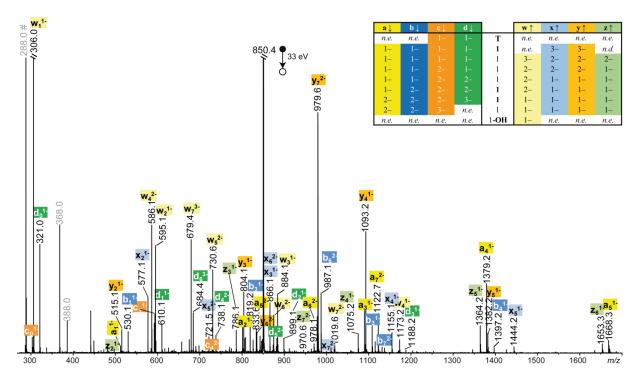
Supplementary Figure 33. ¹H NMR spectrum recorded at RT in CD₃OD for copolymer **P9**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



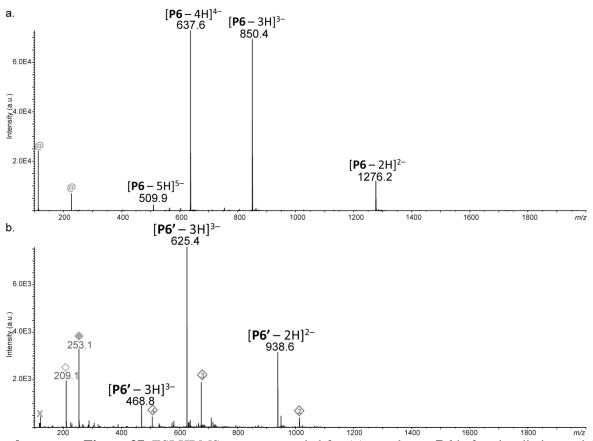
Supplementary Figure 34. ¹H NMR spectrum recorded at RT CD₃OD for copolymer **P10**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



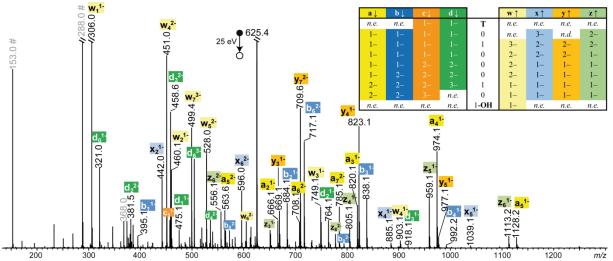
Supplementary Figure 35. ¹H NMR spectrum recorded at RT CD₃OD for copolymer **P11**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



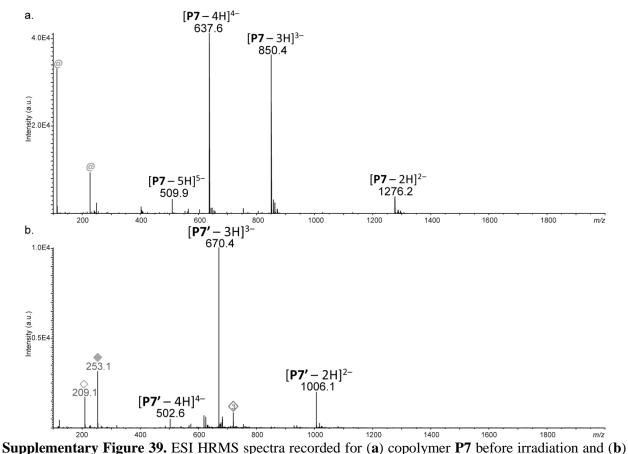
Supplementary Figure 36. MS/MS spectrum recorded for copolymer P10 before irradiation, using a 33 eV collision energy (laboratory frame) to activate the triply deprotonated precursor at m/z 850.4. Peaks annotated in grey correspond to secondary fragments, including deprotonated units (both at m/z 288.0) designated by #. The inset table shows that all (but one) expected members of the eight fragment series are detected and evidence the monotonic sequence of P10 (*n.d.*: not detected; *n.e.*: not expected).



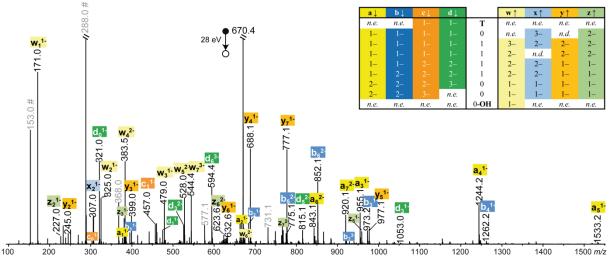
Supplementary Figure 37. ESI HRMS spectra recorded for (**a**) copolymer **P6** before irradiation and (**b**) the resulting polymer **P6'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@), clusters of trichloroacetic acid (x) or photo-deprotection by-products (diamonds).



