Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Approaching the top of the emissive properties of CH_3PbBr_3 perovskite nanoparticles

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Electronic Supplementary Information

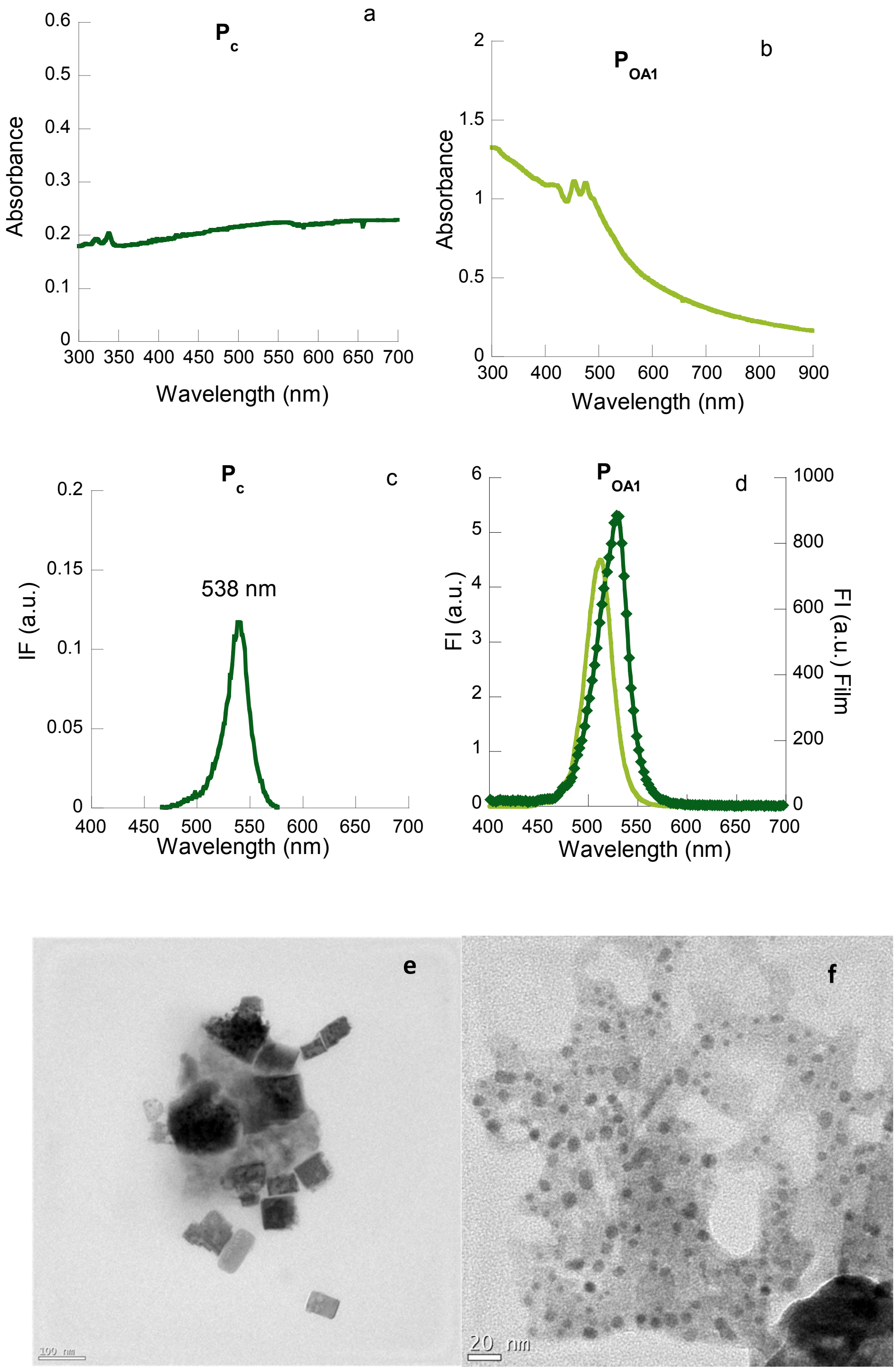


Figure S1: Absorption spectra of **Pc** (a) and $\mathbf{P}_{\mathbf{OA1}}$ (b) in toluene. Emission spectra of **Pc** (c) and $\mathbf{P}_{\mathbf{OA1}}$ in toluene (light green) (d); and $\mathbf{P}_{\mathbf{OA1}}$ film (dark green) (d). Emission recorded at λ_{exc}= 350 nm. (d) HRTEM images (scale bar 20 nm) of **Pc** (e) and $\mathbf{P}_{\mathbf{OA1}}$ (f).

Table S1: Synthesis of $\mathbf{P_{OA}}$ perovskites in the presence and in the absence of ODE and OLA

Name	OABr (mmol)	MABr (mmol)	$PbBr_2$ (mmol)	ODE (mmol)	OLA (mmol)	Emission properties (λ, nm)	ϕ_F
$\mathbf{P_{OA1}}$	0.16	0.24	0.1	6.26	0.3	513	0.67
$\mathbf{P_{OA2}}$	0.16	0.24	0.1	6.26	-	526	0.83
$\mathbf{P_{OA3}}$	0.16	0.24	0.1	-	0.3	525	0.52

Table S2: Study of the influence of the alkyl-chain length of the longer ammonium salt on the emissive properties of the perovskites in the absence of OLA

Name	Ammonium salt	Ammonium salt (mmol)	MABr (mmol)	$PbBr_2$ (mmol)	ODE (mmol)	Emission maximum (λ, nm)	ϕ_F
$\mathbf{P_{EA}}$	EABr	0.16	0.24	0.1	6.26	[a]	-
$\mathbf{P_{HA}}$	HABr	0.16	0.24	0.1	6.26	526	0.58

[a] An orange solid not dispersible in toluene was obtained.

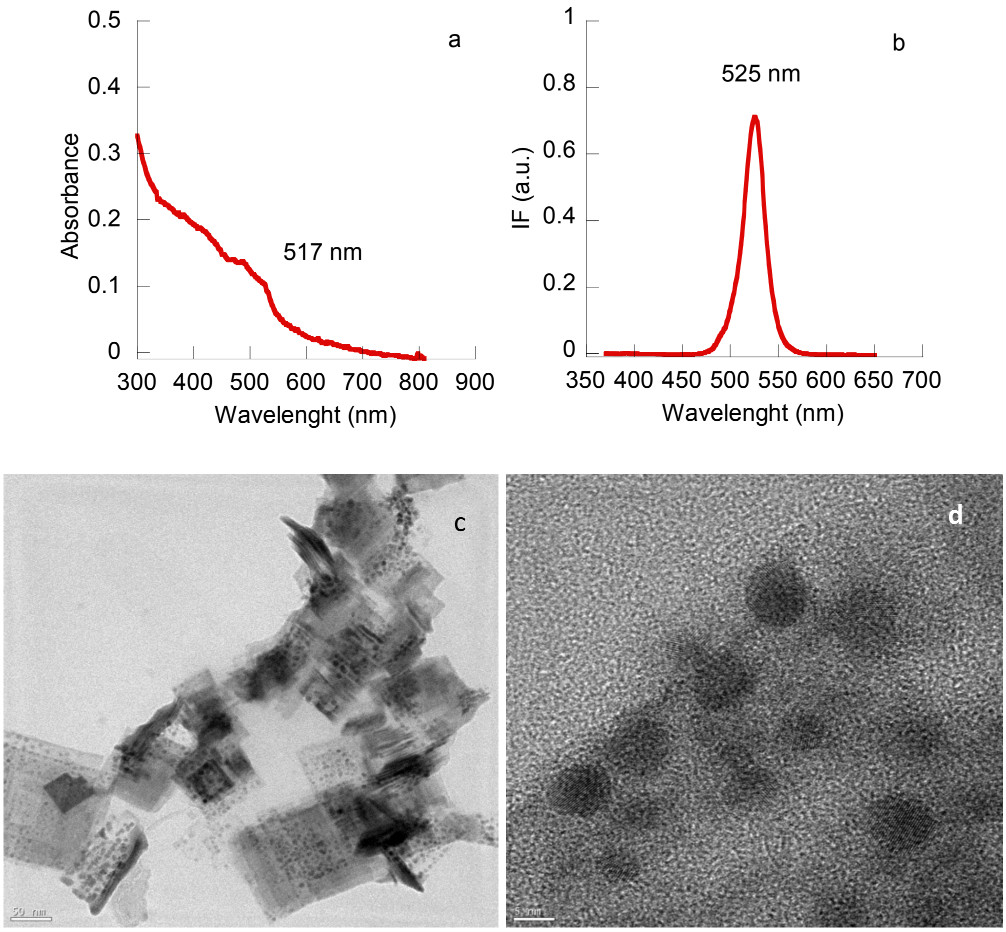


Figure S2: Absorption (a) and emission (b) spectra of $\mathbf{P_{OA3}}$ in toluene; emission recorded at λ_{exc}= 350 nm. (c) and (d) HRTEM images at 50 and 5 nm scale, respectively. Nanoparticle size 5.92 ± 1.79 nm.

