Supplementary Information (SI) for Analyst.

Identification of common textile microplastics via autofluorescence spectroscopy coupled with k-means cluster analysis supplementary information

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FT-IR spectral processing

Baseline removal was performed on the FT-IR spectra using the peak analyser function in OriginPro 2023 (OriginLab (Northampton, MA)). The asymmetric least squares smoothing mode was used for this with the parameters kept constant for each polymer type (Supplementary Information, Table S2). The baseline removal resulted in negative transmittance values with a maximum value of zero.

Normalization of the baseline-subtracted FT-IR spectra was performed as a two-step process: Firstly, the spectrum was adjusted such that the minimum transmittance value of the spectrum (T_{min}) was equal to zero, i.e. all transmittance values became positive, Equation S1:

$$T_{\nu,min} = T_{\nu} - T_{min} \tag{S1}$$

where $T_{\nu,min}$ is the value of the spectrum transmittance at wavenumber ν after adjustment of the minimum spectrum transmittance, and T_{ν} is the original transmittance value at wavenumber ν.

Secondly, the spectrum was normalized to the maximum transmittance value of the new spectrum ($T_{min,max}$), Equation S2:

$$T_{\nu,norm} = T_{\nu,min}/T_{min,max} \tag{S2}$$

where $T_{\nu,norm}$ is the normalized value of the spectrum transmittance at wavenumber ν. The manipulation produced a spectrum with a transmittance range between one and zero. This effectively stretched the spectra to minimize differences in spectral values between samples of the same polymer type that may have arisen due to variation in the acquisition process, such as contact between the sample and the ATR crystal. However, it must be noted that, upon application of this normalization procedure, a change in the transmittance of the dominant FT-IR band upon a chemical change, such as photooxidation, would result in a slight shift in the transmittance of the other bands in the normalized spectra. This occurs because the dominant FT-IR band always has a transmittance value of zero.

FT-IR band ratio determination

Given the recording of the FT-IR data as transmittance, rather than absorbance, the ratios between bands were determined by deducting the transmittance values from one prior to determination of the ratio, Equation S3:

$$R_{\nu_1,\nu_2} = 1 - T_{\nu_1}/1 - T_{\nu_2} \tag{S3}$$

where R_{ν_1,ν_2} is the ratio between the band transmittance at wavenumber ν_1 (T_{ν_1}) and the band transmittance at wavenumber ν_2 (T_{ν_2}).

Fluorescence spectral processing

Normalization of the autofluorescence spectra was performed as a two-step process: Firstly, the minimum band intensity of the spectrum (I_{min}) was subtracted from each of the bands at the other emission wavelengths (I_{λ}), Equation S4:

$$I_{\lambda,min} = I_{\lambda} - I_{min} \tag{S4}$$

where $I_{\lambda,min}$ is the value of band intensity at wavelength λ after subtraction of the minimum band intensity. The manipulation produced a spectrum with the minimum band intensity of zero.

Secondly, the spectrum was normalized to the maximum band intensity of the new spectrum ($I_{min,max}$), Equation S5:

$$I_{\lambda,norm} = I_{\lambda,min}/I_{min,max} \tag{S5}$$

where $I_{\lambda,norm}$ is the normalized intensity of the emission band at wavelength λ. This manipulation produced a spectrum with an intensity range between one and zero.

Statistical analysis

Statistical analysis was performed using IBM SPSS Statistics software. A one-way analysis of variance (ANOVA) test was used to determine the statistical differences between the means of three, or more, samples, assuming equal variance, with Tukey posthoc comparison. Differences were considered significant with a confidence level of 0.95 (95% confidence).

Table S1. Physical properties of synthetic polymer samples investigated as provided by manufacturers.

Polymer	Sample ID	Density [g cm^{-3}]	Length [µm]	Width [µm]
Acrylic (PAN/ secondary polymer)	AC3/30	1.17-1.18	2700-3300	10-19
	PAN60	1.17-1.18	75-175	19-25
	PAN1200	1.17-1.18	450-650	29-25
Polyamide (Nylon-6,6)	N3/10	1.3-1.4	700-1300	16-20
	N3/20	1.3-1.4	1800-2200	16-20
	N3/30	1.3-1.4	2700-3300	18
	WN60	1.3-1.4	125-250	16-20
Polyester (PET)	PES1000	1.3-1.4	350-800	6-18
	ZZ	1.3-1.4	122	6-18
	P6/30	1.3-1.4	2700-3300	16-20
	PE60	1.3-1.4	75-175	10-30
Polyethylene (PE)	HMPE35A	0.95	10-15	10-15
	HMPE95A	0.95	40-60	40-60
	HMPE125A	0.95	60-90	60-90
	HMPE500A	0.95	300-450	300-450
Polypropylene (PP)	DA3/15	0.91	1300-1800	22
	DA3/30	0.91	2700-3300	22
	DA3/50	0.91	4500-5500	22

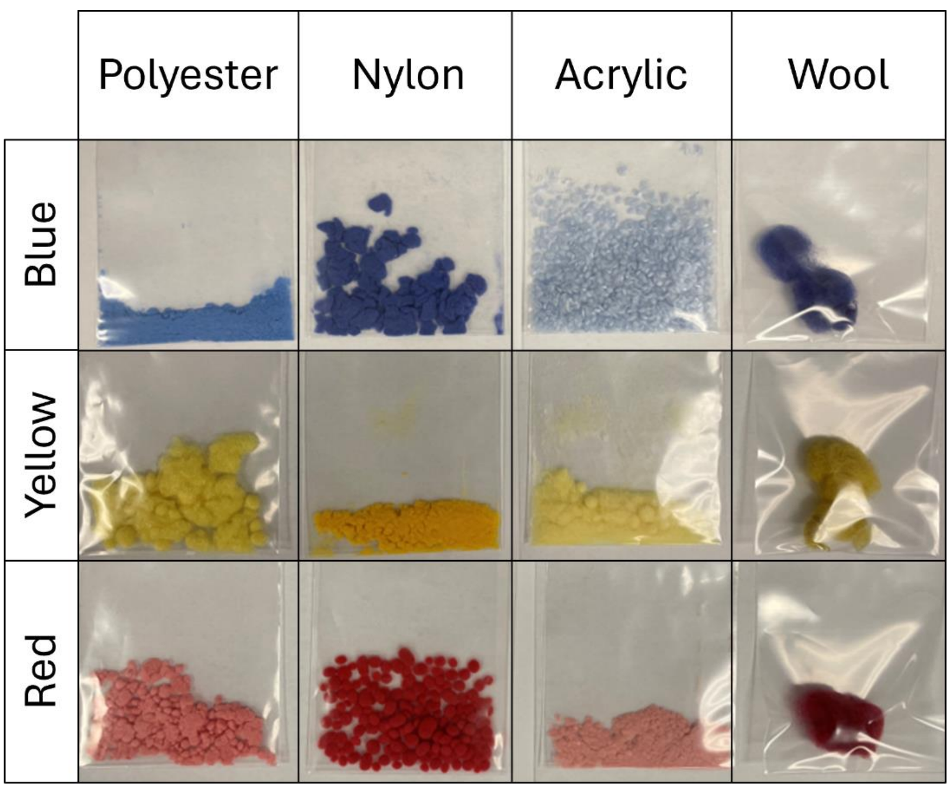

Figure S1. Photos of dyed polymer and wool samples.

Table S2. Baseline subtraction parameters used to remove FT-IR baseline from polymer samples in Origin Pro 2023.

Sample	Baseline subtraction parameters			
	Asymmetric factor	**Threshold**	**Smoothing factor**	**No. of iterations**
Acrylic	0.99	0.01	4	20
Polyamide	0.9999	0.01	5	20
Polyester	0.9999	0.004	5	20
PE	0.9999	0.01	8	20
PP	0.9999	0.01	7	20
Cellulose	0.9999	0.004	5	20
Wool	0.9999	0.005	5	20

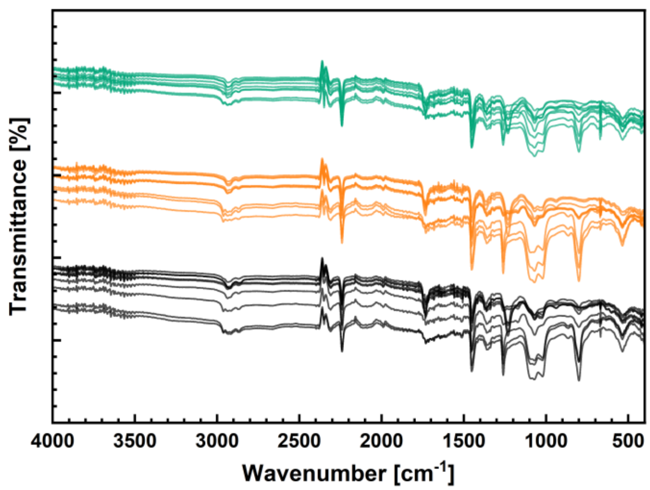

Figure S2. Raw FT-IR spectra prior to processing for acrylic samples (black line: 0 min UV-ozone exposure, orange line: 10 min UV-ozone exposure, green line: 60 min UV-ozone exposure; three repeats per sample)

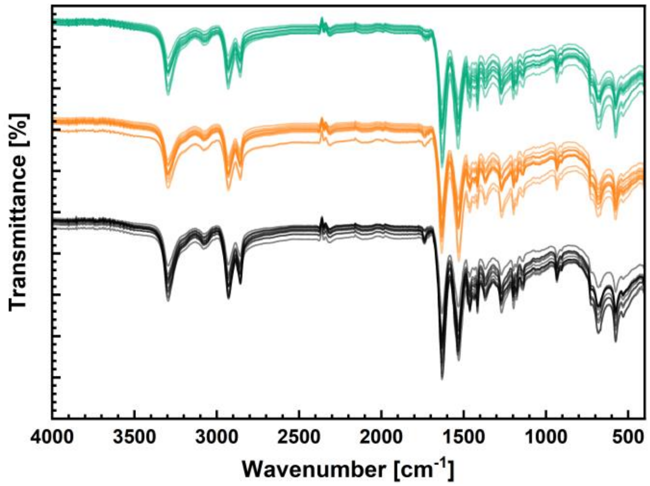

Figure S3. Raw FT-IR spectra prior to processing for polyamide samples (black line: 0 min UV-ozone exposure, orange line: 10 min UV-ozone exposure, green line: 60 min UV-ozone exposure; three repeats per sample)