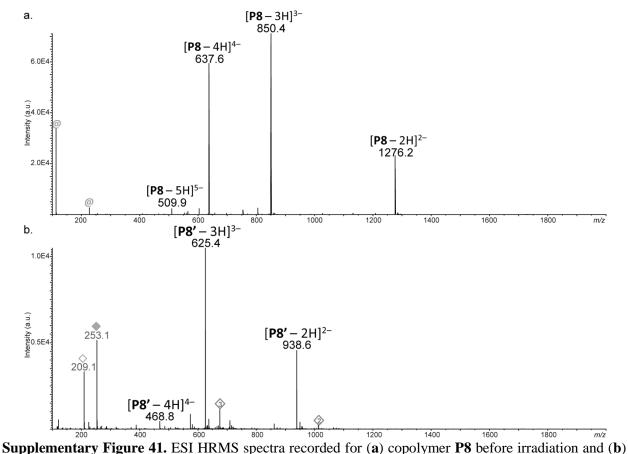
Supplementary Figure 38. MS/MS spectrum recorded for copolymer P6' obtained after irradiation of P6, using a 25 eV collision energy (laboratory frame) to activate the triply deprotonated precursor at m/z 625.4. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 153.0 and $[1 - H]^-$ at m/z 288.0, both designated by #. Inset Table: Sequence coverage of P6' (*n.d.*: not detected; *n.e.*: not expected). Before photo-exposure, copolymer P6 exhibits the same MS/MS spectrum as P10 in Supplementary Figure 35.



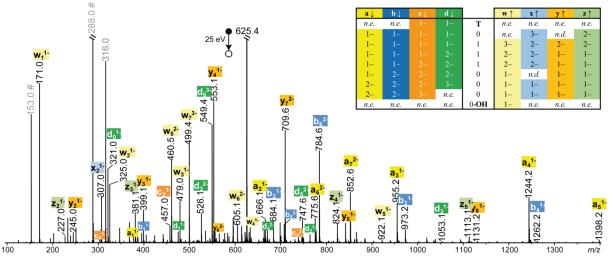
the resulting polymer **P7'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@) or photo-deprotection by-products (diamonds).



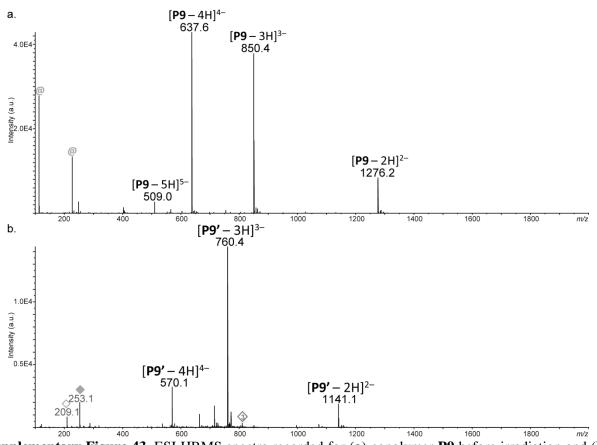
Supplementary Figure 40. MS/MS spectra recorded for copolymer P7' obtained after irradiation of P7, using a 28 eV collision energy (laboratory frame) to activate the triply deprotonated precursor at m/z 670.4. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 153.0 and $[1 - H]^-$ at m/z 288.0, both designated by #. Inset Table: Sequence coverage of P7' (*n.d.*: not detected; *n.e.*: not expected). Before photo-exposure, copolymer P7 exhibits the same MS/MS spectrum as P10 in Supplementary Figure 35.



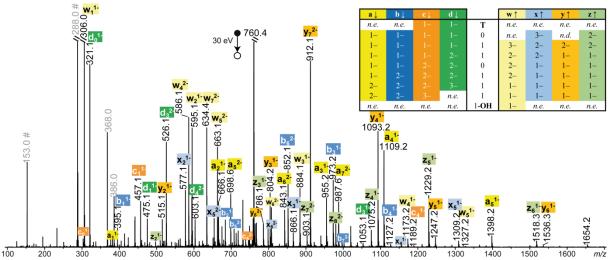
the resulting polymer **P8'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@) or photo-deprotection by-products (diamonds).



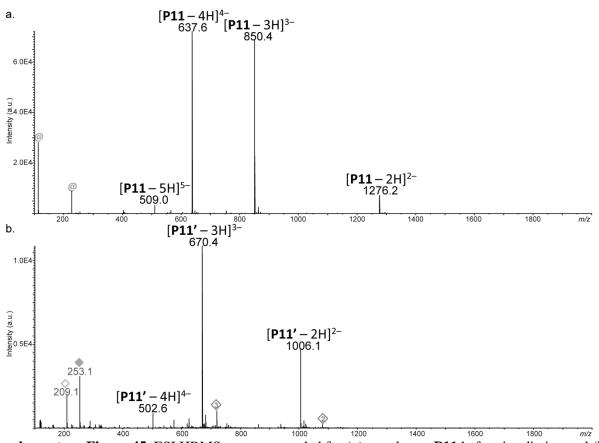
Supplementary Figure 42. MS/MS spectra recorded for copolymer P8' obtained after irradiation of P8, using a 25 eV collision energy (laboratory frame) to activate the triply deprotonated precursor at m/z 625.4. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 153.0 and $[1 - H]^-$ at m/z 288.0, both designated by #. Inset Table: Sequence coverage of P8' (*n.d.*: not detected; *n.e.*: not expected). Before photo-exposure, copolymer P8 exhibits the same MS/MS spectrum as P10 in Supplementary Figure 35.