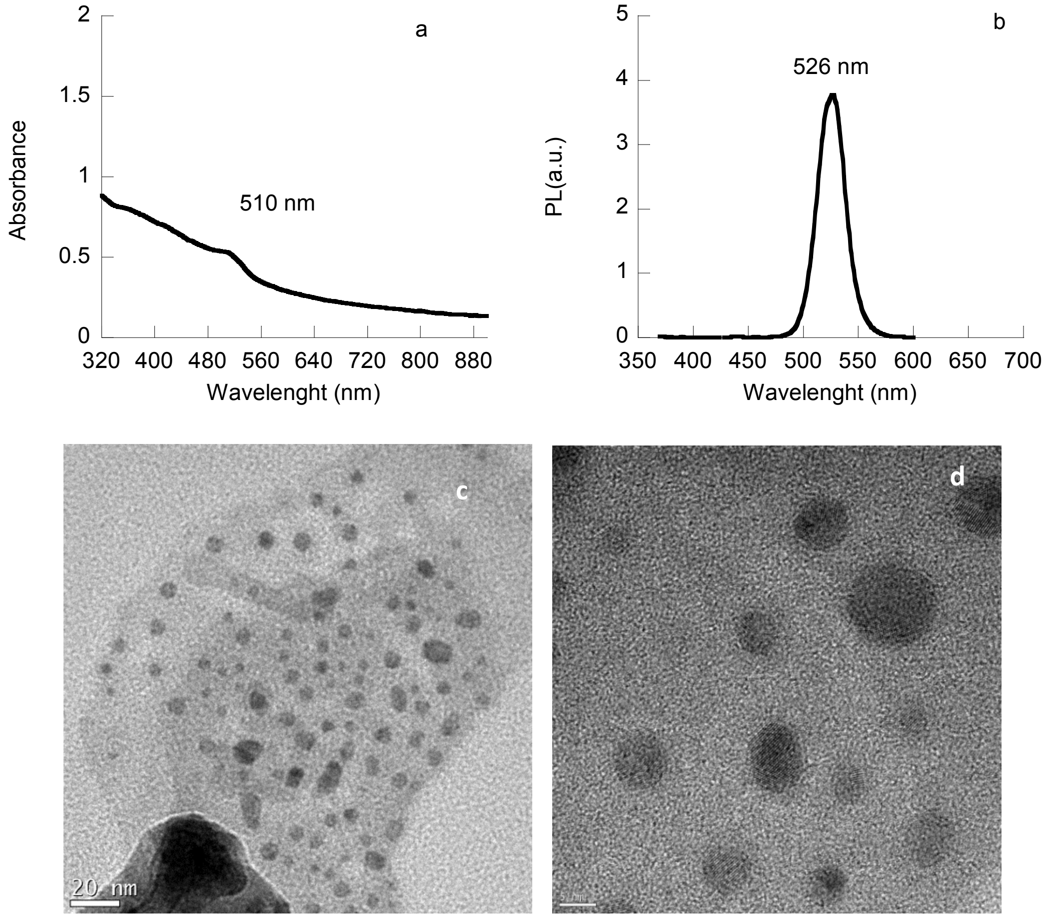


Figure S3: Absorption and emission spectra of $\mathbf{P_{HA}}$ (a, b) in toluene; emission recorded at λ_{exc}= 350 nm, and HRTEM images with a scale bar of 20 (c) and 5 nm (d). Size 5.92 ± 2.05 nm

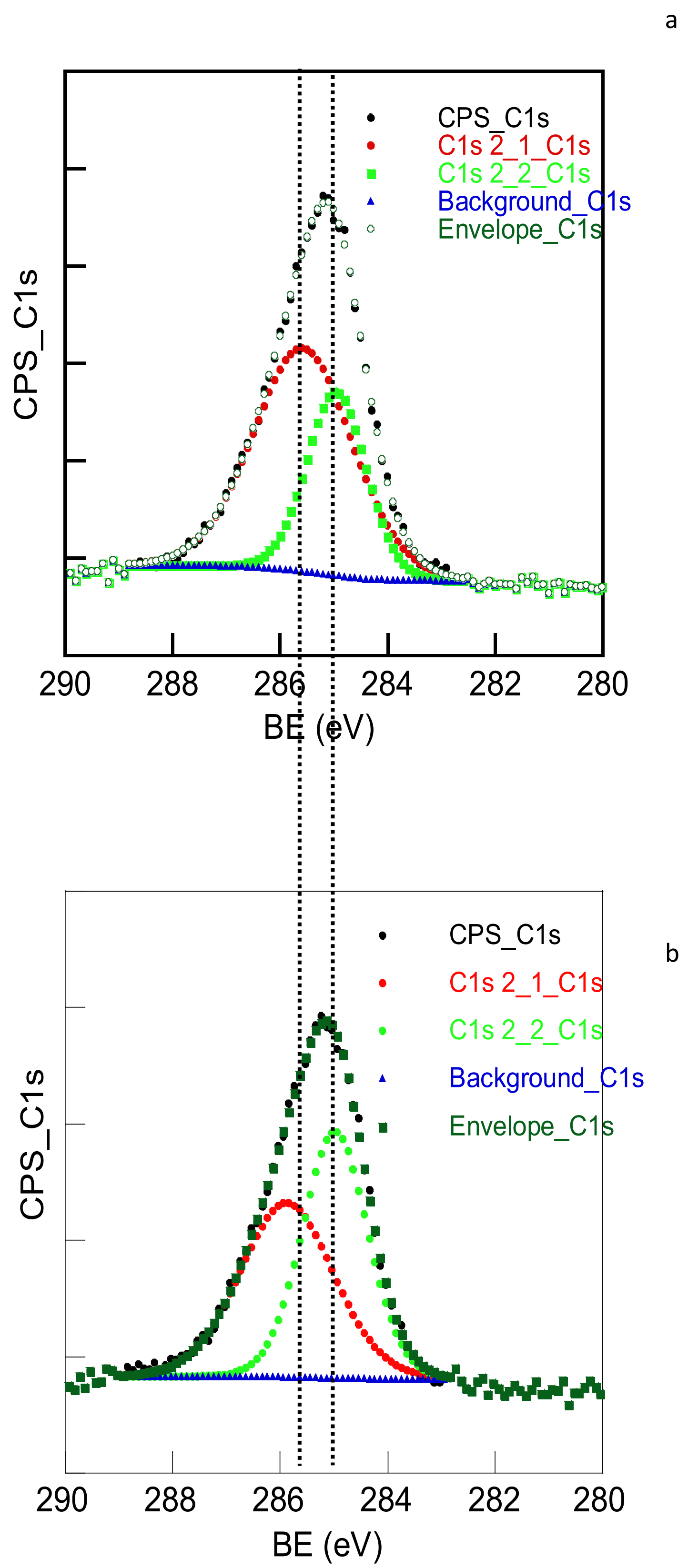
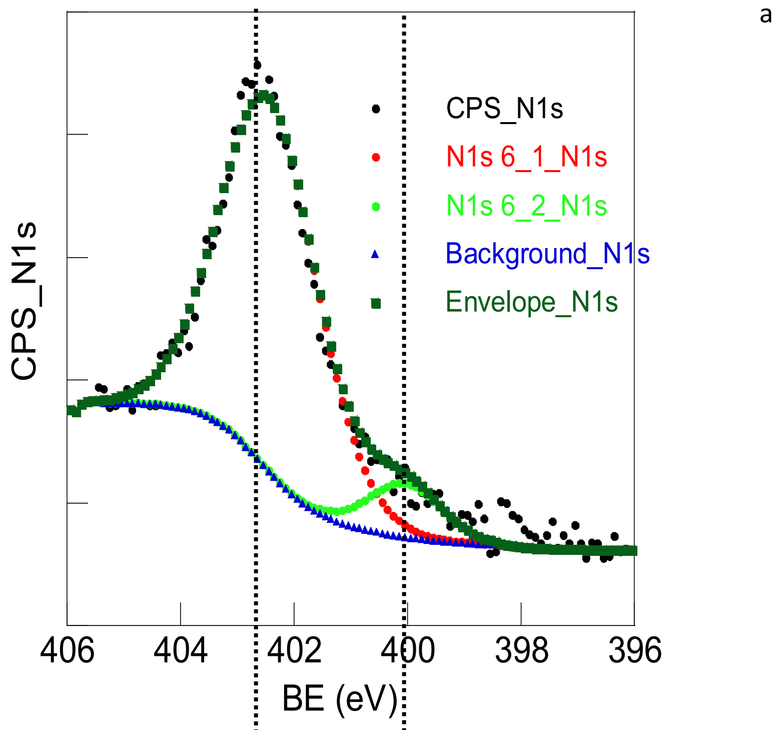