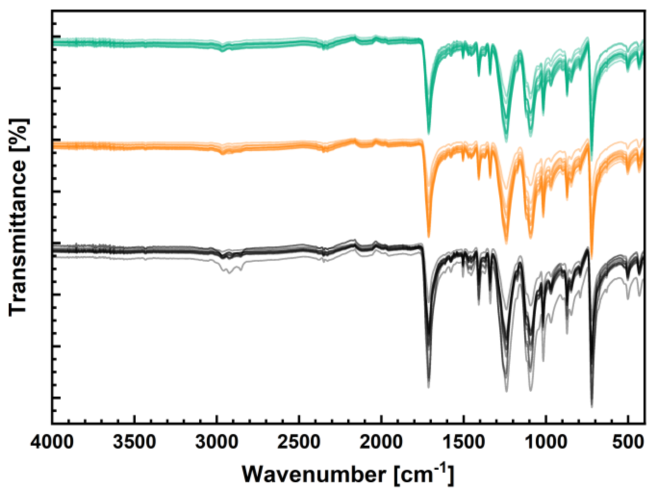

Figure S4. Raw FT-IR spectra prior to processing for polyester samples (black line: 0 min UV-ozone exposure, orange line: 10 min UV-ozone exposure, green line: 60 min UV-ozone exposure; three repeats per sample)

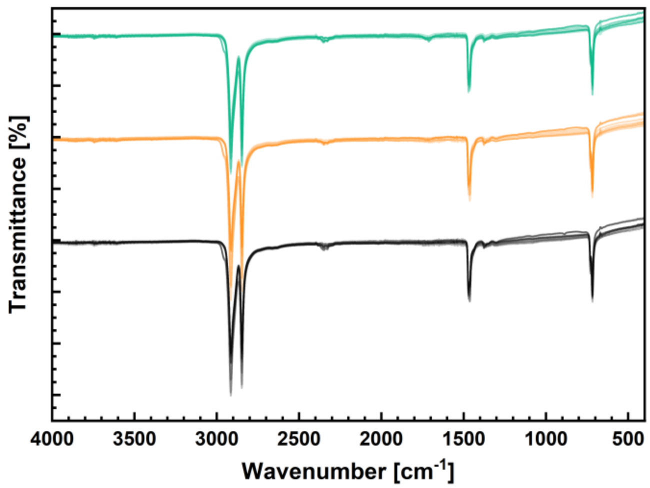

Figure S5. Raw FT-IR spectra prior to processing for polyethylene samples (black line: 0 min UV-ozone exposure, orange line: 10 min UV-ozone exposure, green line: 60 min UV-ozone exposure; three repeats per sample)

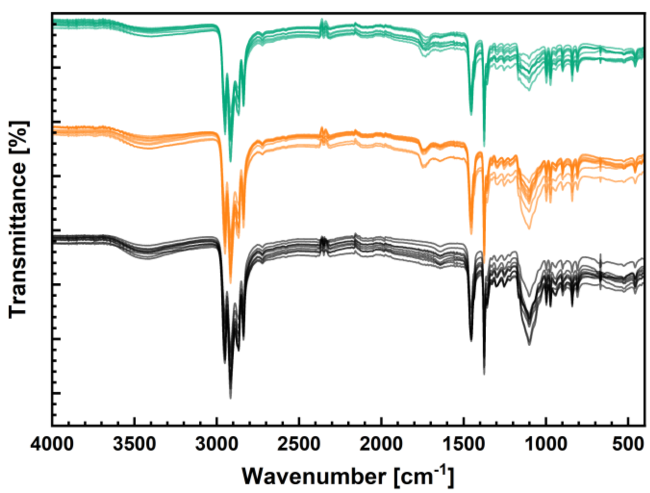

Figure S6. Raw FT-IR spectra prior to processing for polypropylene samples (black line: 0 min UV-ozone exposure, orange line: 10 min UV-ozone exposure, green line: 60 min UV-ozone exposure; three repeats per sample)

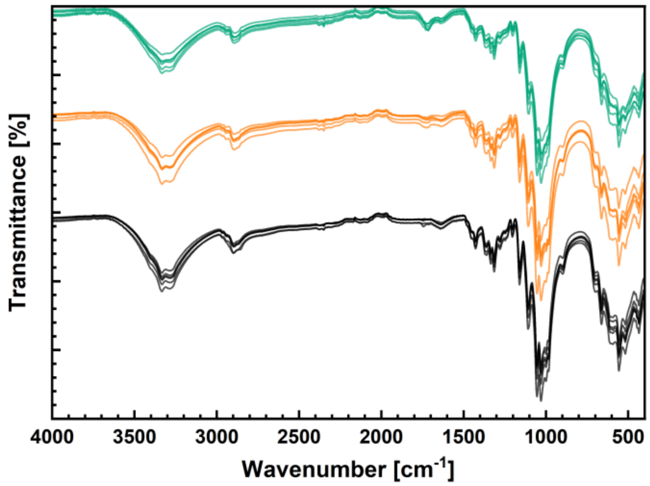

Figure S7. Raw FT-IR spectra prior to processing for cellulose samples (black line: 0 min UV-ozone exposure, orange line: 10 min UV-ozone exposure, green line: 60 min UV-ozone exposure; three repeats per sample)

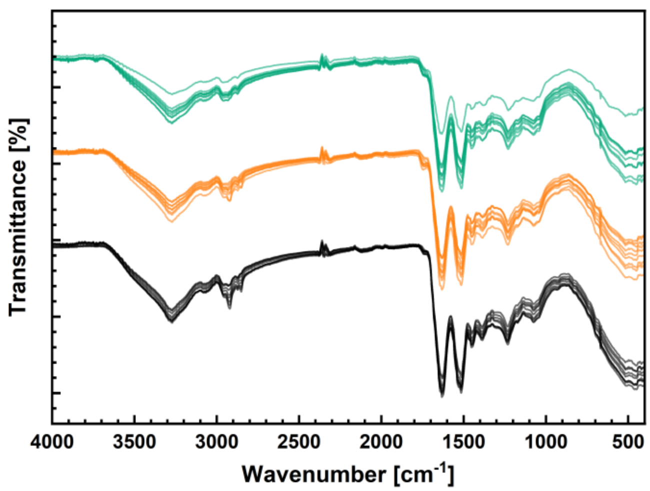

Figure S8. Raw FT-IR spectra prior to processing for wool samples (black line: 0 min UV-ozone exposure, orange line: 10 min UV-ozone exposure, green line: 60 min UV-ozone exposure; three repeats per sample)

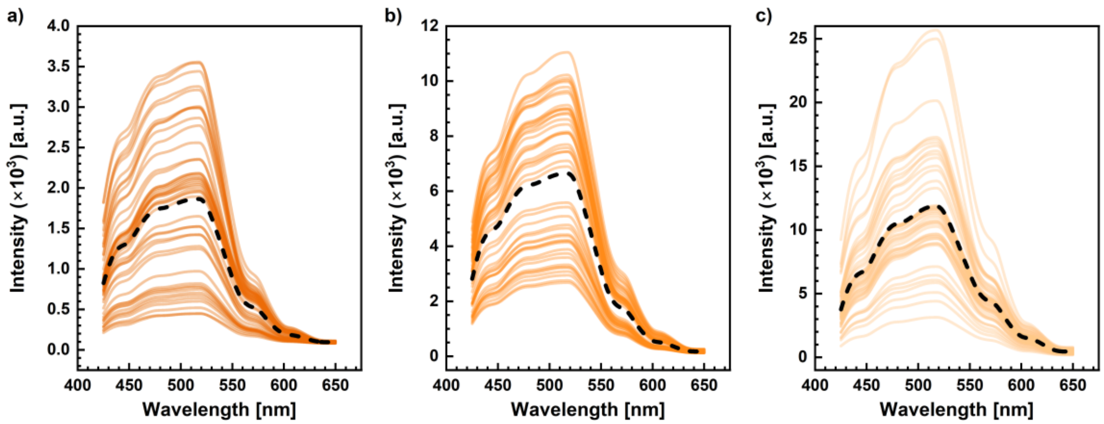

Figure S9. Raw autofluorescence spectra for acrylic samples after **a)** 0 min, **b)** 10 min and **c)** 60 min UV-ozone exposure (black dashed line: average spectrum). Laser power: 60%, correction factor: 2.94.

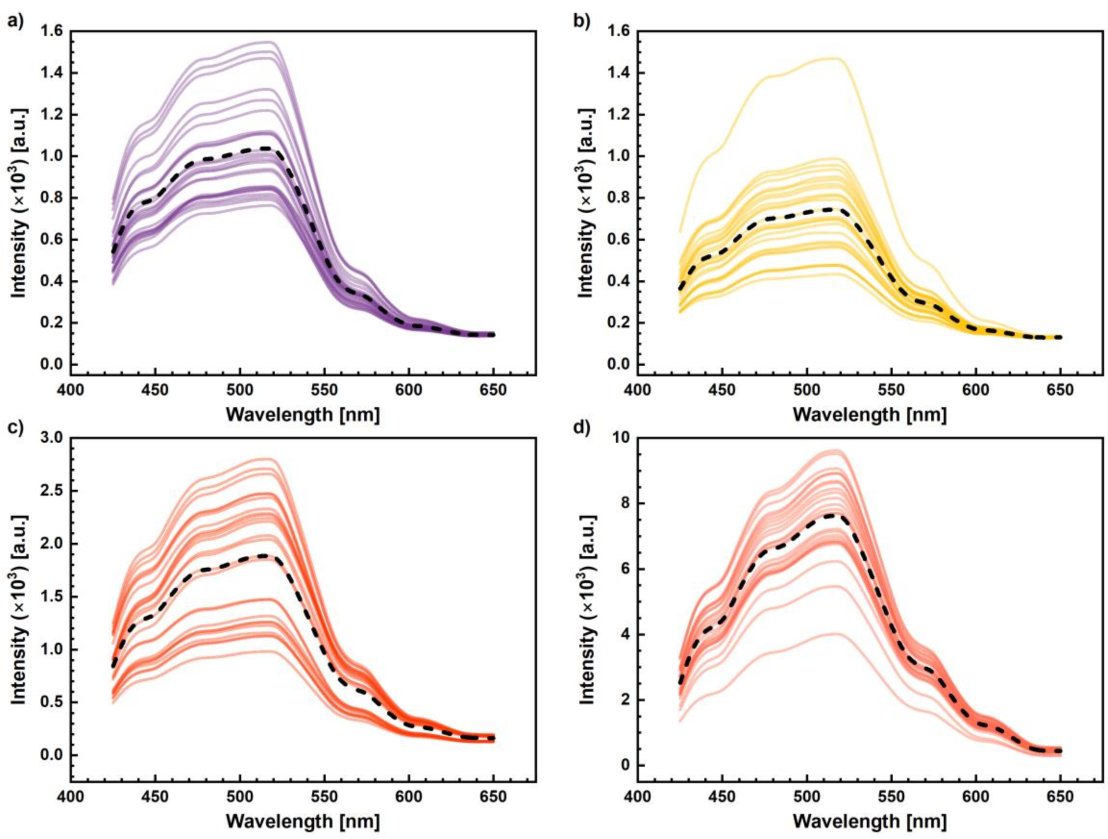

Figure S10. Raw autofluorescence spectra for acrylic samples **a)** dyed blue, **b)** dyed yellow, **c)** dyed red and **d)** dyed red followed by 60 min UV-ozone exposure (black dashed line: average spectrum). Laser power: 60%, correction factor: 2.94.

