Electronic Supplementary Information

Molecular structure – intrinsic photostability relationships for diketopyrrolopyrrole-based conjugated polymers

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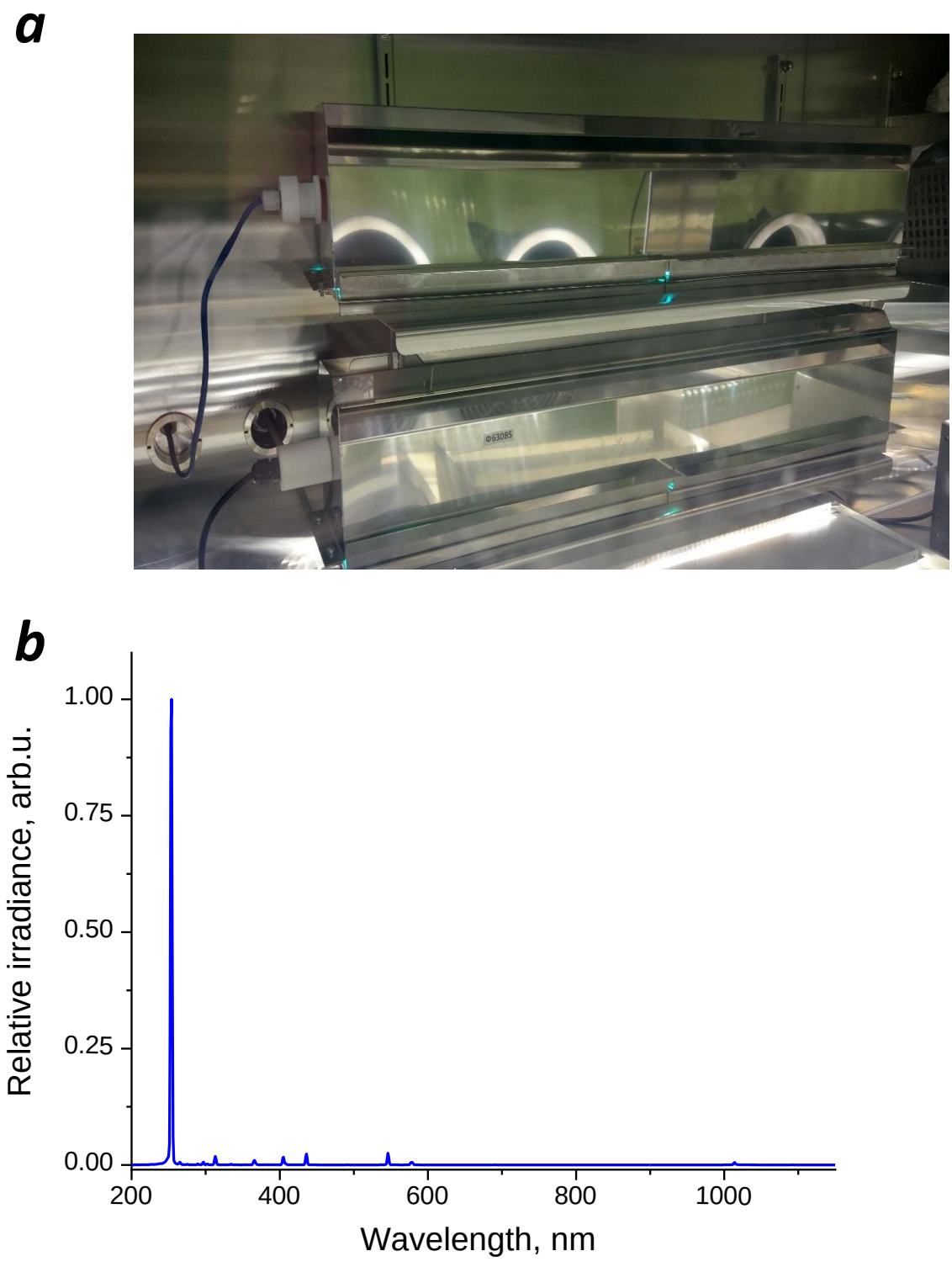

Figure S1. Photograph of the experimental setup: two UV lamps in metal shielding are placed inside the glove box (a) and emission spectrum of the lamp measured in 200-1150 nm range (b)