Figure S4: XPS spectra of C1s for P_{OA1} (a) and P_{OA2} (b)



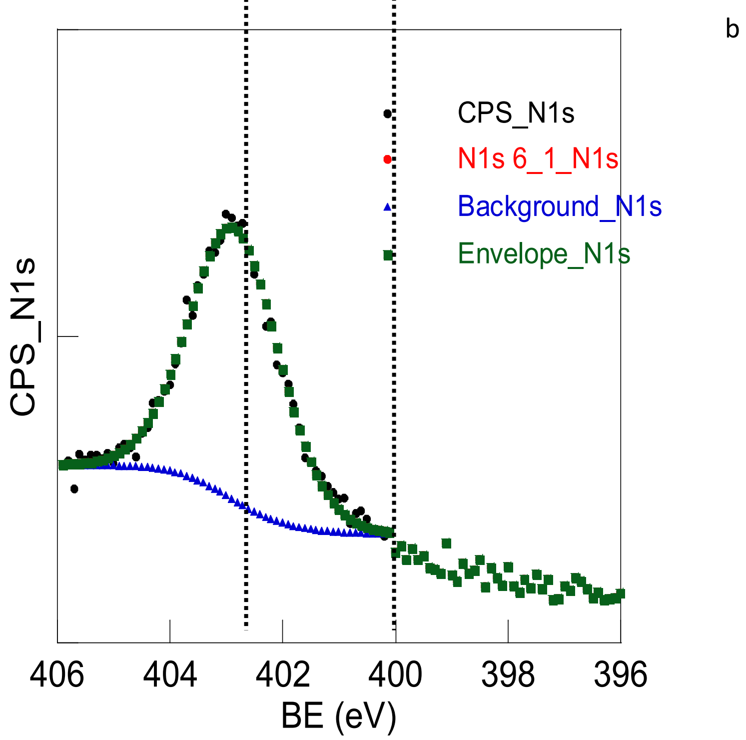
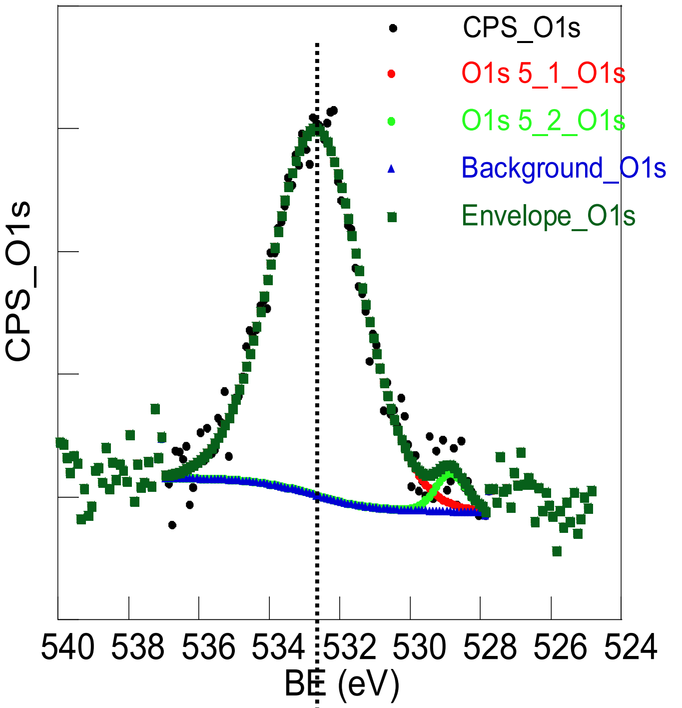


Figure S5: XPS spectra of N1s for P_{OA1} (a) and P_{OA2} (b) a



b

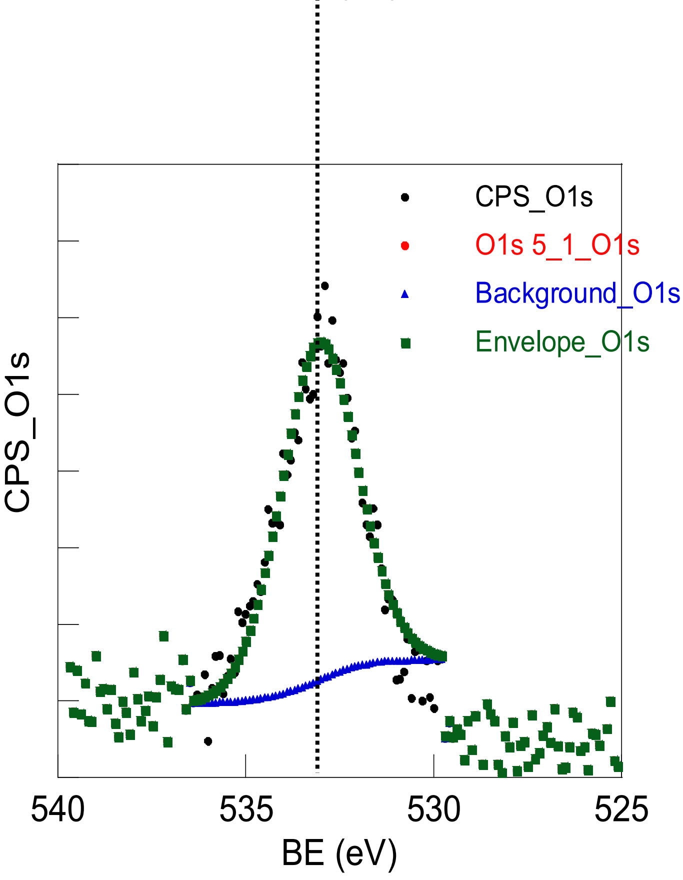


Figure S6: XPS spectra of O1s for P_{OA1} (a) and P_{OA2} (b)