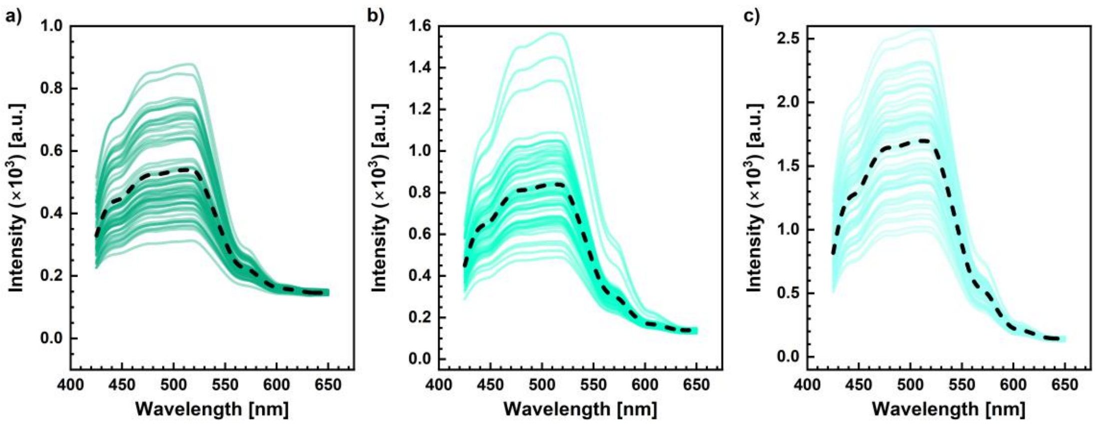

Figure S11. Raw autofluorescence spectra for polyamide samples after **a)** 0 min, **b)** 10 min and **c)** 60 min UV-ozone exposure (black dashed line: average spectrum). Laser power: 100%.

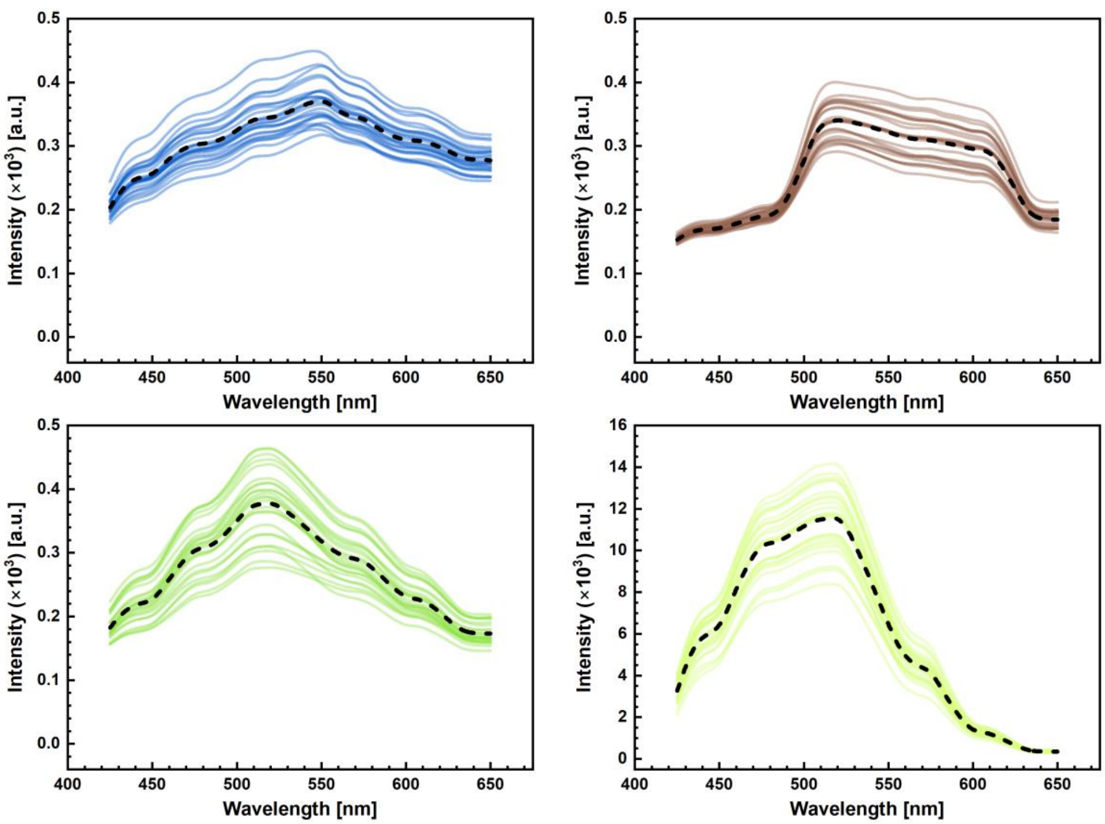

Figure S12. Raw autofluorescence spectra for polyamide samples **a)** dyed blue, **b)** dyed red, **c)** dyed yellow and **d)** dyed yellow followed by 60 min UV-ozone exposure (black dashed line: average spectrum). Laser power: 100%.

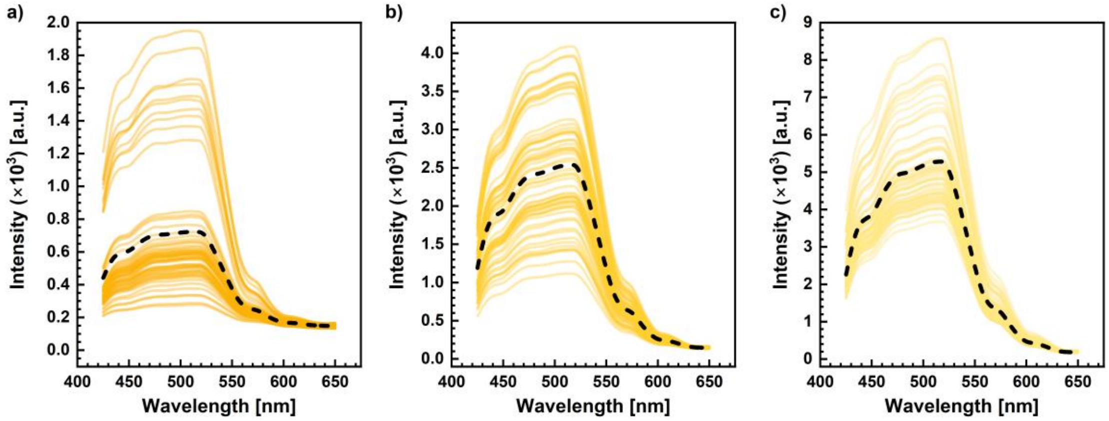

Figure S13. Raw autofluorescence spectra for polyester samples after **a)** 0 min, **b)** 10 min and **c)** 60 min UV-ozone exposure (black dashed line: average spectrum). Laser power: 100%.

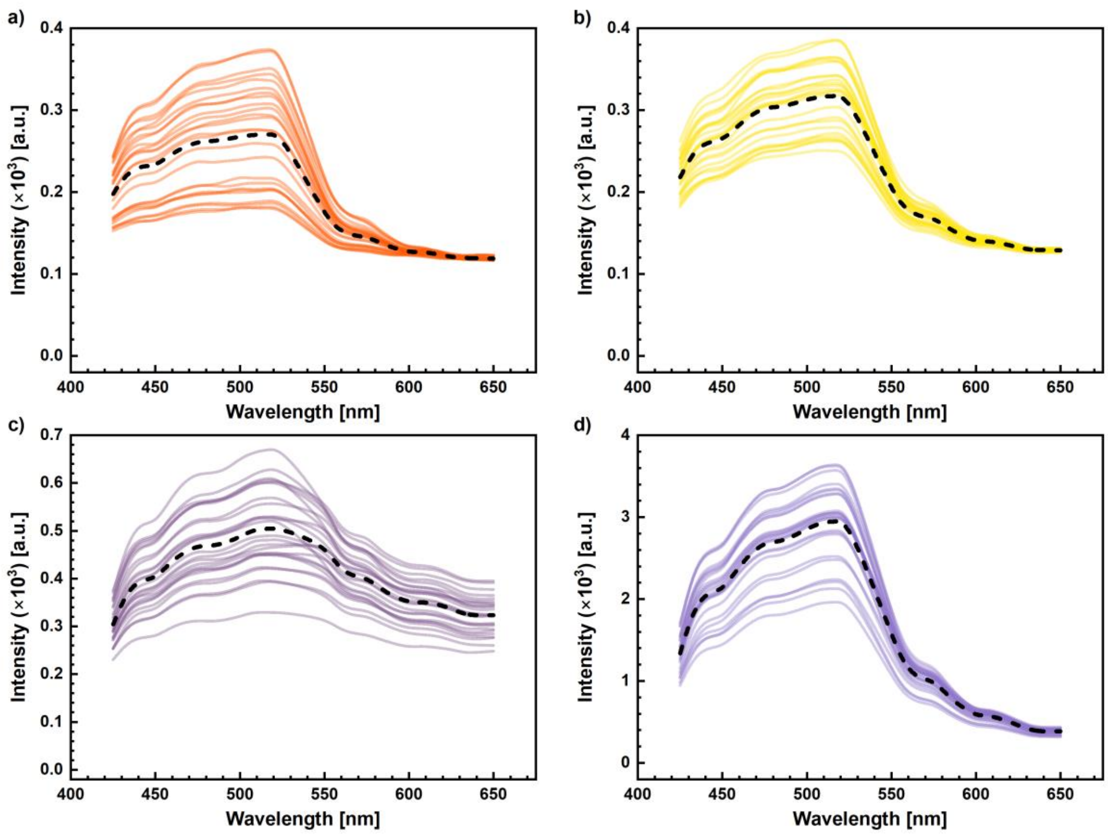

Figure S14. Raw autofluorescence spectra for polyester samples **a)** dyed red, **b)** dyed yellow, **c)** dyed blue and **d)** dyed blue followed by 60 min UV-ozone exposure (black dashed line: average spectrum). Laser power: 100%.