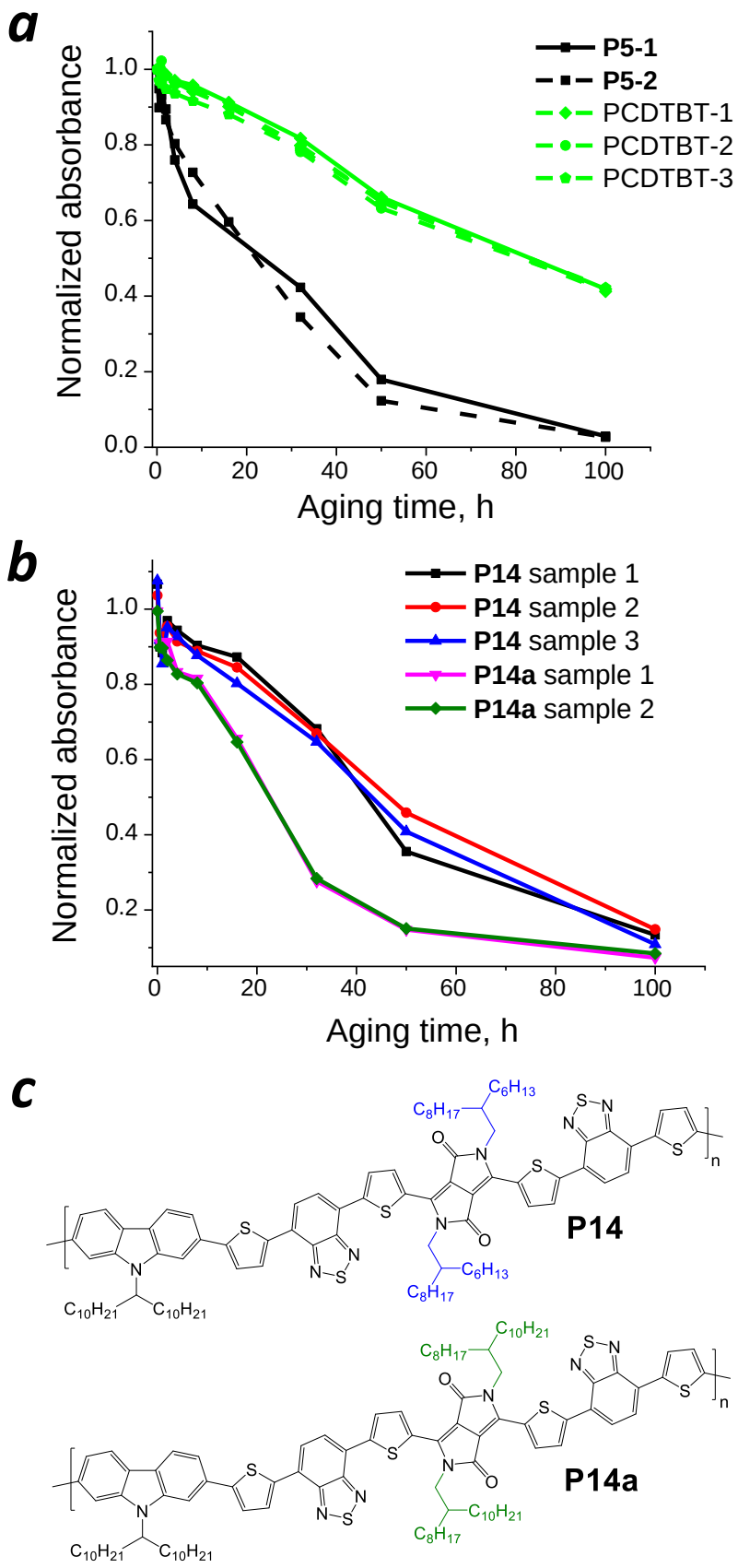

Figure S2. UV aging dynamics of two independent batches of polymer **P5** and three independent batches of PCDTBT (a). Sample-to-sample reproducibility of the aging behavior of polymer **P14** and similar polymer **P14a** with bulkier solubilizing side chains (b); molecular structures of these polymers (c).