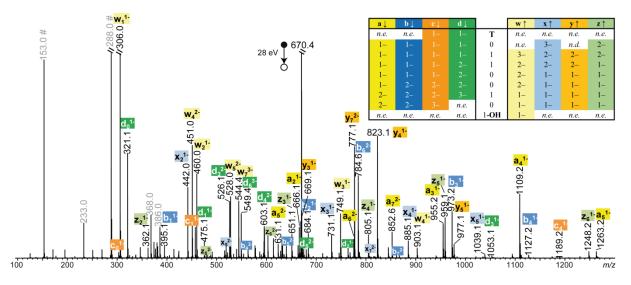
Supplementary Figure 43. ESI HRMS spectra recorded for (**a**) copolymer **P9** before irradiation and (**b**) the resulting polymer **P9'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@) or photo-deprotection by-products (diamonds).



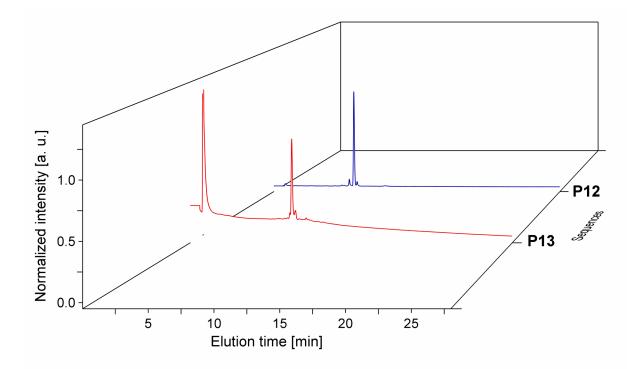
Supplementary Figure 44. MS/MS spectra recorded for copolymer P9' obtained after irradiation of P9, using a 30 eV collision energy (laboratory frame) to activate the triply deprotonated precursor at m/z 760.4. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 153.0 and $[1 - H]^-$ at m/z 288.0, both designated by #. Inset Table: Sequence coverage of P9' (*n.d.*: not detected; *n.e.*: not expected). Before photo-exposure, copolymer P9 exhibits the same MS/MS spectrum as P10 in Supplementary Figure 35.



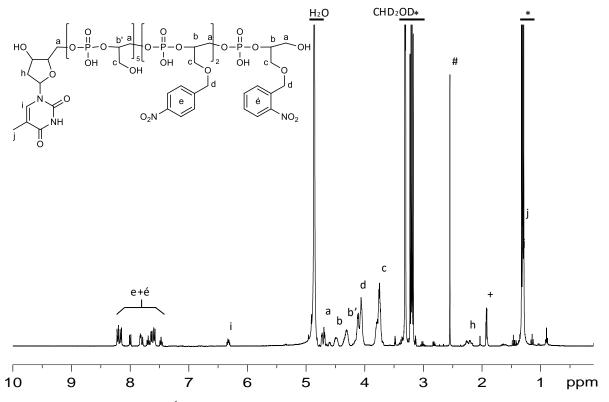
Supplementary Figure 45. ESI HRMS spectra recorded for (**a**) copolymer **P11** before irradiation and (**b**) the resulting polymer **P11'** after photo-exposure. Grey symbols designate clusters of trifluoroacetic acid (@) or photo-deprotection by-products (diamonds).



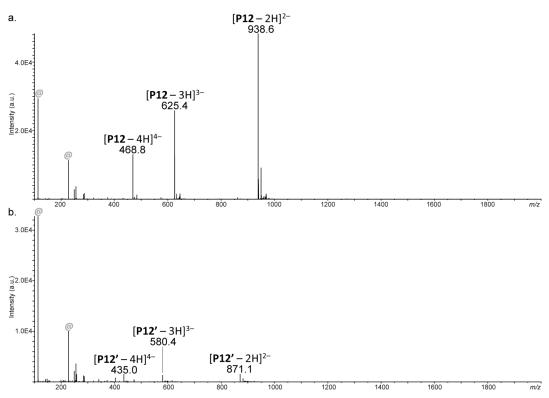
Supplementary Figure 46. MS/MS spectra recorded for copolymer P11' obtained after irradiation of P11, using a 28 eV collision energy (laboratory frame) to activate the triply deprotonated precursor at m/z 670.4. Peaks annotated in grey correspond to secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 153.0 and $[1 - H]^-$ at m/z 288.0, both designated by #. Inset Table: Sequence coverage of P11' (*n.d.*: not detected; *n.e.*: not expected). Before photo-exposure, copolymer P11 exhibits the same MS/MS spectrum as P10 in Supplementary Figure 35.