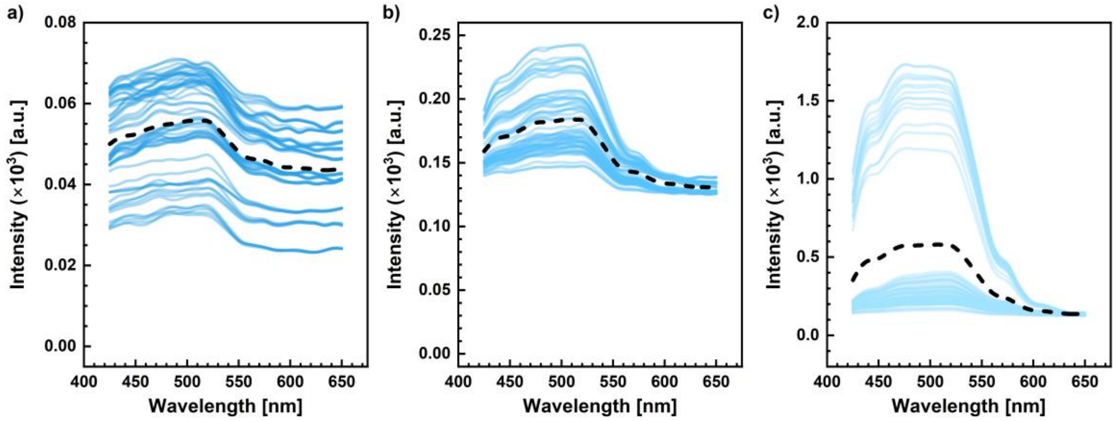

Figure S15. Raw autofluorescence spectra for polyethylene samples after **a)** 0 min, **b)** 10 min and **c)** 60 min UV-ozone exposure (black dashed line: average spectrum). Highest fluorescence intensities after 60 min UV-ozone exposure only observed for HMPE 35A sample. Laser power: 100%.

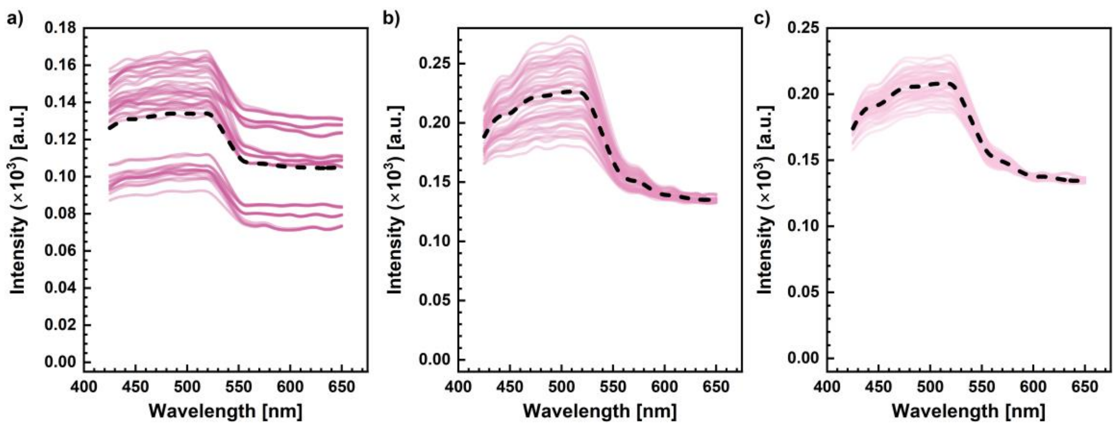

Figure S16. Raw autofluorescence spectra for polypropylene samples after **a)** 0 min, **b)** 10 min and **c)** 60 min UV-ozone exposure (black dashed line: average spectrum). Lowest fluorescence intensities after 0 min UV-ozone exposure only observed for DA3/15 sample. Laser power: 100%.

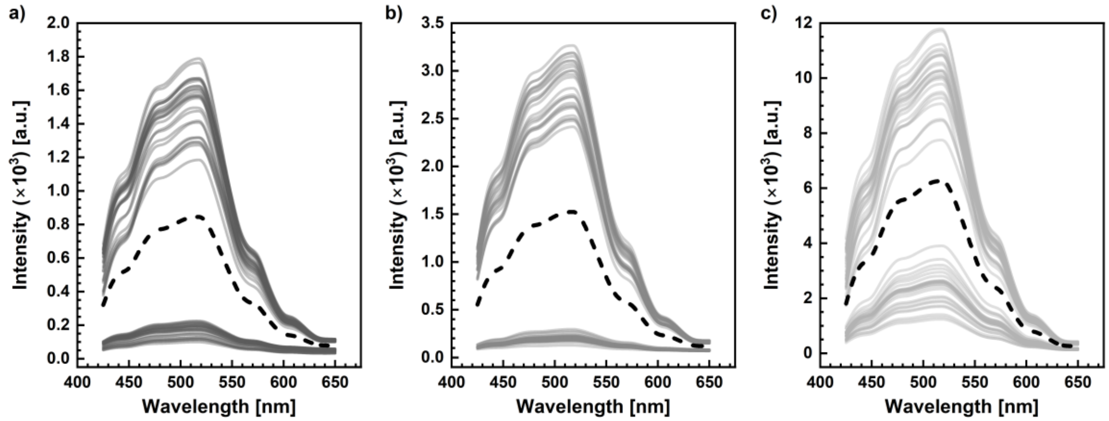

Figure S17. Raw autofluorescence spectra for cellulose samples after **a)** 0 min, **b)** 10 min and **c)** 60 min UV-ozone exposure (black dashed line: average spectrum). The pulped sample had a higher intensity than the as received sample, most likely due to the higher surface area. Laser power: 100%.

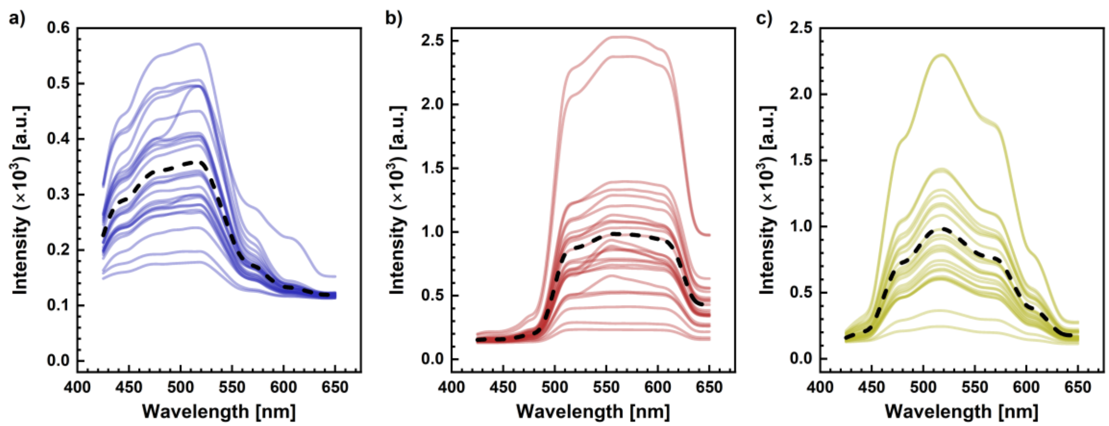

Figure S18. Raw autofluorescence spectra for cellulose samples **a)** dyed blue, **b)** dyed red and **c)** dyed yellow (black dashed line: average spectrum). Laser power: 100%.

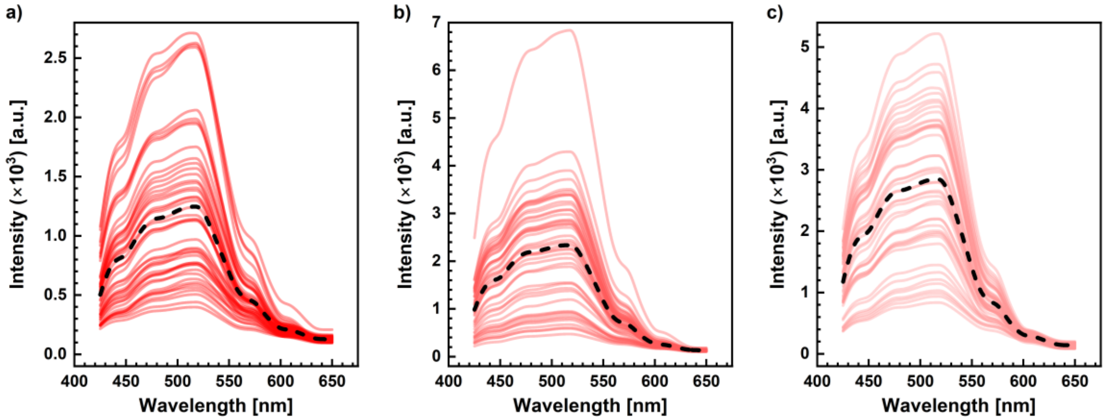

Figure S19. Raw autofluorescence spectra for wool samples after **a)** 0 min, **b)** 10 min and **c)** 60 min UV-ozone exposure (black dashed line: average spectrum). Laser power: 100%.