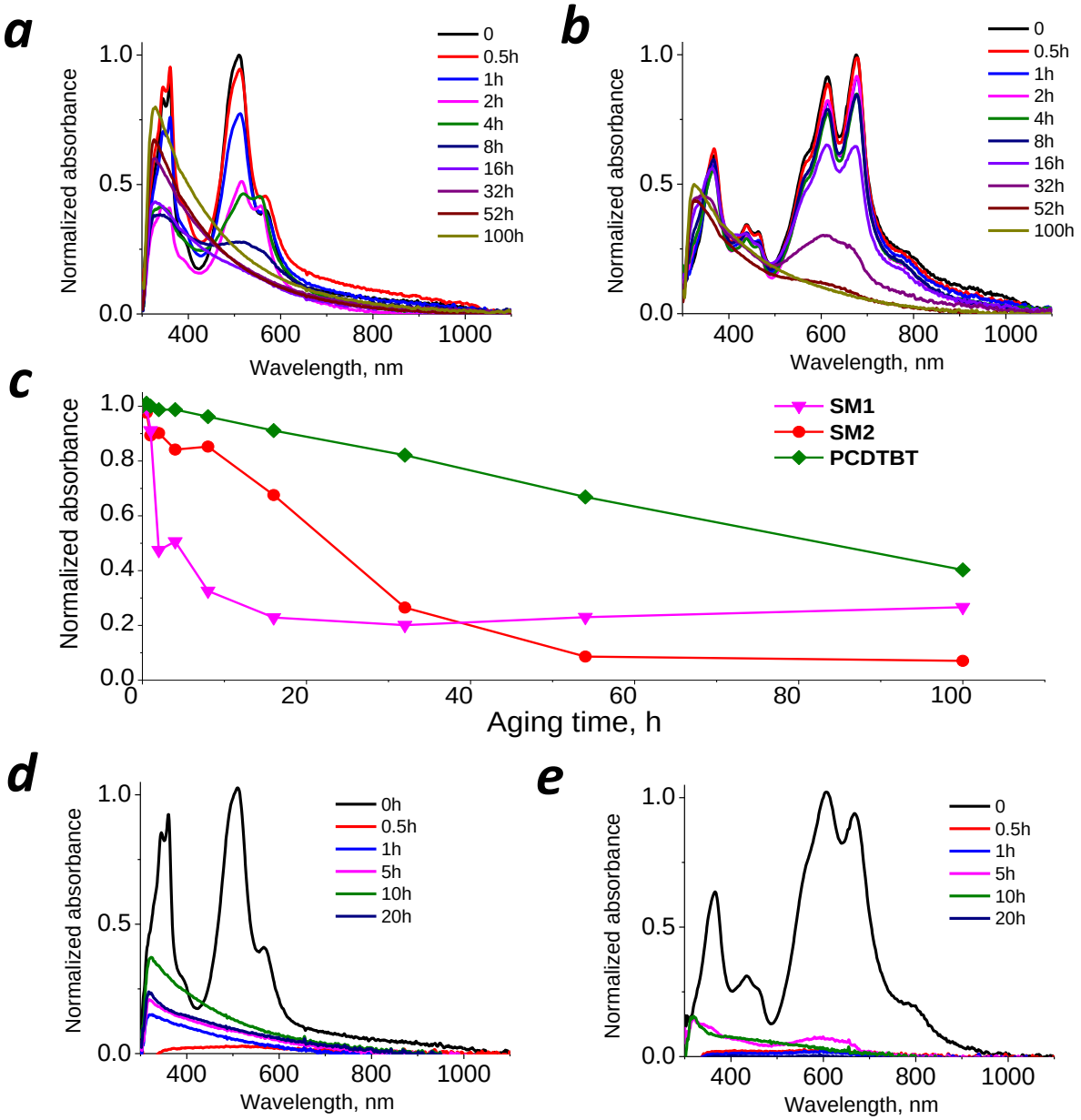

Figure S3. The evolution of the UV-vis absorption spectra of **SM1** (a) and **SM2** (b) films upon exposure to UV light inside the glove box. The maximal absorbance vs. aging time plots for **SM1** and **SM2** (c). The evolution of the UV-vis absorption spectra of the insoluble residues obtained after repeatable washing the exposed **SM1** (d) and **SM2** (e) films with CS_2-acetone-d6 solvent mixture (preparation of samples for NMR spectroscopy).

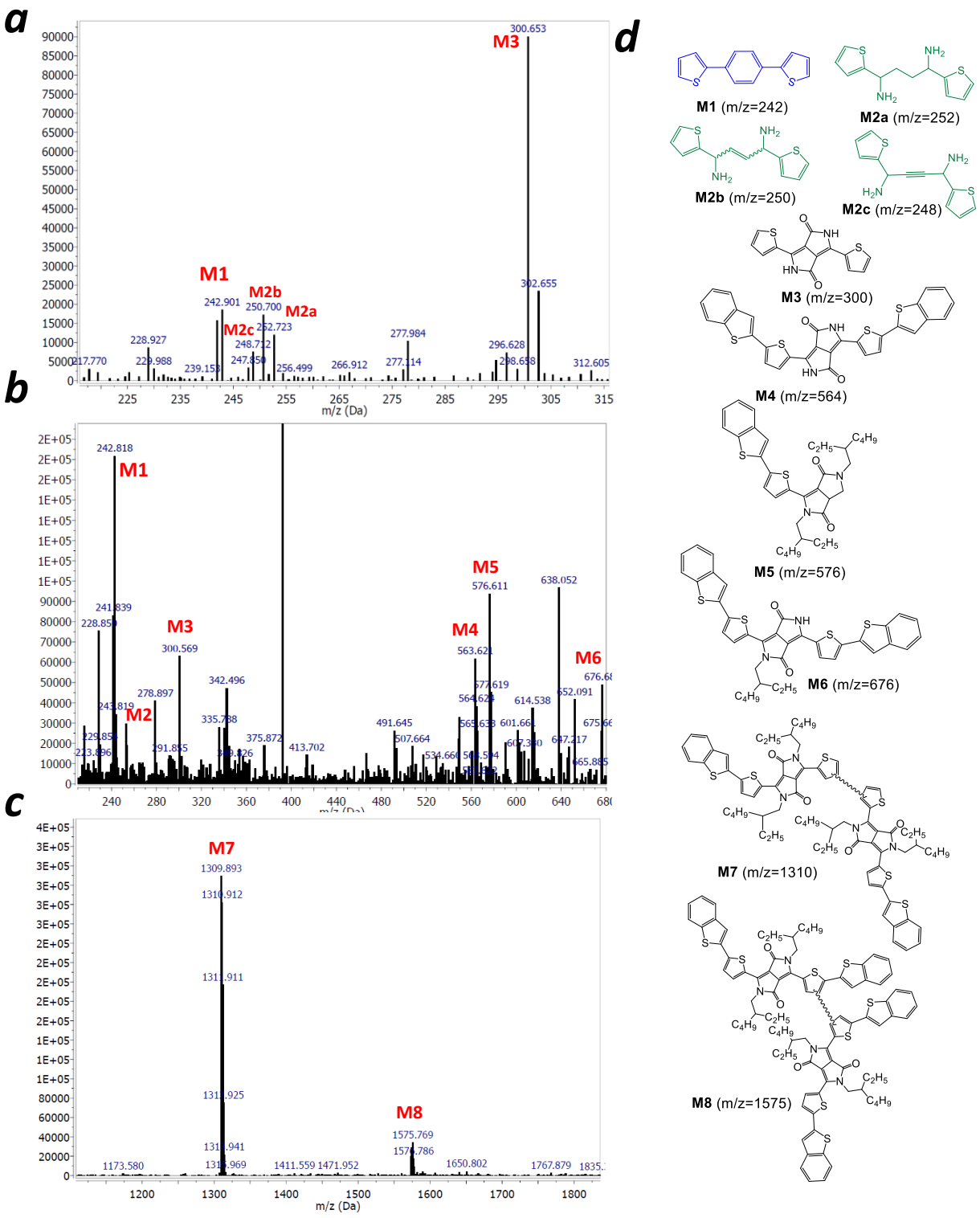

Figure S4. MALDI TOF mass spectra of **SM2** films exposed to UV light for 30 min (a) and 20 h (b, c); the ranges with m/z<700 (a, b) and m/z>1000 (c) are shown to avoid interference with intense **SM2** molecular ion. The assignment of some peaks is shown at the mass spectra, while the structures of the corresponding molecular species are shown in (d).