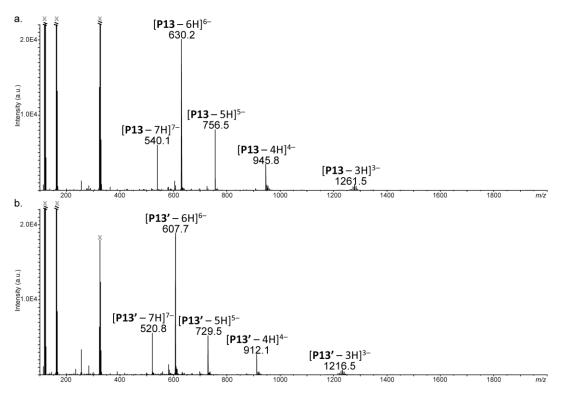
Supplementary Figure 47. HPLC traces measured for copolymers P12 and P13. The chromatogram is recorded at λ =260 nm. Experimental conditions: phase A: 10 % ACN 20 % 2M NH₃ in water, phase B: 2.5 M NaCl in water; gradient: 0-3 min 5 % B, 3-23 min 5 % B-30 % B, 23-28 min 30 %B, 28-35 min 30% \rightarrow 5 % B; flow rate: 1 mL·min⁻¹.



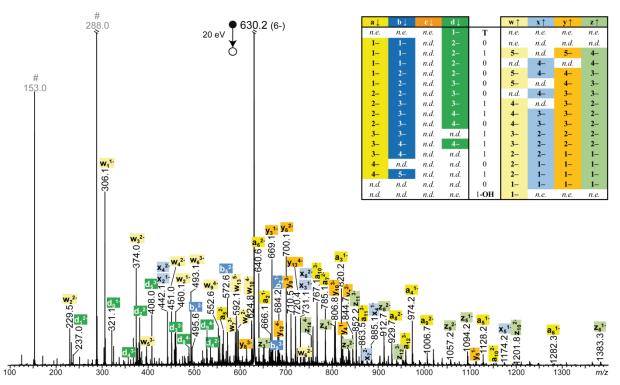
Supplementary Figure 48. ¹H NMR spectrum recorded at RT in CD₃OD for copolymer **P12**. The star symbols indicate signals of triethylammonium counterions. (#) Methylamine, (+) acetonitrile.



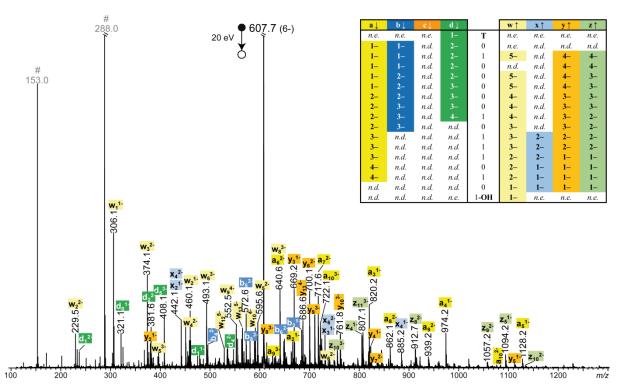
Supplementary Figure 49. ESI HRMS spectra recorded for (**a**) copolymer **P12** before irradiation and (**b**) the resulting polymer **P12**' after photo-exposure. Grey symbols indicate trifluoroacetic acid clusters (@).



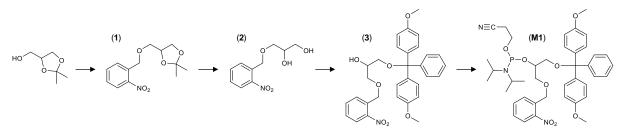
Supplementary Figure 50. ESI HRMS spectra recorded for (**a**) copolymer **P13** before irradiation and (**b**) the resulting polymer **P13'** after photo-exposure. Numerous H/Na exchanges in the lowest charge state species account for the more complex pattern observed for the - ions. Grey symbols designate clusters of trifluoroacetic acid (x).



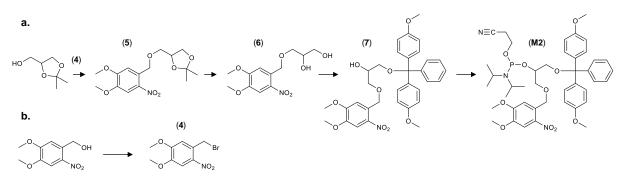
Supplementary Figure 51. MS/MS spectra recorded for copolymer **P13** before irradiation, using a 20 eV collision energy (laboratory frame) to activate the $[P13 - 6H]^{6-}$ precursor at m/z 630.2. In grey: secondary fragments, including the deprotonated units, $[0 - H]^{-}$ at m/z 153.0 and $[1 - H]^{-}$ at m/z 288.0, both designated by #. Inset Table: Sequence coverage of **P13** (*n.d.*: not detected; *n.e.*: not expected), with detailed assignments reported in Supplementary Table 7.