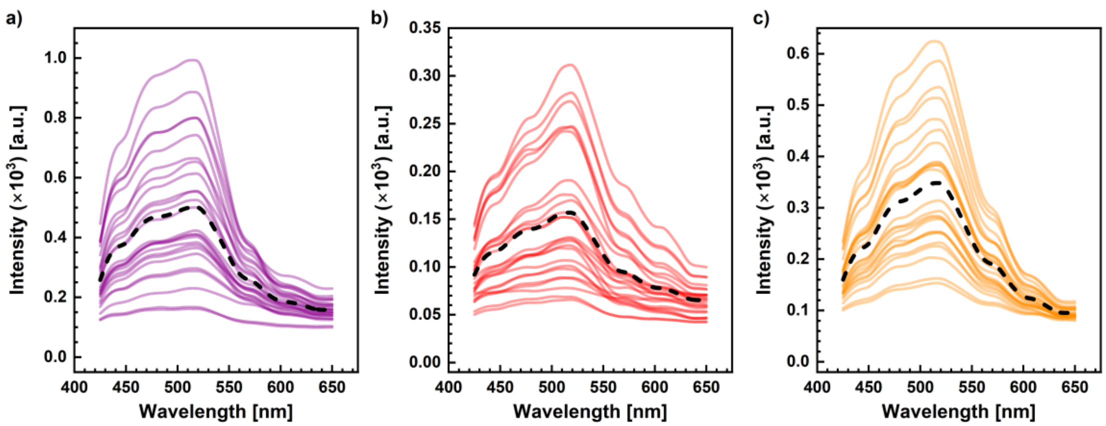

Figure S20. Raw autofluorescence spectra for wool samples **a)** dyed blue, **b)** dyed red and **c)** dyed yellow (black dashed line: average spectrum). Laser power: 100%.

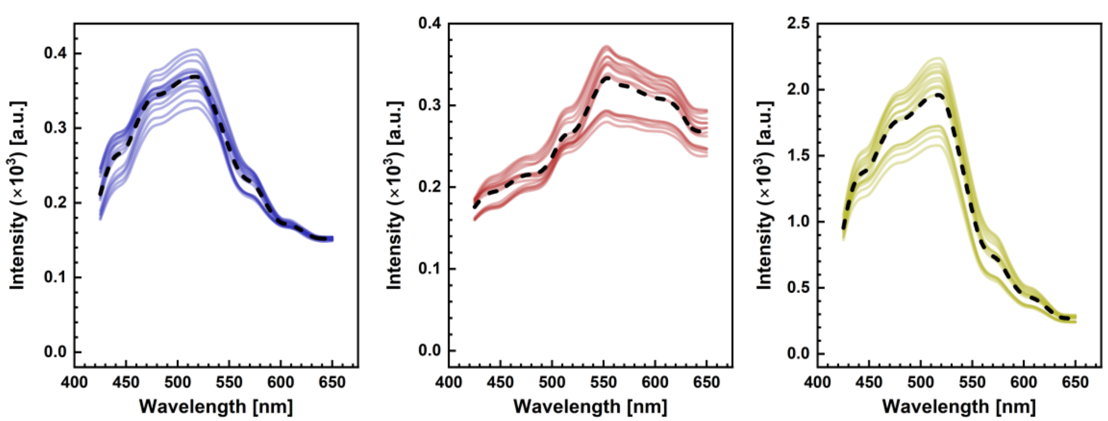

Figure S21. Raw autofluorescence spectra for dyes **a)** sapphire blue, **b)** racing red and **c)** daffodil yellow (black dashed line: average spectrum). Laser power: 100%.

Table S3. Average values of the normalized emission intensity input parameters used for the initial cluster centers in the k-means cluster analysis of dry polymers.

Sample			Normalized emission intensity at wavelength λ nm																									
Polymer	Color	UV-ozone exposure [min]	425	433	442	450	458	467	475	483	492	500	508	517	525	550	558	567	575	583	592	600	608	617	625	633	642	650
Acrylic	Undyed	0	0.41	0.61	0.68	0.69	0.79	0.88	0.93	0.93	0.96	0.98	1.00	1.00	1.00	0.43	0.30	0.25	0.24	0.16	0.10	0.05	0.05	0.04	0.02	0.00	0.00	0.00
		10	0.41	0.61	0.68	0.69	0.80	0.88	0.93	0.93	0.95	0.98	1.00	1.00	1.00	0.44	0.30	0.25	0.24	0.16	0.10	0.05	0.05	0.04	0.02	0.00	0.00	0.00
		60	0.29	0.47	0.54	0.55	0.69	0.80	0.88	0.88	0.92	0.96	0.99	1.00	1.00	0.53	0.40	0.35	0.34	0.24	0.16	0.10	0.09	0.07	0.03	0.00	0.00	0.00
	Blue	0	0.45	0.65	0.71	0.72	0.82	0.89	0.94	0.94	0.96	0.98	1.00	1.00	1.00	0.41	0.27	0.22	0.21	0.14	0.08	0.05	0.05	0.03	0.02	0.00	0.00	0.00
	Red	0	0.40	0.59	0.66	0.66	0.77	0.86	0.92	0.92	0.95	0.98	1.00	1.00	1.00	0.45	0.32	0.26	0.25	0.17	0.11	0.06	0.06	0.04	0.02	0.00	0.00	0.00
		60	0.29	0.46	0.52	0.54	0.66	0.78	0.86	0.86	0.90	0.95	0.99	1.00	1.00	0.52	0.40	0.35	0.34	0.25	0.17	0.11	0.11	0.08	0.04	0.01	0.00	0.00
	Yellow	0	0.38	0.57	0.64	0.65	0.77	0.87	0.93	0.93	0.95	0.98	1.00	1.00	1.00	0.46	0.33	0.27	0.26	0.17	0.11	0.06	0.06	0.04	0.02	0.00	0.00	0.00
Nylon	Undyed	0	0.47	0.69	0.75	0.76	0.85	0.92	0.96	0.96	0.97	0.99	1.00	1.00	0.99	0.41	0.26	0.20	0.19	0.12	0.07	0.04	0.04	0.03	0.01	0.00	0.00	0.00
		10	0.45	0.66	0.73	0.73	0.84	0.92	0.96	0.96	0.97	0.99	1.00	1.00	1.00	0.44	0.29	0.24	0.23	0.14	0.08	0.04	0.04	0.03	0.01	0.00	0.00	0.00
		60	0.43	0.65	0.73	0.73	0.84	0.92	0.97	0.96	0.97	0.99	1.00	1.00	0.99	0.47	0.31	0.25	0.24	0.15	0.09	0.05	0.04	0.03	0.01	0.00	0.00	0.00
	Blue	0	0.00	0.20	0.27	0.28	0.42	0.51	0.57	0.57	0.61	0.66	0.78	0.80	0.80	1.00	0.87	0.81	0.80	0.70	0.64	0.60	0.60	0.56	0.50	0.44	0.42	0.42
	Red	0	0.00	0.07	0.09	0.09	0.13	0.16	0.20	0.20	0.37	0.66	0.95	1.00	1.00	0.90	0.86	0.84	0.84	0.81	0.79	0.75	0.76	0.64	0.42	0.20	0.17	0.17
	Yellow	0	0.05	0.18	0.23	0.24	0.39	0.53	0.65	0.66	0.74	0.86	0.99	1.00	1.00	0.70	0.62	0.58	0.56	0.47	0.36	0.27	0.27	0.20	0.10	0.01	0.00	0.00
		60	0.26	0.44	0.51	0.52	0.67	0.80	0.89	0.89	0.93	0.97	1.00	1.00	1.00	0.54	0.42	0.37	0.35	0.24	0.15	0.08	0.08	0.06	0.03	0.00	0.00	0.00
Polyester	Undyed	0	0.51	0.72	0.78	0.78	0.87	0.93	0.97	0.97	0.98	0.99	1.00	1.00	1.00	0.38	0.23	0.18	0.17	0.11	0.06	0.03	0.03	0.02	0.01	0.00	0.00	0.00
		10	0.44	0.66	0.73	0.74	0.83	0.90	0.95	0.95	0.96	0.98	1.00	1.00	1.00	0.42	0.27	0.21	0.20	0.13	0.08	0.04	0.04	0.03	0.01	0.00	0.00	0.00
		60	0.41	0.63	0.70	0.71	0.81	0.89	0.94	0.94	0.96	0.98	1.00	1.00	1.00	0.44	0.29	0.23	0.22	0.15	0.09	0.05	0.05	0.03	0.02	0.00	0.00	0.00
	Blue	0	0.00	0.35	0.47	0.48	0.64	0.75	0.82	0.82	0.85	0.91	0.99	1.00	1.00	0.83	0.59	0.50	0.48	0.37	0.28	0.23	0.23	0.21	0.16	0.10	0.09	0.10
		60	0.37	0.59	0.66	0.67	0.77	0.85	0.90	0.90	0.93	0.96	0.99	1.00	1.00	0.46	0.31	0.25	0.24	0.17	0.12	0.08	0.08	0.06	0.03	0.00	0.00	0.00
	Red	0	0.52	0.69	0.75	0.74	0.83	0.90	0.94	0.94	0.96	0.98	1.00	1.00	1.00	0.35	0.23	0.18	0.17	0.12	0.08	0.05	0.05	0.03	0.01	0.00	0.00	0.00
	Yellow	0	0.47	0.65	0.70	0.71	0.80	0.87	0.93	0.93	0.95	0.98	1.00	1.00	1.00	0.38	0.27	0.22	0.21	0.15	0.09	0.06	0.06	0.04	0.02	0.00	0.00	0.00
PE	Undyed	0	0.53	0.66	0.70	0.71	0.81	0.85	0.91	0.92	0.95	0.99	0.99	1.00	0.98	0.34	0.25	0.22	0.20	0.11	0.06	0.06	0.04	0.04	0.01	0.00	0.01	0.04
		10	0.54	0.69	0.74	0.75	0.83	0.90	0.96	0.96	0.97	0.99	1.00	0.99	0.99	0.38	0.27	0.23	0.22	0.15	0.09	0.06	0.05	0.04	0.01	0.01	0.00	0.00
		60	0.49	0.72	0.79	0.78	0.88	0.95	0.99	0.98	0.99	1.00	1.00	0.99	0.98	0.48	0.31	0.24	0.23	0.15	0.09	0.05	0.05	0.03	0.01	0.00	0.00	0.00
PP	Undyed	0	0.72	0.82	0.89	0.87	0.91	0.93	0.96	0.99	0.98	0.98	0.97	0.98	1.00	0.14	0.10	0.08	0.08	0.05	0.03	0.02	0.01	0.01	0.00	0.00	0.01	0.01
		10	0.58	0.73	0.79	0.78	0.87	0.92	0.96	0.96	0.97	0.99	1.00	0.99	0.99	0.32	0.22	0.17	0.18	0.12	0.07	0.04	0.05	0.03	0.01	0.00	0.00	0.01
		60	0.54	0.71	0.77	0.77	0.84	0.92	0.96	0.97	0.97	0.99	1.00	1.00	1.00	0.36	0.26	0.21	0.18	0.12	0.07	0.04	0.05	0.04	0.02	0.01	0.00	0.01
Cellulose	Undyed	0	0.33	0.52	0.59	0.60	0.73	0.83	0.90	0.90	0.93	0.97	1.00	1.00	1.00	0.49	0.37	0.32	0.31	0.21	0.13	0.08	0.08	0.06	0.03	0.00	0.00	0.00
		10	0.30	0.49	0.56	0.57	0.71	0.82	0.90	0.90	0.93	0.97	1.00	1.00	1.00	0.51	0.38	0.33	0.32	0.22	0.14	0.08	0.08	0.06	0.03	0.00	0.00	0.00
		60	0.26	0.44	0.51	0.53	0.67	0.80	0.88	0.88	0.92	0.96	1.00	1.00	1.00	0.53	0.41	0.36	0.34	0.24	0.15	0.09	0.09	0.06	0.03	0.00	0.00	0.00
	Blue	0	0.45	0.64	0.71	0.72	0.81	0.89	0.93	0.94	0.95	0.98	0.99	1.00	1.00	0.41	0.28	0.22	0.21	0.14	0.09	0.06	0.06	0.04	0.02	0.00	0.00	0.00
	Red	0	0.00	0.01	0.00	0.00	0.01	0.03	0.06	0.06	0.19	0.50	0.82	0.86	0.86	1.00	0.99	0.99	0.99	0.98	0.97	0.94	0.94	0.84	0.61	0.37	0.33	0.33
	Yellow	0	0.00	0.03	0.05	0.08	0.29	0.51	0.69	0.69	0.78	0.90	0.99	1.00	1.00	0.77	0.75	0.73	0.72	0.57	0.41	0.28	0.27	0.20	0.11	0.03	0.02	0.02
Wool	Undyed	0	0.34	0.54	0.61	0.62	0.74	0.84	0.91	0.91	0.94	0.97	1.00	1.00	1.00	0.49	0.35	0.30	0.29	0.20	0.12	0.07	0.07	0.05	0.02	0.00	0.00	0.00
		10	0.39	0.59	0.67	0.68	0.79	0.88	0.94	0.93	0.96	0.98	1.00	1.00	1.00	0.46	0.32	0.26	0.25	0.16	0.10	0.06	0.05	0.04	0.02	0.00	0.00	0.00
		60	0.38	0.59	0.66	0.67	0.79	0.88	0.93	0.93	0.95	0.98	1.00	1.00	1.00	0.46	0.32	0.26	0.25	0.17	0.10	0.06	0.06	0.04	0.02	0.00	0.00	0.00
	Blue	0	0.29	0.54	0.62	0.63	0.76	0.85	0.90	0.90	0.92	0.95	0.99	1.00	1.00	0.52	0.36	0.29	0.28	0.19	0.12	0.08	0.08	0.06	0.03	0.00	0.00	0.00
	Red	0	0.29	0.49	0.55	0.57	0.67	0.75	0.81	0.81	0.86	0.93	0.99	1.00	1.00	0.51	0.38	0.32	0.32	0.24	0.18	0.14	0.14	0.11	0.06	0.01	0.00	0.00
	Yellow	0	0.26	0.42	0.50	0.51	0.65	0.77	0.86	0.86	0.89	0.95	0.99	1.00	1.00	0.55	0.43	0.38	0.37	0.26	0.18	0.12	0.11	0.08	0.04	0.00	0.00	0.00