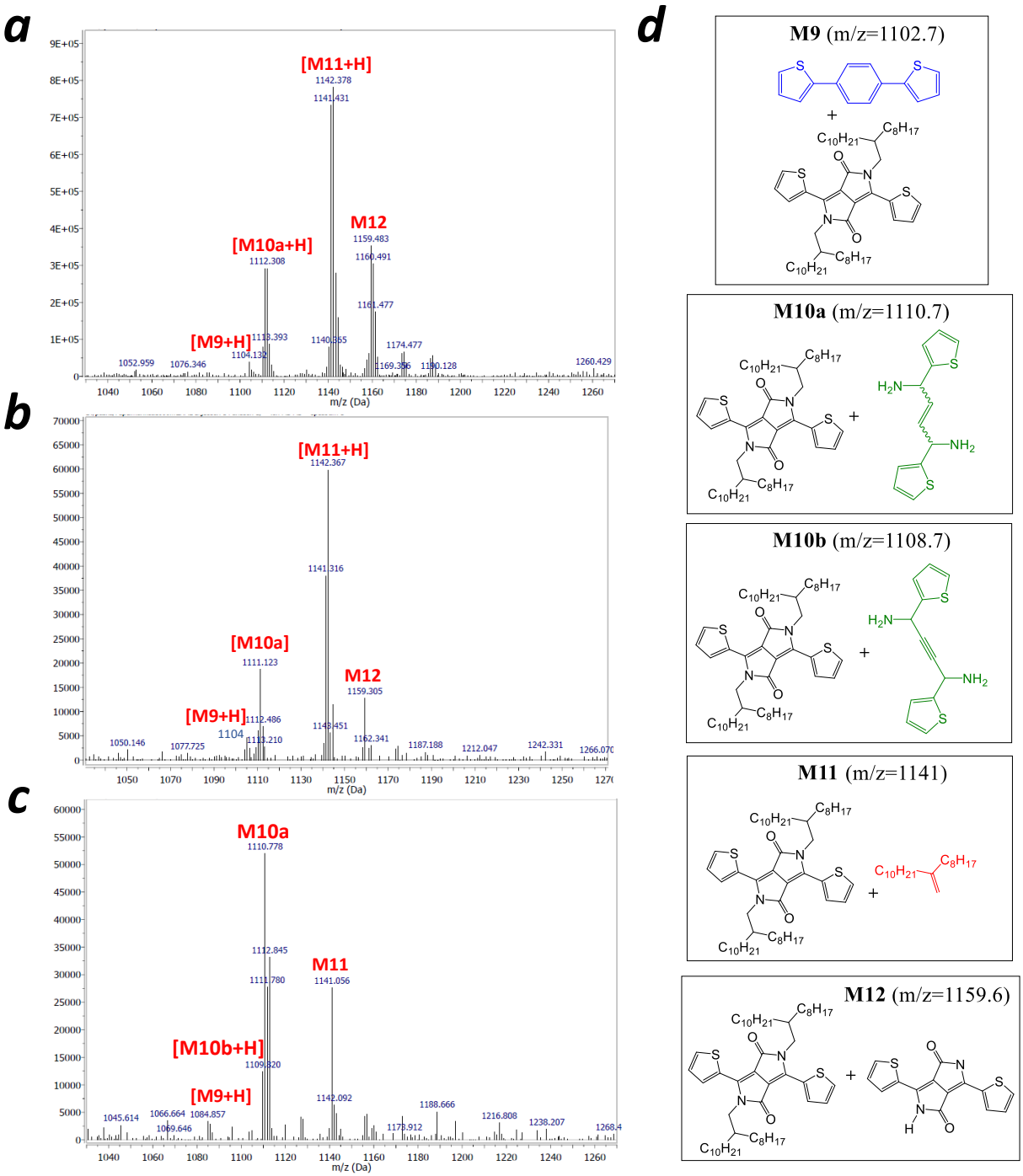

Figure S5. MALDI TOF mass spectra of **SM1** films exposed to UV light for 15 min (a), 30 min (b), and 20 h (c) recorded in the range of m/z>1000 to avoid interference with intense **SM1** molecular ion. The assignment of some peaks is shown at the mass spectra, while the structures of the corresponding molecular species are shown in (d).