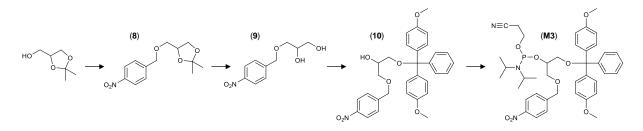
Supplementary Figure 52. MS/MS spectra recorded for copolymer P13' obtained after irradiation of P13, using a 20 eV collision energy (laboratory frame) to activate $[P13' - 6H]^{6-}$ at m/z 607.7. In grey: secondary fragments, including the deprotonated units, $[0 - H]^-$ at m/z 153.0 and $[1 - H]^-$ at m/z 288.0, both designated by #. Inset Table: Sequence coverage of P13' (*n.d.*: not detected; *n.e.*: not expected), with detailed assignments reported in Supplementary Table 8.



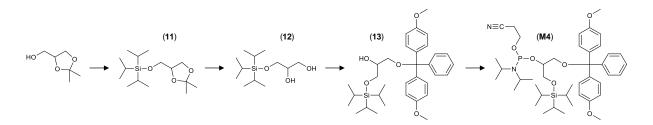
Supplementary Figure 53. Synthetic route used in this work for the preparation of M1.



Supplementary Figure 54. Synthetic route used in this work for the preparation of **M2**: (**a**) main synthesis route; (**b**) synthesis of 4,5-dimethoxy-2-nitrobenzyl bromide.



Supplementary Figure 55. Synthetic route used in this work for the preparation of M3.



Supplementary Figure 56. Synthetic route used in this work for the preparation of M4.

Supplementary Tables.

	Bef	ore irradiation		After irradiation					
	Sequence ^a	m/z_{th}^{b}	m/z_{exp}		Sequence ^a	m/z_{th}^{b}	m/z_{exp}^{c}		
H1	T 00000000	850.4499	850.4451	H1'	T ••••••	490.3644	490.3584		
Н2	T 11111111	1010.5062	1010.5081	Н2'	$T \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet$	490.3644	$n.d.^{d}$		
P1	T 01000101	910.4710	910.4710	P1'	T •••••	490.3644	490.3555		
P2	T 01110010	930.4780	930.4785	P2'	T •••••	490.3644	490.3559		
P3	T 01100001	910.4710	910.4711	P3'	T ••••••	490.3644	490.3589		
P4	T 01110011	950.4851	950.4839	P4'	T ••••••	490.3644	490.3585		
P5	T 01100101	930.4780	930.4795	P5'	T ••••••	490.3644	490.3573		

Supplementary Table 1. ESI-HRMS characterization of photo-erasable polymers.

^a Before irradiation, bits 0 and 1 correspond to monomers **M1** and **M2**, respectively. After irradiation, the symbol • represents the monomer unit of a non-decodable homopolymer. ^b The displayed m/z values correspond to $[M-3H]^{3-}$. ^c After irradiation, targeted species were of too low abundance to allow high accuracy mass measurements, accounting for relative error of 10-20 ppm. ^d Due to its very low abundance, the triply deprotonated **H2**' polymer could not be accurately mass measured (*n.d.*: not determined).

Supplementary	Table 2. ESI-HRMS	S characterization o	f polymer	s coded wit	h an invisible ink.
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	Before	e irradiation		After irradiation					
	Sequence ^a	m/z_{th}^{b}	m/z_{exp}		Sequence ^a	m/z_{th}^{b}	m/z_{exp}		
Н3	T 11111111	850.4499	850.4520	Н3'	T 11111111	850.4499	850.4484		
P6	T 1 1 111 11	850.4499	850.4504	P6'	T 01000101	625.3965	625.3934		
P7	T 1 1111 111	850.4499	850.4527	P7'	T 01111000	670.4072	670.4061		
P8	T 1 111 1111	850.4499	850.4489	P8'	T 01110000	625.3965	625.3924		
P9	T 1 11 1 1111	850.4499	850.4538	Р9'	T 01101111	760.4285	760.4254		
P10	T 1 111 11 11	850.4499	850.4537	P10'	T 01110011	715.4178	715.4148		
P11	T 11111111	850.4499	850.4522	P11'	T 01100101	670.4072	670.4073		

^a Before irradiation, **1** and 1 correspond to isobaric monomers **M1** and **M3**, respectively. After irradiation, bit 0 corresponds to a photo-deprotected **M1** unit. ^b The displayed m/z values correspond to $[M-3H]^{3-}$.

Supplementary Table 3. ESI-HRMS characterization of photo-mutable polymers.