Table S4. Cluster number and average values of the optional input parameters (normalized total emission intensity, color mode values, shape factor) used for the initial cluster centers in the k-means cluster analysis of dry polymers.

Sample			Cluster no.	Normalized total emission intensity (NTEI)	Color mode value			Shape factor	Reduced NTEI
Polymer	Color	UV-ozone exposure [min]			R	G	B		
Acrylic	Undyed	0	1	0.076	1	1	1	0.01	0.074
		10	2	0.26	1	1	1	0.01	0.25
		60	3	0.47	1	1	1	0.01	0.48
	Blue	0	4	0.016	0	0	1	0.01	0.047
	Red	0	5	0.027	1	0	0	0.01	0.080
		60	6	0.10	1	0	0	0.01	0.32
	Yellow	0	7	0.012	0	1	1	0.01	0.036
Nylon	Undyed	0	8	0.0031	1	1	1	0.01	0.0099
		10	9	0.0045	1	1	1	0.01	0.014
		60	10	0.0085	1	1	1	0.01	0.025
	Blue	0	11	0.0028	0	0	1	0.01	0.011
	Red	0	12	0.0023	1	0	0	0.01	0.0090
	Yellow	0	13	0.0025	0	1	1	0.01	0.0090
		60	14	0.052	0	1	1	0.01	0.15
Polyester	Undyed	0	15	0.0040	1	1	1	0.01	0.012
		10	16	0.012	1	1	1	0.01	0.034
		60	17	0.025	1	1	1	0.01	0.069
	Blue	0	18	0.0038	0	0	1	0.01	0.014
		60	19	0.015	0	0	1	0.01	0.045
	Red	0	20	0.0018	1	0	0	0.01	0.0059
	Yellow	0	21	0.0020	0	1	1	0.01	0.0068
PE	Undyed	0	22	0.00046	1	1	1	1.00	0.0017
		10	23	0.0015	1	1	1	1.00	0.0052
		60	24	0.0034	1	1	1	1.00	0.011
PP	Undyed	0	25	0.0011	1	1	1	0.01	0.0040
		10	26	0.0017	1	1	1	0.01	0.0058
		60	27	0.0016	1	1	1	0.01	0.0056
Cellulose	Undyed	0	28	0.0041	1	1	1	0.01	0.013
		10	29	0.0073	1	1	1	0.01	0.023
		60	30	0.029	1	1	1	0.01	0.084
	Blue	0	31	0.0022	0	0	1	0.01	0.0071
	Red	0	32	0.0055	1	0	0	0.01	0.024
	Yellow	0	33	0.0050	0	1	1	0.01	0.018
Wool	Undyed	0	34	0.0062	1	1	1	0.01	0.019
		10	35	0.011	1	1	1	0.01	0.032
		60	36	0.013	1	1	1	0.01	0.038
	Blue	0	37	0.0030	0	0	1	0.01	0.0098
	Red	0	38	0.0010	1	0	0	0.01	0.0034
	Yellow	0	39	0.0020	0	1	1	0.01	0.0066

Table S5. Assigned cluster number and average total emission intensity for polymer samples. Sample labelling uses the following convention: (polymer type, color of dye, UV-ozone exposure time period). Superscript letters denote samples within a polymer type for which the total intensities are not significantly different from one another, $p \leq 0.05$. Error: ± S.D.