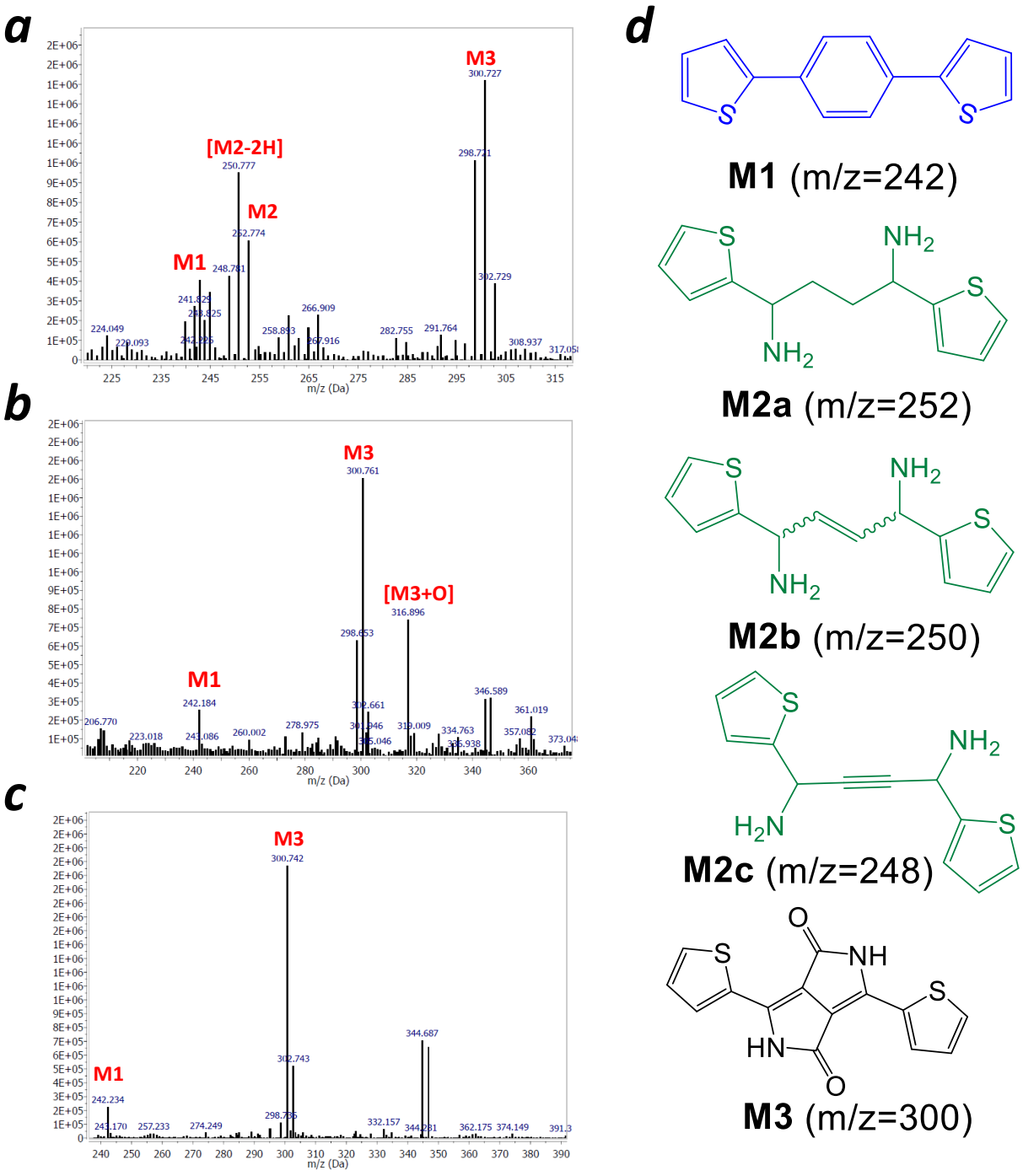

Figure S6. MALDI TOF mass spectra of thin films of **P6** (a-b) and **P7 (c)** exposed to UV light for 15 min (a and c) or 20 h (b). The assignment of some peaks is shown at the mass spectra, while the structures of the corresponding molecular species are shown in (d).