Before irradi	iation		After irradiation					
Sequence ^a	m/z_{th}	m/z _{exp}		Sequence ^a	m/z_{th}	m/zexp		
T 0100001 1	938.5983 ^b	938.5995	P12'	T 01000010	871.0823 ^b	871.0818		
T 010000 1 101110101	756.4726°	756.4720	P13'	T 0100000101110101	729.4662°	729.4660		
,	Sequence ^a T 0100001 1	Sequence ^a m/z_{th} T 01000011 938.5983 ^b	Sequence ^a m/z_{th} m/z_{exp} T 01000011 938.5983 ^b 938.5995	Sequence ^a m/z_{th} m/z_{exp} T 01000011 938.5983 ^b 938.5995 P12'	Sequence ^a m/z_{th} m/z_{exp} Sequence ^a T 01000011 938.5983 ^b 938.5995 P12' T 01000010	Sequence ^a m/z_{th} m/z_{exp} Sequence ^a m/z_{th} T 01000011 938.5983 ^b 938.5995 P12' T 01000010 871.0823 ^b		

^a Before irradiation, **1** and 1 correspond to isobaric monomers **M1** and **M3**, respectively. Bit 0 corresponds to an OH-functional unit. ^b The displayed m/z values correspond to $[M-2H]^{2-}$. ^c The displayed m/z values correspond to $[M-5H]^{5-}$, measured at isotopic maximum.

a↓	b ↓	c ↓	d↓		$\mathbf{w}\uparrow$	x ↑	y ↑	z↑
n.e.	n.e.	1–	1–	Т	n.e.	n.e.	n.e.	n.e.
1–	1–	1–	2–	0	n.e.	n.d.	2–	n.d.
1–	1–	n.d.	2–	1	2-/3-	3–	2–	2–
1–	2–	n.d.	n.d.	0	2-/3-	n.d.	2–	2–
1–	2–	n.d.	3–	0	2-/3-	2–	1—/2—	1–
1-/2-	2–	n.d.	n.d.	0	2—	n.d.	1–	1—
2–	2-/3-	n.d.	3-/4-	1	1—/2—	1–	1–	1–
2-/3-	n.d.	n.d.	n.e.	0	1-/2-	1–	1–	n.d.
n.e.	n.e.	n.e.	n.e.	1 -OH	1–	n.e.	n.e.	n.e.

Supplementary Table 4. Full coverage of the T01000101 sequence of **P1** using MS/MS data shown in Figure 2c.

Values indicate the fragment charge state. n.d.: not detected. n.e.: not expected.

Supplementary Table 5. Full coverage of the T01110011 sequence of **P10'** using MS/MS data shown in Figure 3c.

a↓	b ↓	c↓	d↓		$\mathbf{w}\uparrow$	x ↑	y ↑	z↑
n.e.	n.e.	1–	1–	Т	n.e.	n.e.	n.e.	n.e.
1–	1–	1–	1–	0	n.e.	3–	n.d.	2–
1–	1–	1–	1–	1	3–	2–	2–	2–
1–	1–	1–	2—	1	2–	2–	2–	1–
1–	1–	2–	2—	1	2–	1–	1–	1–
1–	2–	2–	2—	0	2–	1–	1–	1–
2–	2–	2–	3–	0	1–	1–	1–	1–
2–	2—	3–	n.e.	1	1–	1–	1–	1–
n.e.	n.e.	n.e.	n.e.	1 -OH	1–	n.e.	n.e.	n.e.

Values indicate the fragment charge state. *n.d.*: not detected. *n.e.*: not expected.

	Т	0	1	0	0	0	0	1	X	
i→	0	1	2	3	4	5	6	7	8	
ai ^{z-}	n.e.	n.d.	666.1 ¹⁻	820.21-	974.2 ¹⁻	1128.3 ¹⁻	1282.3 ¹⁻	785.22-	n.e.	
b_i^{z}	n.e.	395.1 ¹⁻	684.1 ¹⁻	838.21-	992.2 ¹⁻	1146.3 ¹⁻	1300.3 ¹⁻	794.22-	n.e.	
c_i^{z}	n.e.	457.1 ¹⁻	746.1 ¹⁻	900.2 ¹⁻	1054.21-	1208.2 ¹⁻	680.6 ²⁻	n.d.	n.e.	
$\mathbf{d}_{\mathbf{i}}^{\mathbf{z}}$	321.1 ¹⁻	475.1 ¹⁻	764.1 ¹⁻	918.2 ¹⁻	1072.21-	1226.21-	689.6 ²⁻	834.5 ²⁻	n.e.	
		8	7	6	5	4	3	2	1	←j
	n.e.	n.e.	749.6 ²⁻	1211.2 ¹⁻	1057.2 ¹⁻	903.2 ¹⁻	749.1 ¹⁻	595.1 ¹⁻	306.11-	xx. Z-
	n.e.	n.e.	682.1 ²⁻	1076.21-	922.1 ¹⁻	768.1 ¹⁻	614.1 ¹⁻	460.1 ¹⁻	171.1 ¹⁻	Wj ^{z-}
	n.e.	817.6 ²⁻	1482.2 ¹⁻	1193.2 ¹⁻	1039.2 ¹⁻	885.2 ¹⁻	731.1 ¹⁻	577.1 ¹⁻	n.e.	
	n.e.	750.12-	673.1 ²⁻	1058.1 ¹⁻	904.1 ¹⁻	750.1 ¹⁻	596.1 ¹⁻	442.1 ¹⁻	n.e.	Xj ^{z-}
	n.e.	n.d.	1420.2 ¹⁻	1131.3 ¹⁻	977.2 ¹⁻	823.2 ¹⁻	669.1 ¹⁻	515.1 ¹⁻	n.e.	7-
	n.e.	719.12-	1285.3 ¹⁻	996.2 ¹⁻	842.21-	688.1 ¹⁻	534.1 ¹⁻	380.1 ¹⁻	n.e.	Уј ²⁻
	n.e.	777.6 ²⁻	1402.3 ¹⁻	1113.3 ¹⁻	959.2 ¹⁻	805.21-	651.1 ¹⁻	497.1 ¹⁻	n.e.	7.2-
	n.e.	710.1 ²⁻	1267.3 ¹⁻	978.1 ¹⁻	824.21-	670.1 ¹⁻	516.1 ¹⁻	362.1 ¹⁻	n.e.	Zj ^{z-}