Sample no.	Sample (no. of spectra)	Average total emission intensity [a.u.]	Sample no.	Sample (no. of spectra)	Average total emission intensity [a.u.]
1	Acrylic, undyed, 0 min (N = 9, n = 5)	$7.2 \pm 3.4 \times 10^{4}$ [a,d]	22	PE, undyed, 0 min (N = 12, n = 5)	$1.3 \pm 0.29 \times 10^{3}$ [n]
2	Acrylic, undyed, 10 min (N = 9, n = 5)	$2.5 \pm 0.97 \times 10^{5}$ [b]	23	PE, undyed, 10 min (N = 12, n = 5)	$4.1 \pm 0.39 \times 10^{3}$ [p]
3	Acrylic, undyed, 60 min (N = 9, n = 5)	$4.5 \pm 1.8 \times 10^{5}$ [c]	24	PE, undyed, 60 min (N = 12, n = 5)	$9.4 \pm 7.5 \times 10^{3}$ [q]
4	Acrylic, blue, 0 min (N = 5, n = 5)	$4.39 \pm 0.88 \times 10^{4}$ [d]	25	PP, undyed, 0 min (N = 9, n = 5)	$3.1 \pm 0.57 \times 10^{3}$ [r]
5	Acrylic, red, 0 min (N = 5, n = 5)	$7.6 \pm 2.3 \times 10^{4}$ [d]	26	PP, undyed, 10 min (N = 9, n = 5)	$4.7 \pm 0.31 \times 10^{3}$ [s]
6	Acrylic, red, 60 min (N = 5, n = 5)	$2.9 \pm 0.49 \times 10^{5}$ [a]	27	PP, undyed, 60 min (N = 9, n = 5)	$4.4 \pm 0.14 \times 10^{3}$ [t]
7	Acrylic, yellow, 0 min (N = 5, n = 5)	$3.2 \pm 0.83 \times 10^{4}$ [d]	28	Cellulose, undyed, 0 min (N = 6, n = 5)	$1.2 \pm 0.89 \times 10^{4}$ [u]
8	Nylon, undyed, 0 min (N = 12, n = 5)	$8.8 \pm 1.8 \times 10^{3}$ [e,f]	29	Cellulose, undyed, 10 min (N = 6, n = 5)	$2.2 \pm 1.7 \times 10^{4}$ [u]
9	Nylon, undyed, 10 min (N = 12, n = 5)	$1.3 \pm 0.26 \times 10^{4}$ [f]	30	Cellulose, undyed, 60 min (N = 6, n = 5)	$7.9 \pm 4.8 \times 10^{4}$ [v]
10	Nylon, undyed, 60 min (N = 12, n = 5)	$2.4 \pm 0.49 \times 10^{4}$ [g]	31	Cellulose, blue, 0 min (N = 5, n = 5)	$6.1 \pm 1.4 \times 10^{3}$ [u]
11	Nylon, blue, 0 min (N = 5, n = 5)	$7.9 \pm 0.67 \times 10^{3}$ [h]	32	Cellulose, red, 0 min (N = 5, n = 5)	$1.5 \pm 0.78 \times 10^{4}$ [u]
12	Nylon, red, 0 min (N = 5, n = 5)	$6.4 \pm 0.47 \times 10^{3}$ [e]	33	Cellulose, yellow, 0 min (N = 5, n = 5)	$1.4 \pm 0.64 \times 10^{4}$ [u]
13	Nylon, yellow, 0 min (N = 5, n = 5)	$6.9 \pm 0.84 \times 10^{3}$ [e]	34	Wool, undyed, 0 min (N = 9, n = 5)	$1.7 \pm 0.78 \times 10^{4}$ [w]
14	Nylon, yellow, 60 min (N = 5, n = 5)	$1.5 \pm 0.19 \times 10^{5}$ [e]	35	Wool, undyed, 10 min (N = 9, n = 5)	$3.1 \pm 1.6 \times 10^{4}$ [x]
15	Polyester, undyed, 0 min (N = 12, n = 5)	$1.1 \pm 0.53 \times 10^{4}$ [j]	36	Wool, undyed, 60 min (N = 9, n = 5)	$3.7 \pm 1.4 \times 10^{4}$ [x]
16	Polyester, undyed, 10 min (N = 12, n = 5)	$3.4 \pm 0.98 \times 10^{4}$ [k]	37	Wool, blue, 0 min (N = 5, n = 5)	$8.4 \pm 3.1 \times 10^{3}$ [y]
17	Polyester, undyed, 60 min (N = 12, n = 5)	$6.9 \pm 1.5 \times 10^{4}$ [l]	38	Wool, red, 0 min (N = 5, n = 5)	$2.8 \pm 1.1 \times 10^{3}$ [y]
18	Polyester, blue, 0 min (N = 5, n = 5)	$1.1 \pm 0.15 \times 10^{4}$ [j]	39	Wool, yellow, 0 min (N = 5, n = 5)	$5.6 \pm 1.7 \times 10^{3}$ [y]
19	Polyester, blue, 60 min (N = 5, n = 5)	$4.2 \pm 0.61 \times 10^{4}$ [m]	-	Blue dye (N = 3, n = 5)	$6.5 \pm 0.17 \times 10^{3}$
20	Polyester, red, 0 min (N = 5, n = 5)	$5.0 \pm 0.80 \times 10^{3}$ [j]	-	Red dye (N = 3, n = 5)	$7.1 \pm 0.29 \times 10^{3}$
21	Polyester, yellow, 0 min (N = 5, n = 5)	$5.7 \pm 0.54 \times 10^{3}$ [j]	-	Yellow dye (N = 3, n = 5)	$3.0 \pm 0.19 \times 10^{4}$

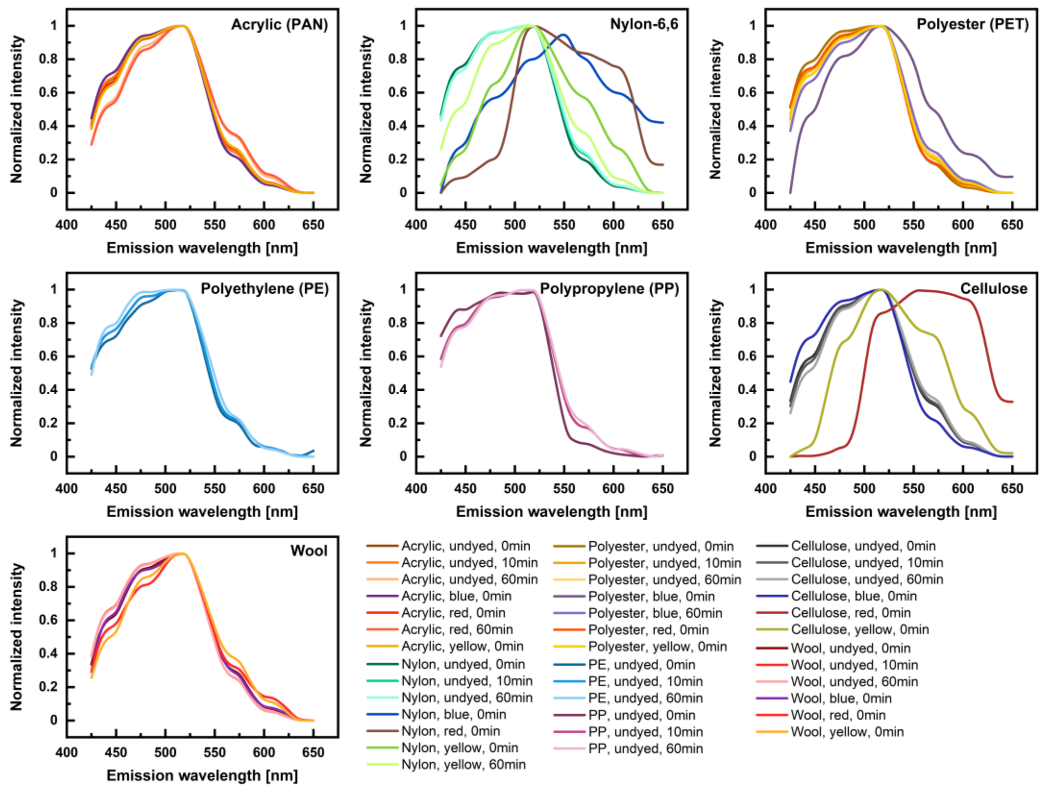

Figure S22. Average normalized autofluorescence spectra of **a)** acrylic, **b)** nylon, **c)** PET, **d)** PE, **e)** PP, **f)** cellulose/cotton and **g)** wool samples as received and after UV-ozone exposure and/or dyeing. Sample labelling uses the following convention: (polymer type, color of dye, UV-ozone exposure time period)

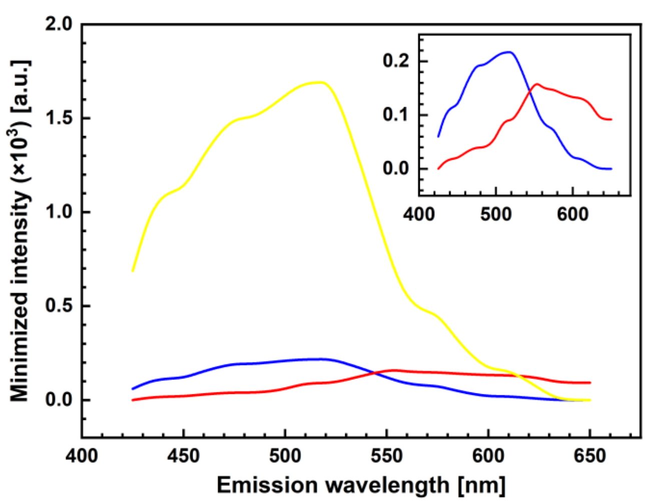

Figure S23. Average minimized autofluorescence spectra of dyes (blue line: blue dye, red line: red dye, yellow line: yellow dye). Inset focusses on minimized spectra for blue and red dyes.

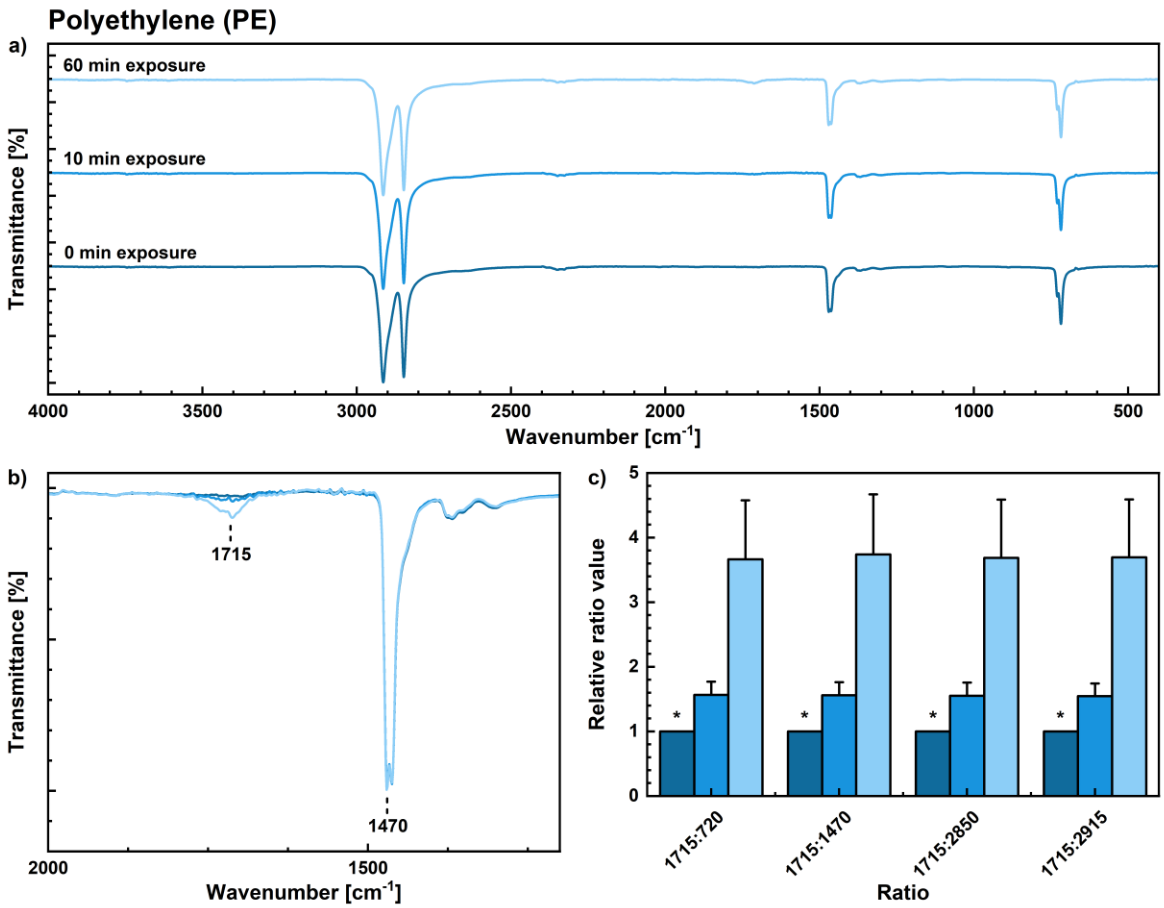

Figure S24. a) Average normalized FT-IR spectra for polyethylene (PE) samples between 400-4000 cm^{-1}; **b)** Average FT-IR spectra for PE samples between 2000-1200 cm^{-1} highlighting region with changes in band transmittance upon UV-ozone exposure; **c)** Change in FT-IR band ratios with exposure to UV-ozone (720 cm^{-1}: rocking of CH_2, 1470 cm^{-1}: bending of CH_2, 1715 cm^{-1}: stretching of C=O, 2850 cm^{-1}: stretching of CH_2, 2915 cm^{-1}: stretching of CH_2; * $p \leq 0.05$ compared to ratio after 60 min UV-ozone exposure) (0 min UV-ozone exposure: dark blue, 10 min UV-ozone exposure: blue, 60 min UV ozone exposure: light blue; N = 3, n = 3; Error: ±S.E.).