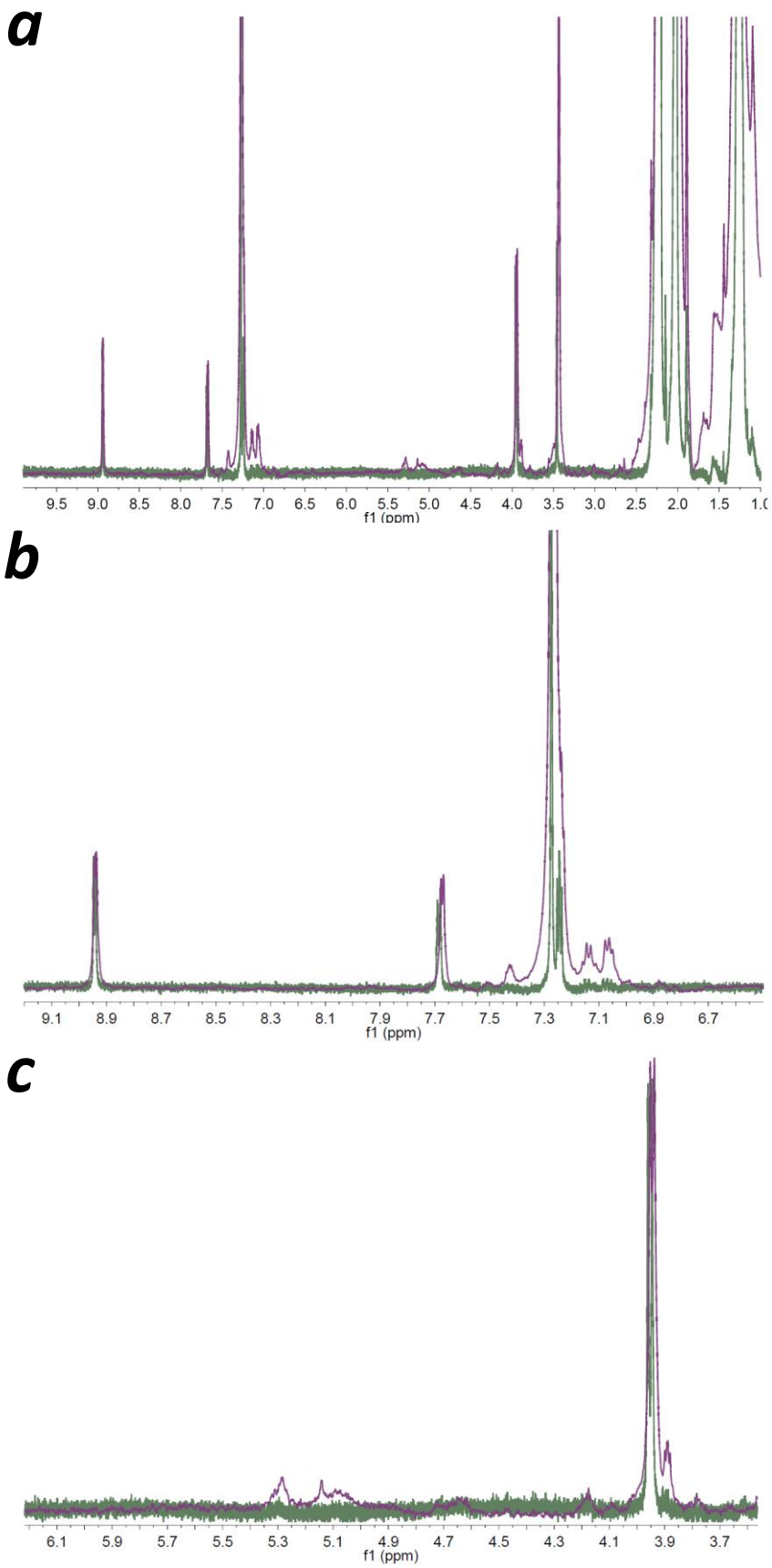

Figure S7. NMR spectra of solutions obtained by dissolving thin films of **SM1** in CS_2-acetone-d^6 solvent mixture prior (olive line) and after (purple line) UV exposure for 20 h. Full range spectra (a) as well as magnified low-field (b) and high-field (c) parts are shown.