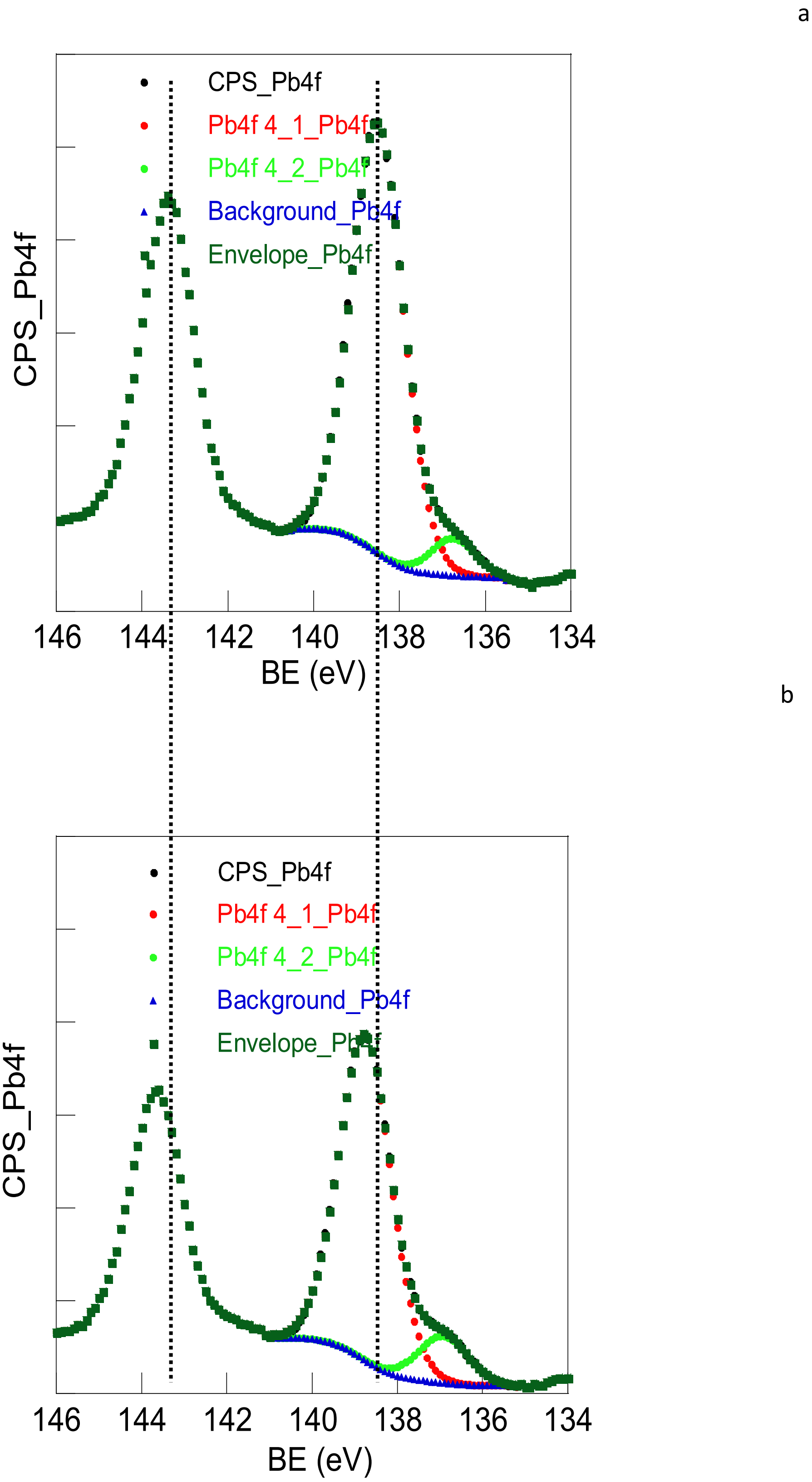
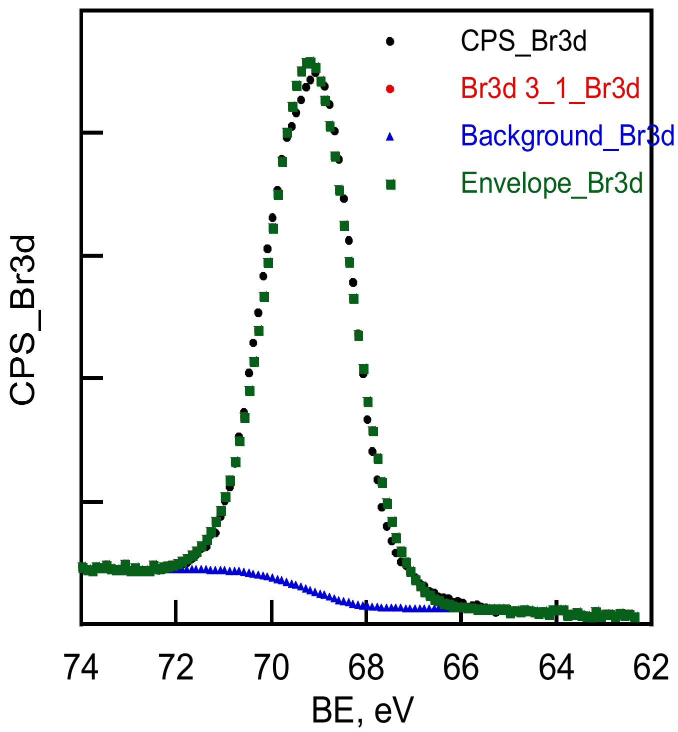


Figure S7: XPS spectra of Pb4f for P_{OA1} (a) and P_{OA2} (b) a



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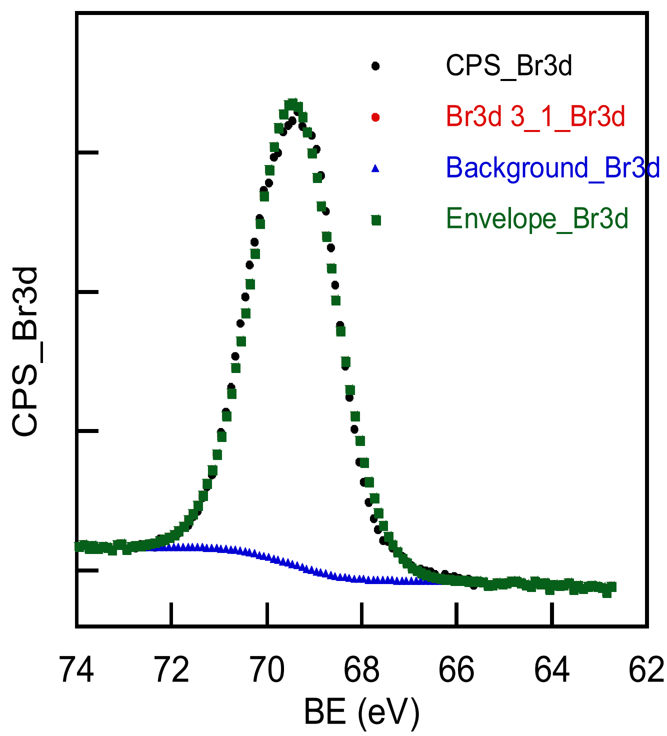

Figure S8: XPS spectra of Br 3d for P_{OA1} (a) and P_{OA2} (b)