Supplementary Table 6. MS/MS data allowing full coverage of the T0100001X sequence of P12 (X = 1) and P12' (X = 0).^a

^a For both polymers **P12** and **P12'**, α -terminated fragments (a_i, b_i, c_i, d_i) are identical since, in these series, species containing all units including the last X one (a₈, b₈, c₈, d₈) are not expected to form (*n.e.*). In contrast, ω -terminated fragments (w_j, x_j, y_j, z_j) all contain the X unit as this is the first unit when counting from the right- to the left-hand side: accordingly, these series are different when X=1 for **P12** (*m*/*z* values in black) or X=0 for **P12'** (*m*/*z* values in red), with a mass shift corresponding to m₁ – m₀ = 135 Da.

n.d.: not detected.

Supplementary Table 7. MS/MS data allowing full coverage of the T0100001101110101 sequence of P13 (*n.e.*: not expected; *n.d.*: not detected). ٦

i↓	ai ^{z-}	b _i ^{z-}	Ci ^{z-}	di _z .		$\mathbf{W_{j}}^{z}$	Xj ^{z-}	yj ^{z-}	Zj ^{z-}	
0	n.e.	n.e.	n.e.	321.1 ¹⁻	Т	n.e.	n.e.	n.e.	n.e.	
1	377.1 ^{1–}	395.1 ¹⁻	n.d.	237.02-	0	n.d.	n.d.	n.d.	n.d.	16
2	666.2 ¹⁻	684.2 ¹⁻	n.d.	381.5 ²⁻	1	680.7 ⁵⁻	n.d.	664.7 ⁵⁻	826.64-	15
3	820.2^{1-}	838.21-	n.d.	458.6^{2-}	0	n.d.	619.3 ⁴⁻	n.d.	754.4^{4-}	14
4	974.2 ^{1–}	495.6 ²⁻	n.d.	535.6 ²⁻	0	592.1 ⁵⁻	735.9 ^{4–}	720.44-	954.8 ³⁻	13
5	1128.2 ^{1–}	572.6 ²⁻	n.d.	408.0^{3-}	0	561.3 ⁵⁻	n.d.	681.9 ^{4–}	903.5 ³⁻	12
6	640.6 ²⁻	649.6 ²⁻	n.d.	459.4^{3-}	0	n.d.	658.8^{4-}	858.2 ³⁻	852.2^{3-}	11
7	785.1 ^{2–}	529.1 ³⁻	n.d.	555.6 ³⁻	1	624.8 ^{4–}	n.d.	806.8 ³⁻	1201.8^{2-}	10
8	929.7 ^{2–}	625.4^{3-}	n.d.	488.84-	1	552.6 ^{4–}	731.1 ³⁻	710.5 ^{3–}	1057.2^{2-}	9
9	1006.7^{2-}	676.8 ³⁻	n.d.	527.3 ⁴⁻	0	480.34-	634.7^{3-}	614.1 ³⁻	912.7 ^{2–}	8
10	767.1 ^{3–}	773.1 ^{3–}	n.d.	n.d.	1	589.4 ³⁻	875.62-	844.7 ^{2–}	835.7 ^{2–}	7
11	863.5 ³⁻	651.84-	n.d.	537.2 ⁵ -	1	493.1 ³⁻	731.1 ^{2–}	700.1^{2-}	691.1 ²⁻	6
12	959.8 ³⁻	724.14-	n.d.	n.d.	1	595.6 ²⁻	586.6 ²⁻	1112.2 ¹⁻	1094.2^{1-}	5
13	758.1 ^{4–}	n.d.	n.d.	n.d.	0	451.0 ²⁻	885.11-	823.2 ^{1–}	805.21-	4
14	830.4 ^{4–}	667.6 ^{5–}	n.d.	n.d.	1	374.02-	731.1 ^{1–}	669.2 ¹⁻	651.1 ¹⁻	3
15	n.d.	n.d.	n.d.	n.d.	0	460.1 ¹⁻	442.1^{1-}	380.1 ¹⁻	362.1 ¹⁻	2
16	n.d.	n.d.	n.d.	n.e.	1-OH	306.1 ¹⁻	n.e.	n.e.	n.e.	1
						-				j↑