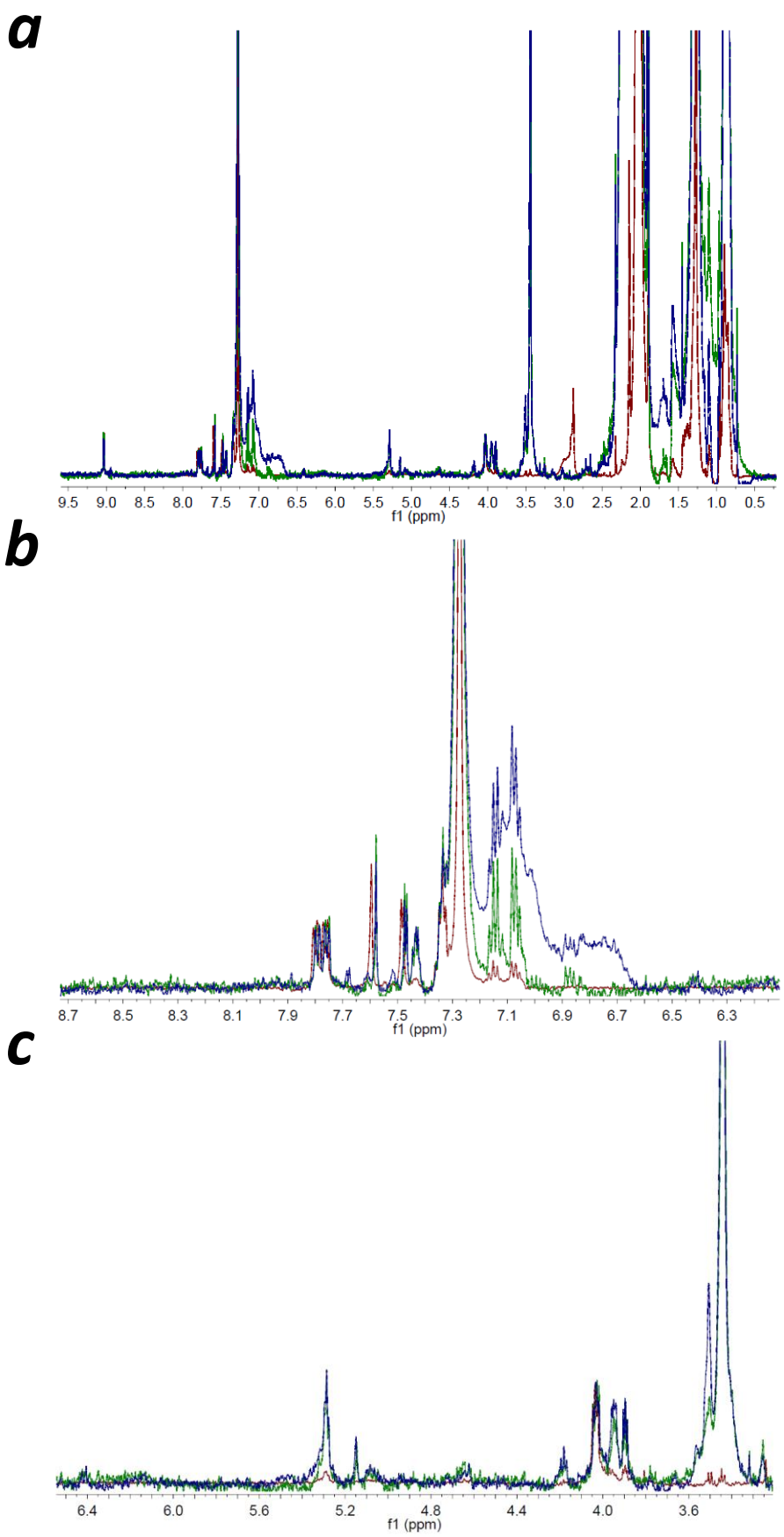

Figure S8. NMR spectra of solutions obtained by dissolving thin films of **SM2** in CS_2-acetone-d^6 solvent mixture after exposure to UV light for 30 min (brown line), 10 h (green line) and 20 h (blue line). Full range spectra (a) as well as magnified low-field (b) and high-field (c) parts are shown.

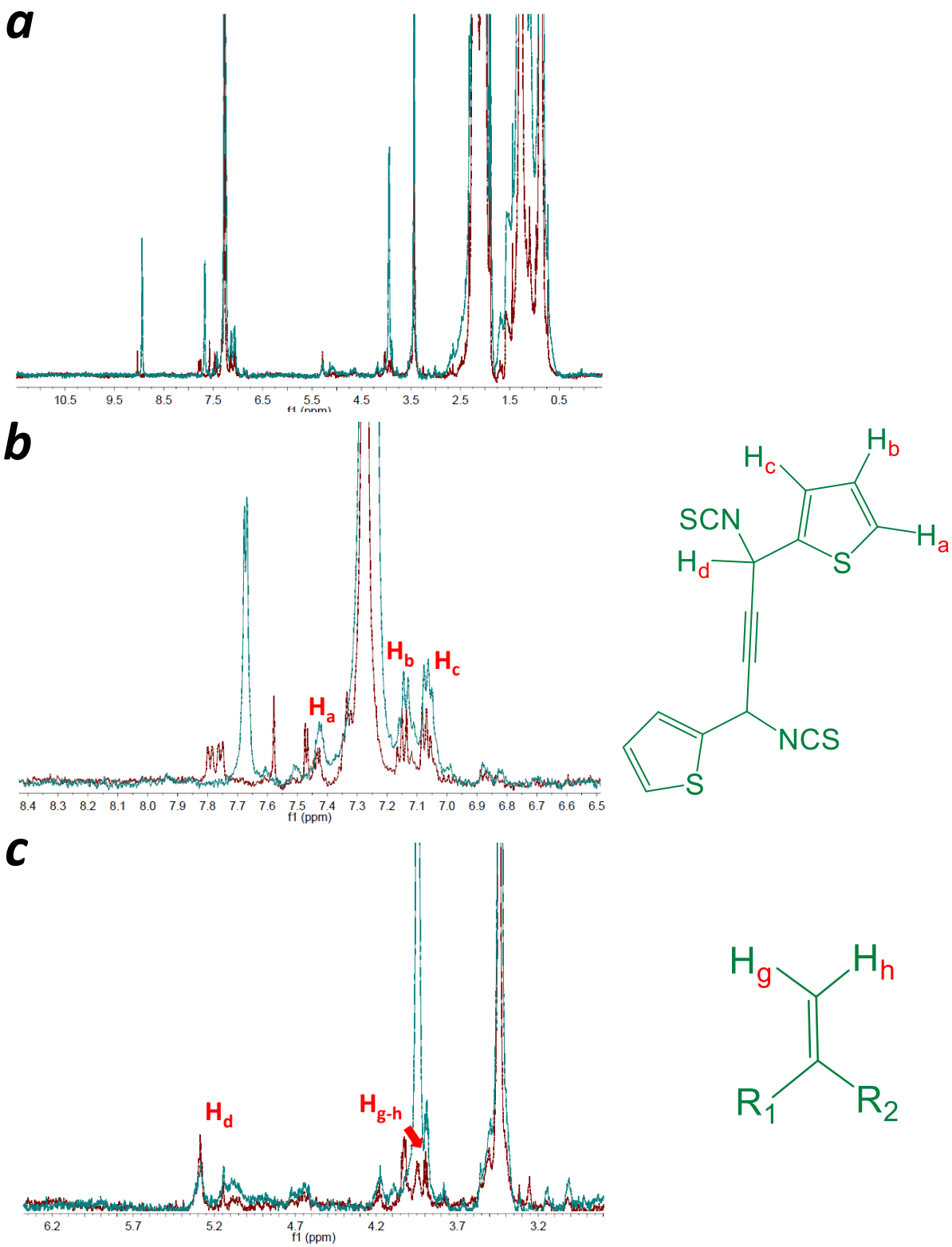

Figure S9. The comparison of the NMR spectra of solutions obtained by dissolving thin films of **SM1** (turquoise) and **SM2** (brown) after exposure to UV light for 20 h and 10 h, respectively. Full range spectra (a) as well as magnified low-field (b) and high-field (c) parts are shown. The reasonable assignments of some signals are also presented with the molecular structures of the identified products drawn on the right side.