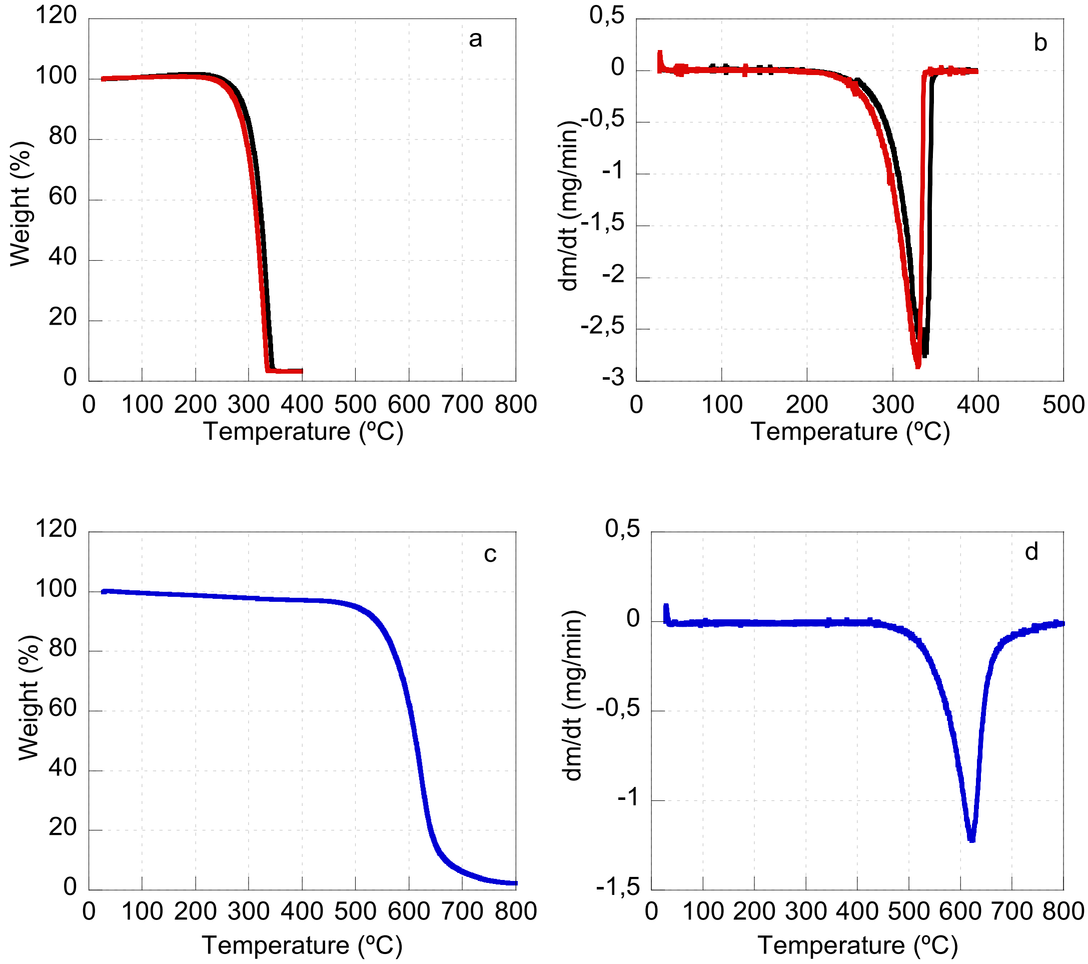

Figure S9: TGA heating curve of MABr and OABr (a, black and red, respectively) and of $PbBr_2$ (c); 1st derivative peaks of MABr and OABr (b, black and red, respectively) and of $PbBr_2$ (d).

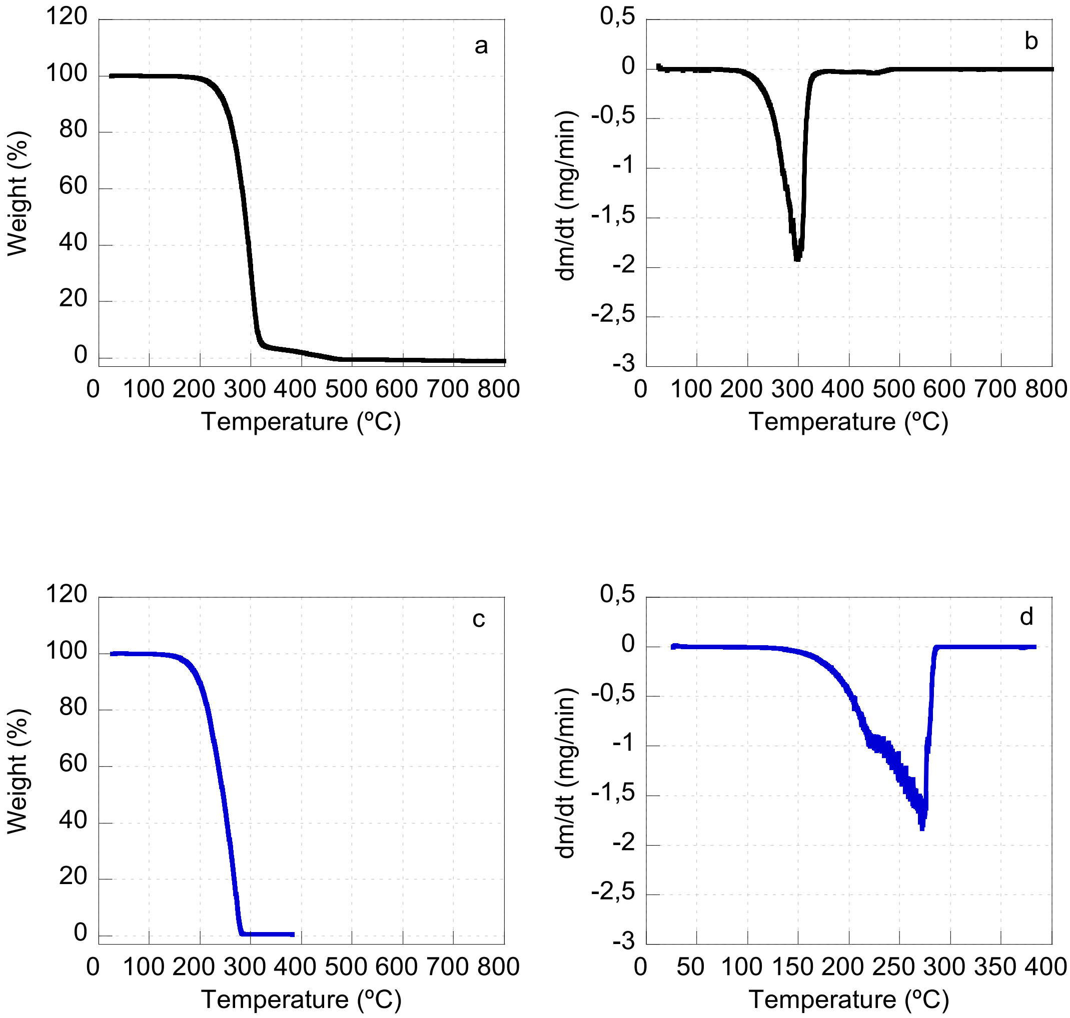

Figure S10: TGA heating curve of OLA and ODE (a and c, in black and blue, respectively) and its 1st derivative peaks (b and d).

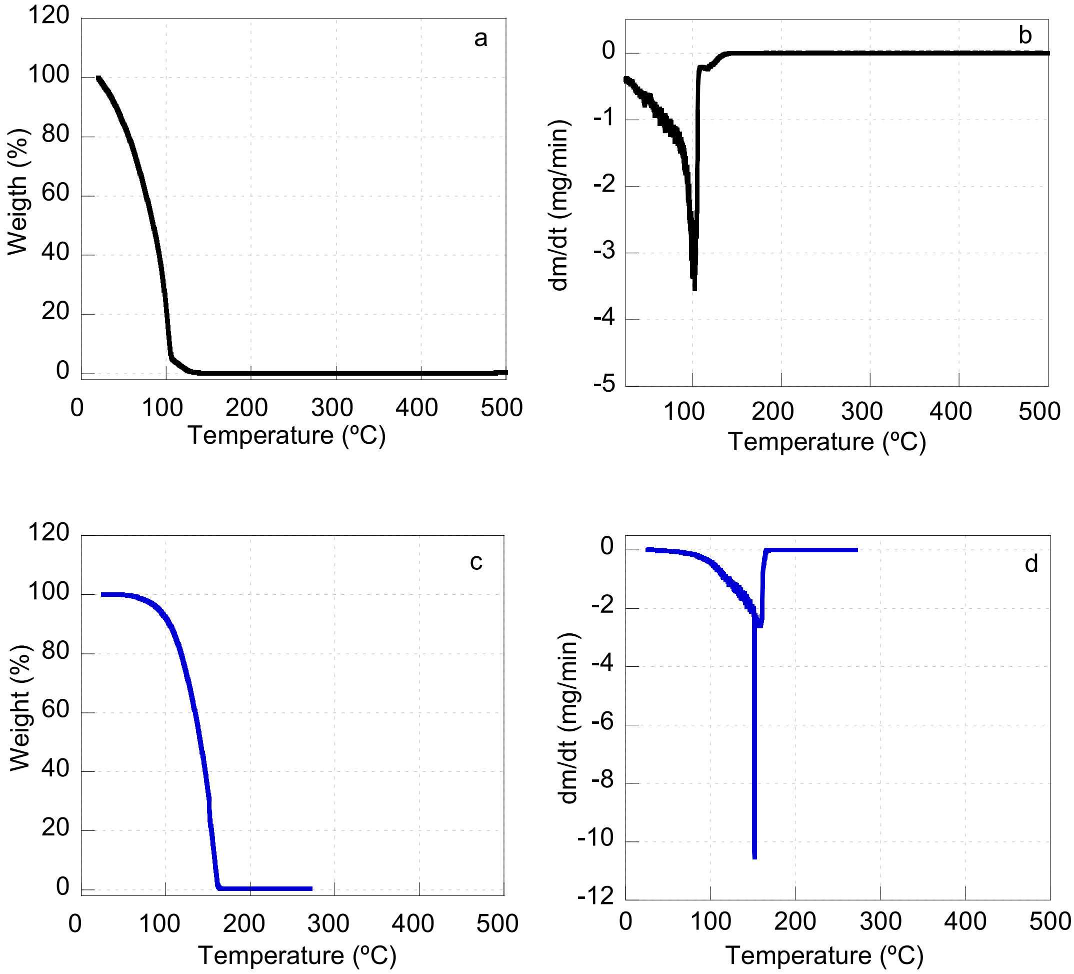

Figure S11: TGA heating curve of MA and OA (a and c, in black and blue, respectively) and its 1st derivative peaks (b and d).