Supplementary Table 8. MS/MS data allowing full coverage of the T0100000101110101 sequence of **P13'** (*n.e.*: not expected; *n.d.*: not detected).

i↓	ai ^{z-}	b₁²-	Ci ^{z-}	d₁²-		$\mathbf{W_j}^{\mathbf{z}}$	Xj ^{z-}	yj ^{z-}	Zj ^{z-}	
0	n.e.	n.e.	n.e.	321.11-	Т	n.e.	n.e.	n.e.	n.e.	
1	377.1 ^{1–}	395.1 ¹⁻	n.d.	237.0^{2-}	0	n.d.	n.d.	n.d.	n.d.	16
2	666.2 ¹⁻	684.2 ^{1–}	n.d.	381.5 ²⁻	1	653.7 ⁵⁻	n.d.	797.4 ^{4–}	792.9 ^{4–}	15
3	820.2 ^{1–}	838.21-	n.d.	458.6^{2-}	0	n.d.	n.d.	725.1 ^{4–}	720.64-	14
4	974.2 ^{1–}	495.6 ^{2–}	n.d.	535.6 ²⁻	0	565.1 ⁵⁻	n.d.	686.6 ^{4–}	909.8 ³⁻	13
5	1128.2^{1-}	572.6 ^{2–}	n.d.	408.0^{3-}	0	534.2 ⁵⁻	n.d.	648.1 ^{4–}	858.5 ³⁻	12
6	640.6 ²⁻	649.6 ²⁻	n.d.	459.4^{3-}	0	629.6 ^{4–} .	n.d.	813.1 ³⁻	807.1^{3-}	11
7	717.6 ^{2–}	484.3 ³⁻	n.d.	510.7 ³⁻	0	691.1 ⁴⁻	n.d.	761.8 ^{3–}	755.8 ^{3–}	10
8	862.1 ^{2–}	580.4 ³⁻	n.d.	455.14-	1	552.6 ^{4–}	n.d.	710.5 ³⁻	1057.2^{2-}	9
9	939.2 ^{2–}	631.7 ³⁻	n.d.	n.d.	0	480.34-	n.d.	614.1 ³⁻	912.7 ^{2–}	8
10	722.1 ^{3–}	n.d.	n.d.	n.d.	1	589.4 ³⁻	875.6 ²⁻	844.7 ^{2–}	835.5 ²⁻	7
11	818.5 ³⁻	n.d.	n.d.	n.d.	1	493.1 ³⁻	731.1 ^{2–}	700.1^{2-}	691.1 ²⁻	6
12	914.8 ^{3–}	n.d.	n.d.	n.d.	1	595.6 ²⁻	586.6 ²⁻	1112.3 ¹⁻	1094.21-	5
13	724.4 ^{4–}	n.d.	n.d.	n.d.	0	451.0 ²⁻	885.1 ¹⁻	823.2 ^{1–}	805.21-	4
14	796.6 ^{4–}	n.d.	n.d.	n.d.	1	374.0 ²⁻	731.1 ¹⁻	669.2 ¹⁻	651.1 ¹⁻	3
15	n.d.	n.d.	n.d.	n.d.	0	460.1 ¹⁻	442.1 ¹⁻	380.1 ¹⁻	362.1 ¹⁻	2
16	n.d.	n.d.	n.d.	n.e.	1-OH	306.11-	n.e.	n.e.	n.e.	1
						-				j↑

Supplementary References.

- Klán, P., Šolomek, T., Bochet, C. G., Blanc, A., Givens, R., Rubina, M., Popik, V., Kostikov, A. & Wirz, J. Photoremovable Protecting Groups in Chemistry and Biology: Reaction Mechanisms and Efficacy. *Chem. Rev.* 113, 119-191 (2013).
- 2 Barltrop, J. A., Plant, P. J. & Schofield, P. Photosensitive protective groups. *Chem. Commun.*, 822-823 (1966).
- 3 Patchornik, A., Amit, B. & Woodward, R. B. Photosensitive protecting groups. J. Am. Chem. Soc. **92**, 6333-6335 (1970).
- 4 Carré, P. Sur la décomposition de l'alcool ortho-nitrobenzylique sous l'influence de la soude aqueuse, et de la soude alcoolique. *C.R. Hebd. Seances Acad. Sci.* **140**, 663-665 (1905).