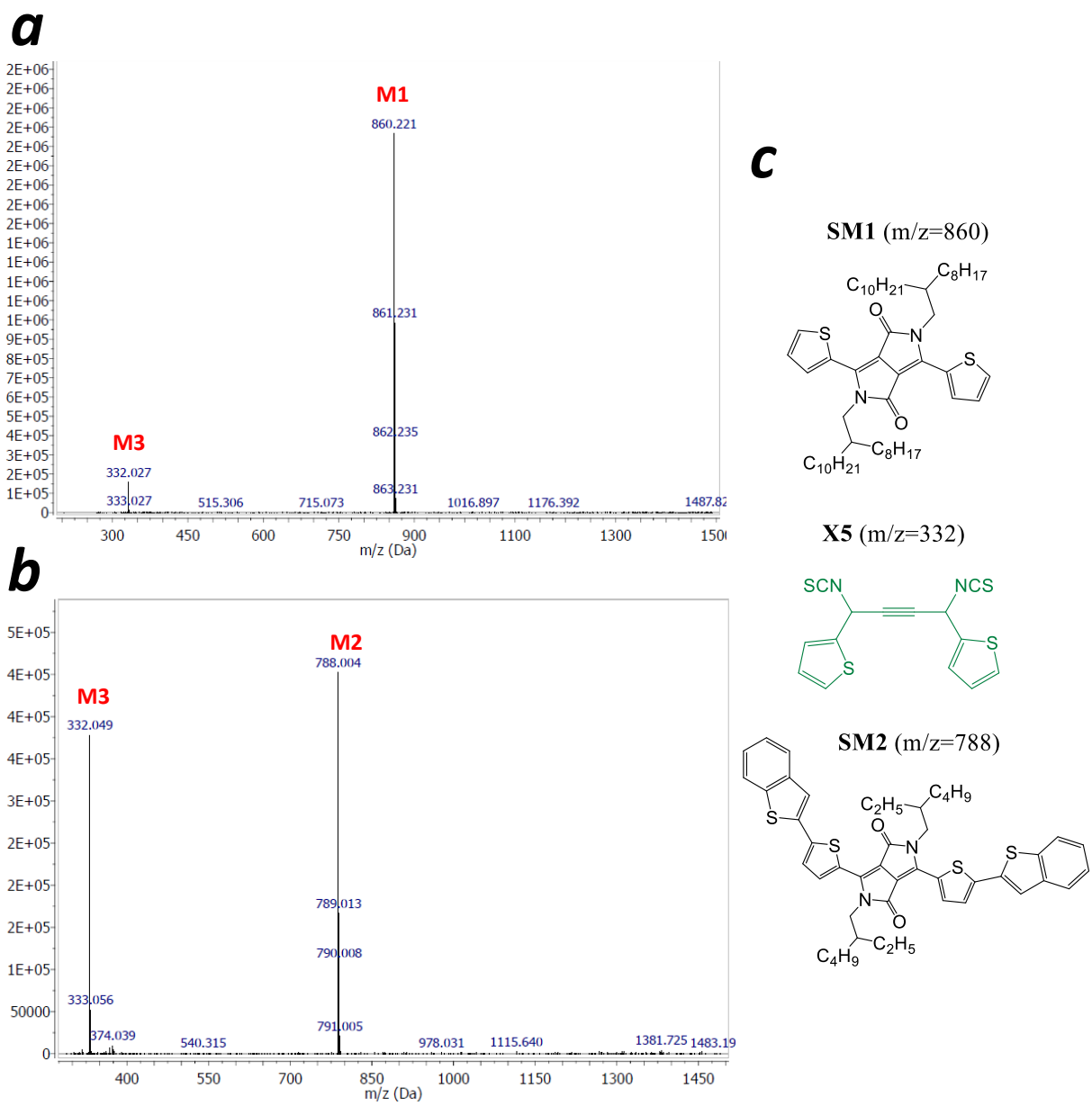

Figure S10. MALDI TOF mass spectra of samples obtained by dissolving thin films of **SM1** (a) and **SM2** (b) exposed to UV light for 5-20 h in acetone-d^6/CS_2 mixture for NMR analysis. The molecular structures of the characteristic ions are shown in (c).

Table S1. Some electronic and physicochemical properties of polymers **P1-P18** and k values, reflecting photostability of these materials

Polymer	M_w, Da	M_w/M_n	$\lambda_{max}^{film}, \lambda_{edge}^{film}$, nm	E_g, eV	$k=A_{20}/A_0$
P1	154400	2.0	796/1024	1.21	0.5
P2	52400	3.03	744/950	1.31	0.7
P3	133300	2.2	700/855	1.45	0.62
P4	80000	2.0	810/1047	1.19	0.5
P5	157500	2.8	915/1006	1.24	0.33
P6	190000	1.5	951/1120	1.11	0.04
P7	96500	1.52	870/970	1.28	0.02
P8	72500	1.7	883/1003	1.24	0.24
P9	60000	1.7	961/>1150	<1.08	0.56
P10	189600	2.2	356/1080	1.15	0.34
P11	142000	1.8	826/936	1.33	0.39
P12	20000	1.3	751/1005	1.24	0.38
P13	14172	2.22	604/714	1.74	0.33
P14	151119	4.2	676/960	1.29	0.65
P15	104000	4.3	740/930	1.34	0.43
P16	41500	1.7	670/836	1.49	0.15
P17	95700	3.7	790/866	1.44	0.47
P18	58000	5.0	695/868	1.43	0.31