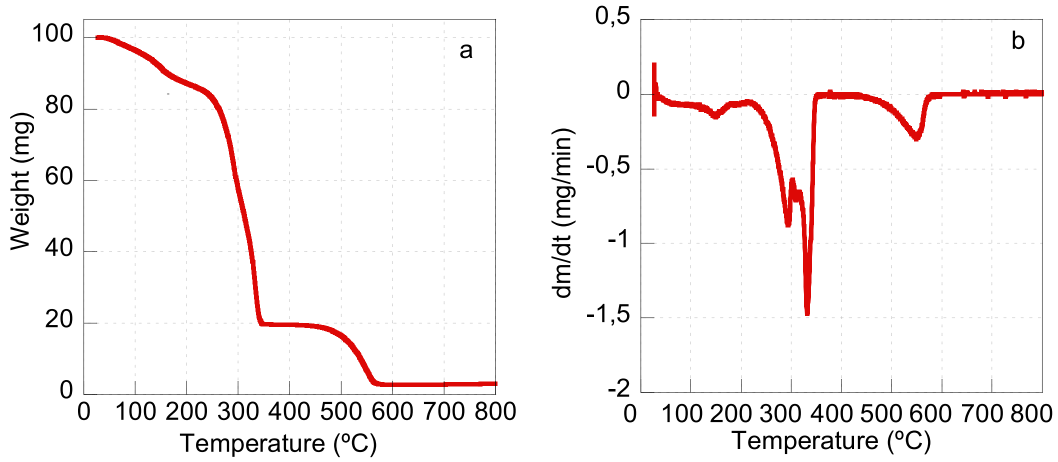

Figure S12: TGA heating curve of **Ss1** (a) and its 1st derivative peaks (b).

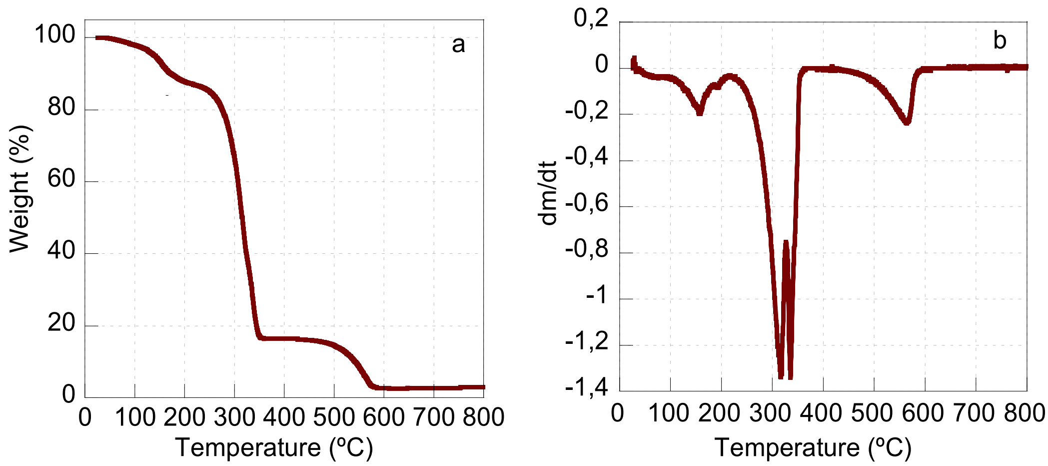

Figure S13: TGA heating curve of **Ss2** (a) and its 1st derivative peaks (b).

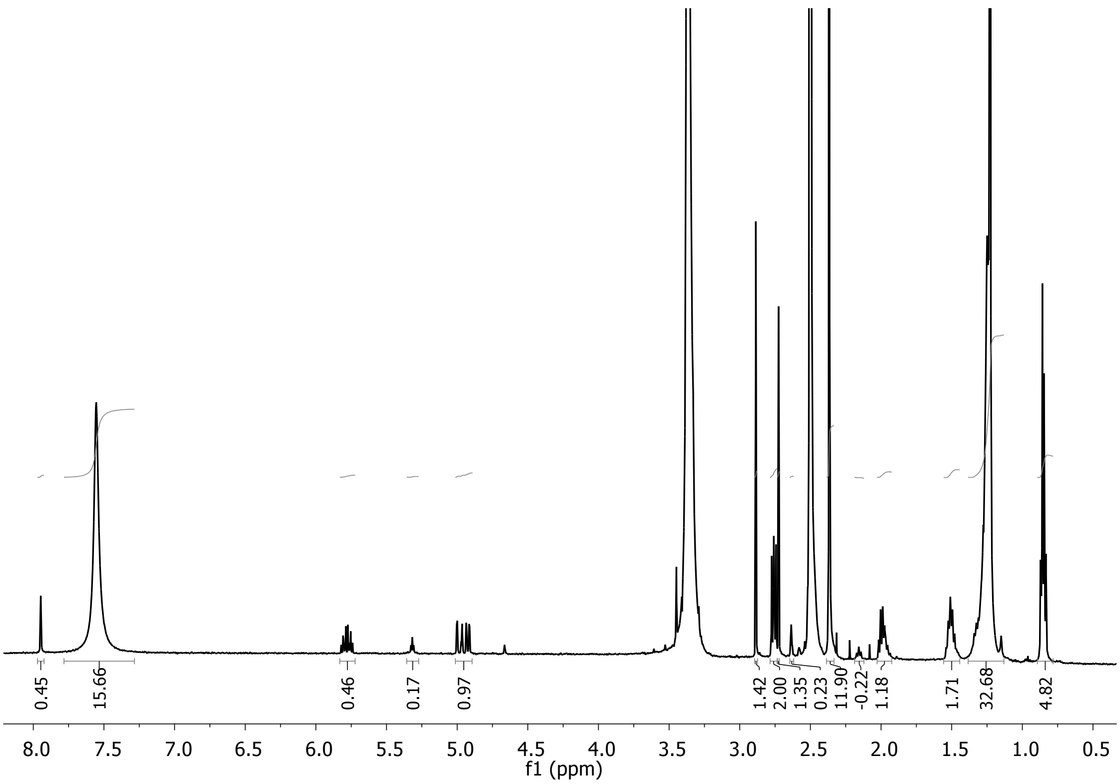

Figure S14: ^{1}H NMR (300 MHz) spectrum of P_{OA1} in deuterated DMSO

[1] H-NMR of the precursors

Methylammonium bromide

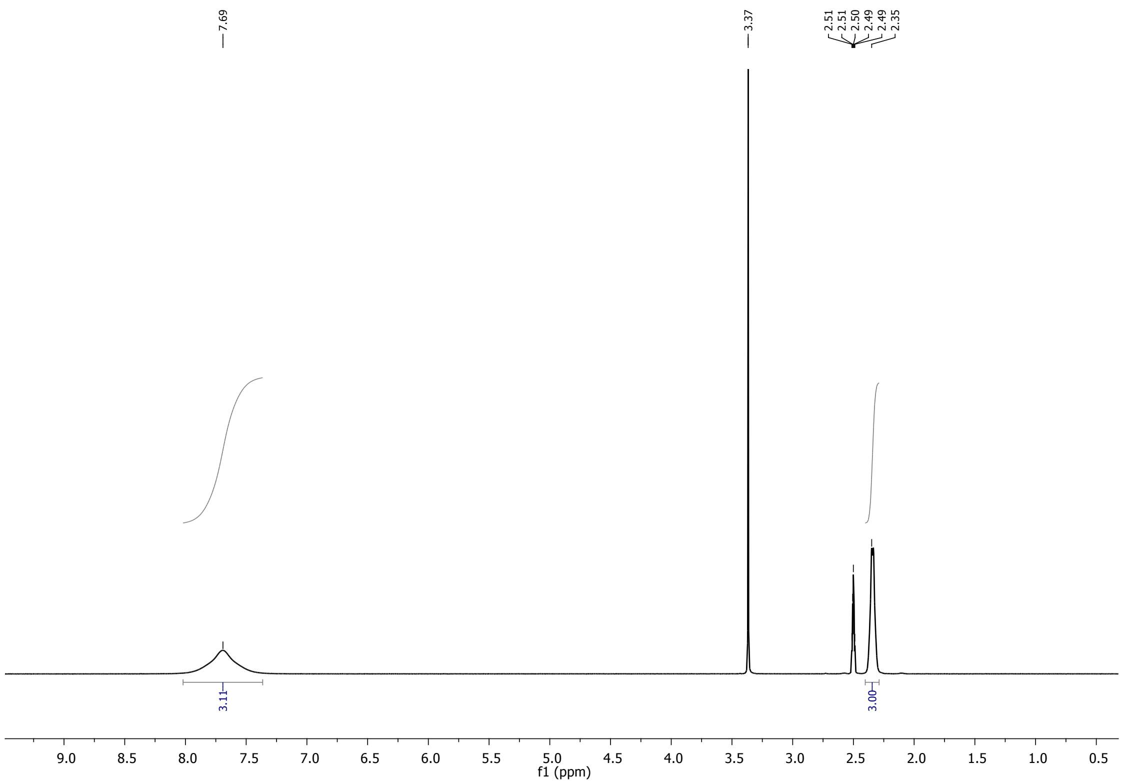

Figure S15. ^{1}H NMR (300 MHz) spectrum of methylammonium bromide in deuterated DMSO.

^{1}H NMR (300 MHz, d-DMSO) δ 7.69 (s, 3H), 2.34 (s, 3H).

Octylammonium bromide

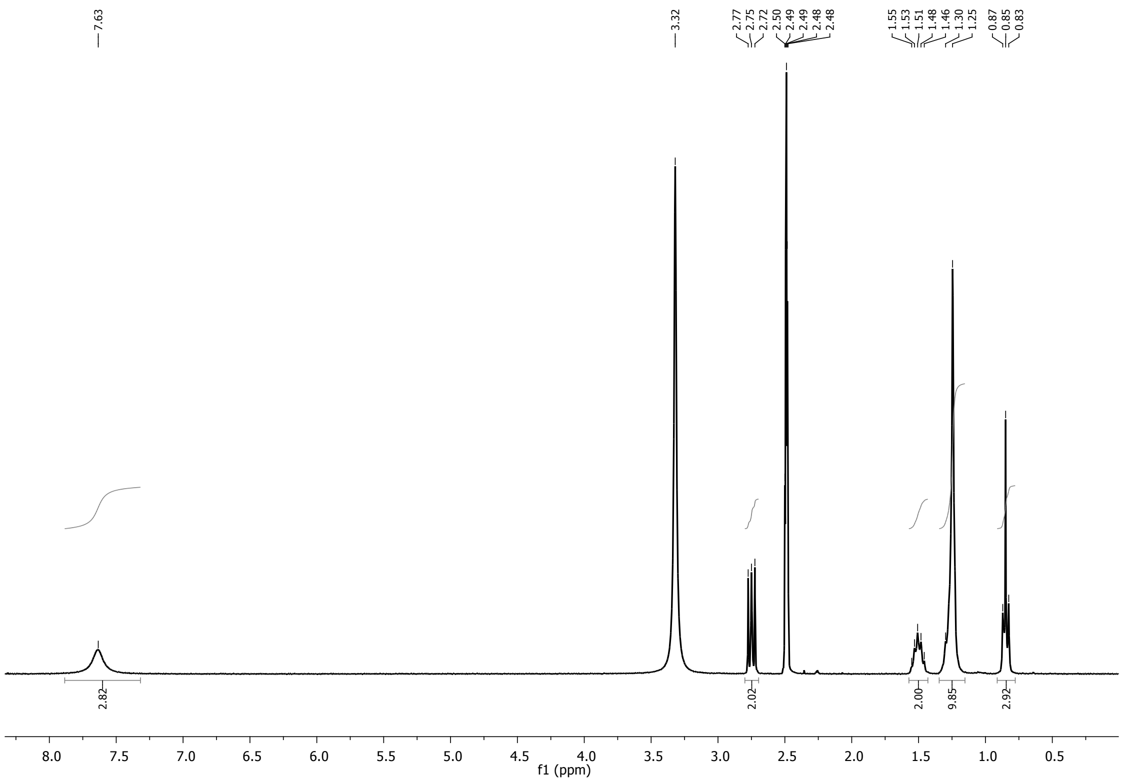

Figure S16. ^{1}H NMR (300 MHz) spectrum of octylammonium bromide in deuterated DMSO.

^{1}H NMR (300 MHz, d-DMSO) δ 7.63 (s, 3H), 2.75 (t, *J* = 7.5 Hz, 2H), 1.59 – 1.41 (m, 2H), 1.27 (s, 10H), 0.85 (t, *J* = 7.0 Hz, 3H).

Oleic acid

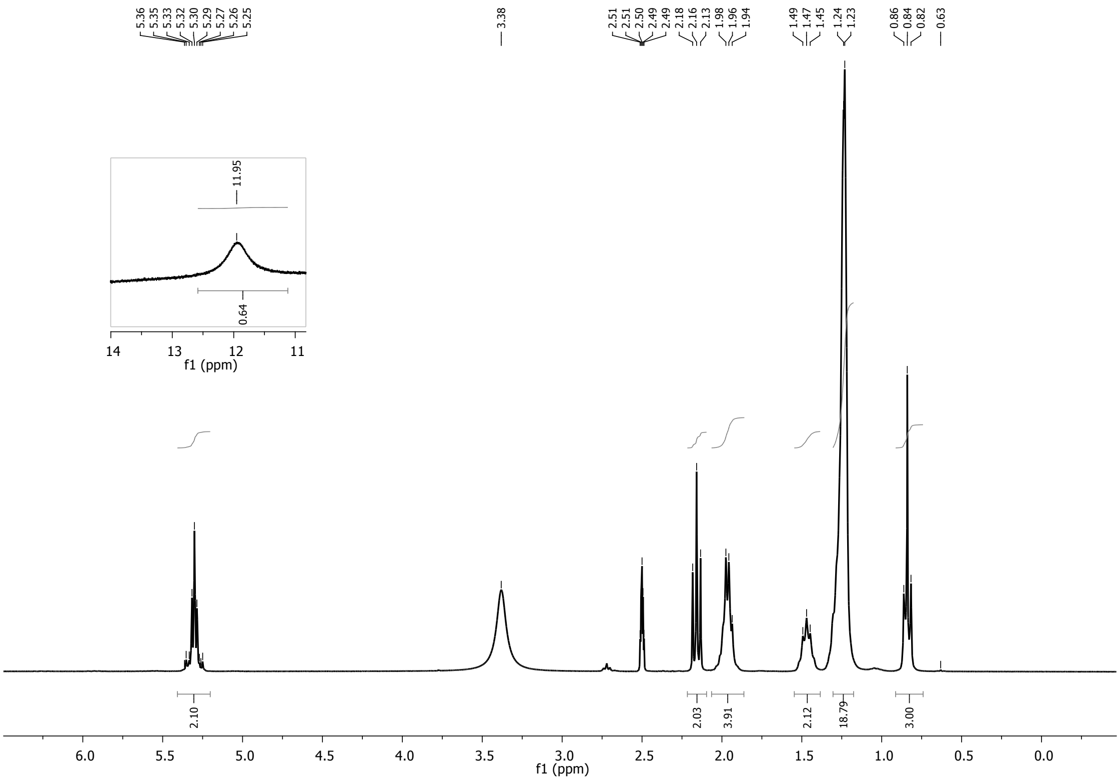

Figure S17. ^{1}H NMR (300 MHz) spectrum of oleic acid in deuterated DMSO.

^{1}H NMR (300 MHz, d-DMSO) δ 11.95 (s, 1H), 5.41 – 5.20 (m, 2H), 2.16 (t, *J* = 7.4 Hz, 2H), 2.06 – 1.86 (m, 4H), 1.55 – 1.38 (m, 2H), 1.23 (d, *J* = 2.3 Hz, 19H), 0.91 – 0.74 (m, 3H).

Octadecene

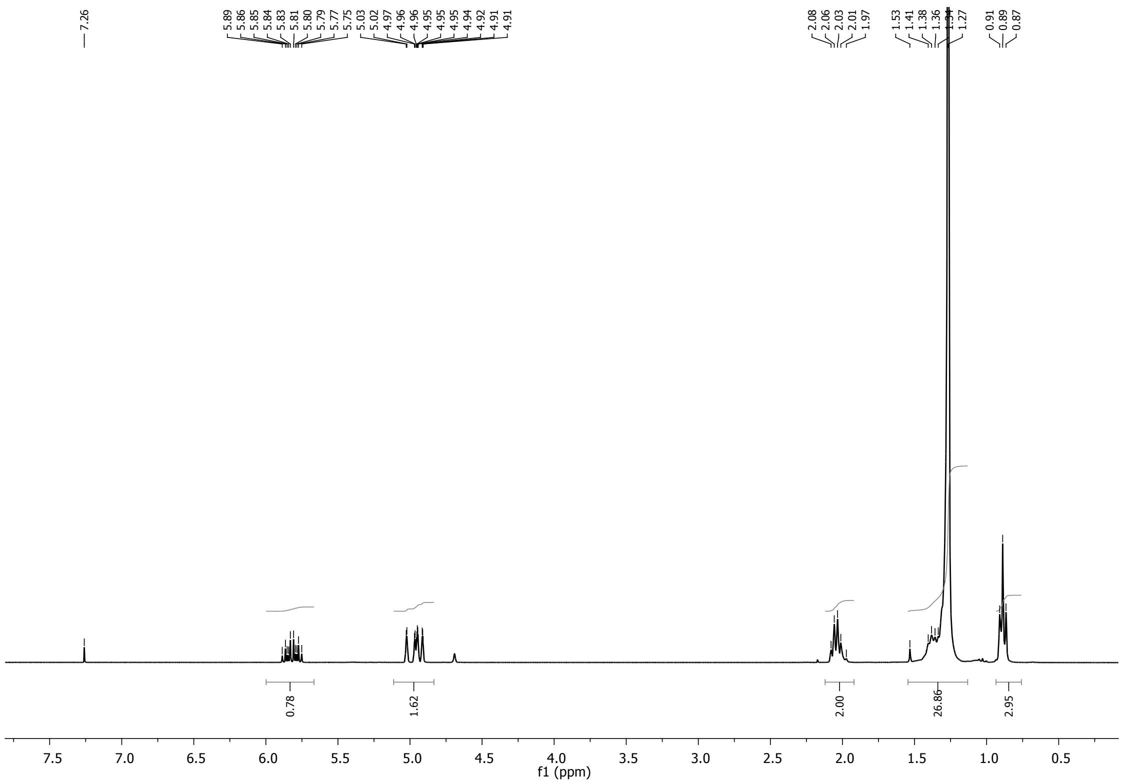

Figure S18. ^{1}H NMR (300 MHz) spectrum of 1-octadecene in deuterated DMSO.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.12 – 4.76 (m, 2H), 2.12 – 1.92 (m, 2H), 1.60 – 0.97 (m, 27H), 0.89 (t, *J* = 6.6 Hz, 3H).

Table S3. Quantification of the component molar ratio in $\mathbf{P_{OA1}}$ by using TGA and ^{1}H-RMN data

Reagents	Reagents mmol	P_{OA1}	
		Component mmol	**Component/$PbBr_2$* Molar ratio**
OABr	0.24	0.031	**0.35**
MABr	0.16	0.122	**1.39**
ODE	6.17	0.015	**0.17**
OLA	0.29	0.003	**0.03**
$PbBr_2$	0.10	0.088	**1.00**

*Moles of $PbBr_2$ calculated by TGA.

Table S4. Quantification of the component molar ratio in $\mathbf{P_{OA2}}$ by using TGA and ^{1}H-RMN data

Reagents	Reagents mmol	P_{OA2}	
		Component mmol	**Component/$PbBr_2$* Molar ratio**
OABr	0.24	0.011	**0.11**
MABr	0.16	0.131	**1.37**
ODE	6.17	0.025	**0.26**
$PbBr_2$	0.10	0.088	**1.00**

*Moles of $PbBr_2$ calculated by TGA.

Table S5. Decay photoluminescence lifetimes (τ) of toluene solutions of $\mathbf{P_{OA1}}$ at different excitation wavelengths (λ_{exc})

λ_{exc}	τ_{av} **(ns)**	τ_1 **(A_1 %) (ns)**	τ_2 **(A_2 %) (ns)**	τ_3 **(A_3 %) (ns)**
340 nm	**411.17**	18.68 (54.62)	123.53 (34.52)	643.80 (10.86)
405 nm	**415.92**	13.22 (61.36)	115.20 (30.20)	661.60 (8.45)
470 nm	**403.78**	18.36 (61.11)	132.29 (29.87)	657.56 (9.02)

Table S6. Decay photoluminescence lifetimes (τ) of toluene solutions of $\mathbf{P_{OA2}}$ at different excitation wavelengths (λ_{exc})

λ_{exc}	τ_{av} **(ns)**	τ_1 **(A_1 %) (ns)**	τ_2 **(A_2 %) (ns)**	τ_3 **(A_3 %) (ns)**
340 nm	**594.45**	19.65 (57.99)	148.88 (32.31)	910.85 (9.71)
405 nm	**611.43**	15.08 (58.27)	138.03 (32.20)	913.33 (9.53)
470 nm	**621.80**	20.10 (55.93)	149.14 (33.55)	931.83 (10.53)

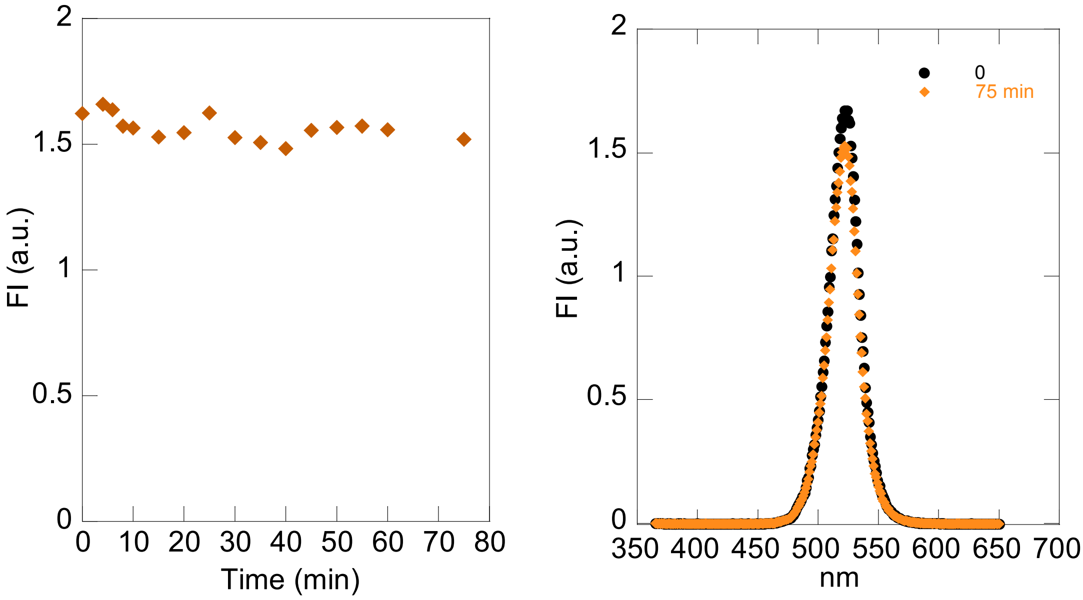

Figure S19. Left: Room-temperature photoluminescence of $\mathbf{P_{OA2}}$ in toluene (λ_{em}= 521 nm) as a function of the illumination time. Right: fluorescence spectra of the sample (λ_{exc}= 350 nm; λ_{em}= 521 nm) before and after 75 minutes irradiation.