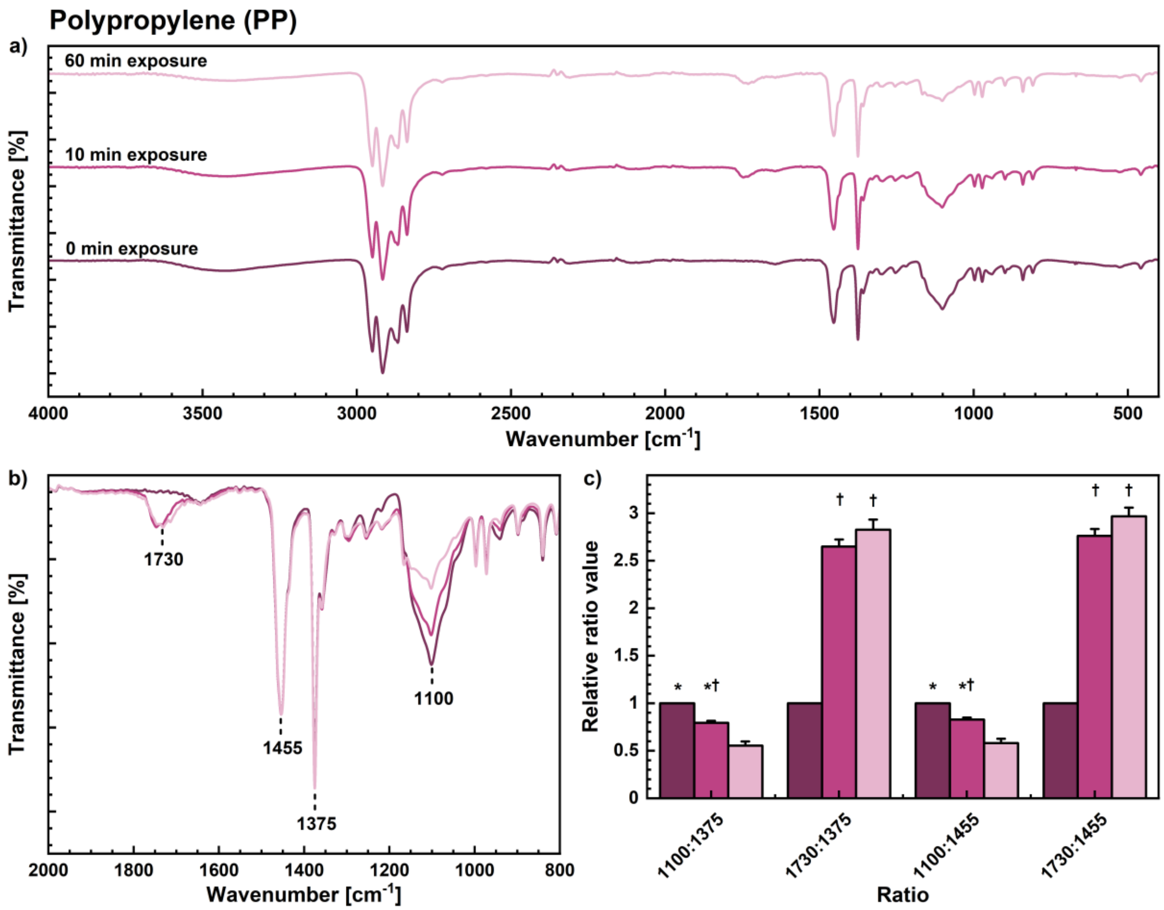

Figure S25. a) Average normalized FT-IR spectra for polypropylene (PP) samples between 400-4000 cm^{-1}; **b)** Average FT-IR spectra for PP samples between 2000-800 cm^{-1} highlighting region with changes in band transmittance upon UV-ozone exposure; **c)** Change in FT-IR band ratios with exposure to UV-ozone (1100 cm^{-1}: wagging of CH_3, 1375 cm^{-1}: bending of CH_3, 1455 cm^{-1}: bending of CH_3, 1730 cm^{-1}: stretching of C=O; * $p \leq 0.05$ compared to ratio after 60 min UV-ozone exposure, † $p \leq 0.05$ compared to ratio after 0 min UV-ozone exposure) (0 min UV-ozone exposure: dark magenta, 10 min UV-ozone exposure: magenta, 60 min UV ozone exposure: light magenta; N = 3, n = 3; Error: ±S.E.).

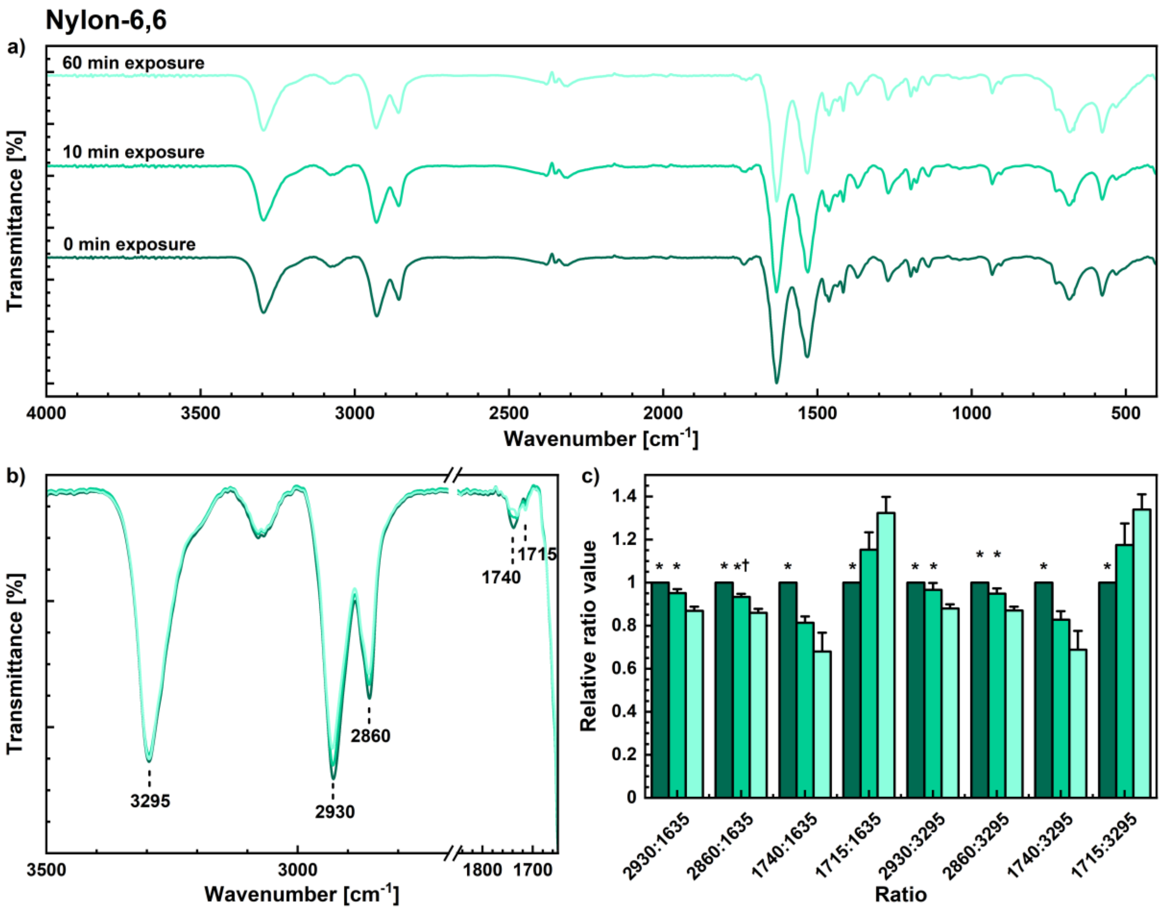

Figure S26. a) Average normalized FT-IR spectra for nylon samples between 400-4000 cm^{-1}; **b)** Average FT-IR spectra for nylon samples between 3500-2500 cm^{-1} and 1850-1650 cm^{-1}, highlighting regions with changes in band transmittance upon exposure to UV-ozone; **c)** Change in FT-IR band ratios upon exposure to UV-ozone (1635 cm^{-1}: amide I stretching, 1715 cm^{-1}: stretching of C=O, 1740 cm^{-1}: stretching of C=O, 2860 cm^{-1}: stretching of CH_2, 2930 cm^{-1}: stretching of CH_2, 3295 cm^{-1}: stretching of N-H; * $p \leq 0.05$ compared to ratio after 60 min UV-ozone exposure, † $p \leq 0.05$ compared to ratio after 0 min UV-ozone exposure) (0 min UV-ozone exposure: dark green-cyan, 10 min UV-ozone exposure: green-cyan, 60 min UV ozone exposure: light green-cyan; N = 4, n = 3; Error: ±S.E.).

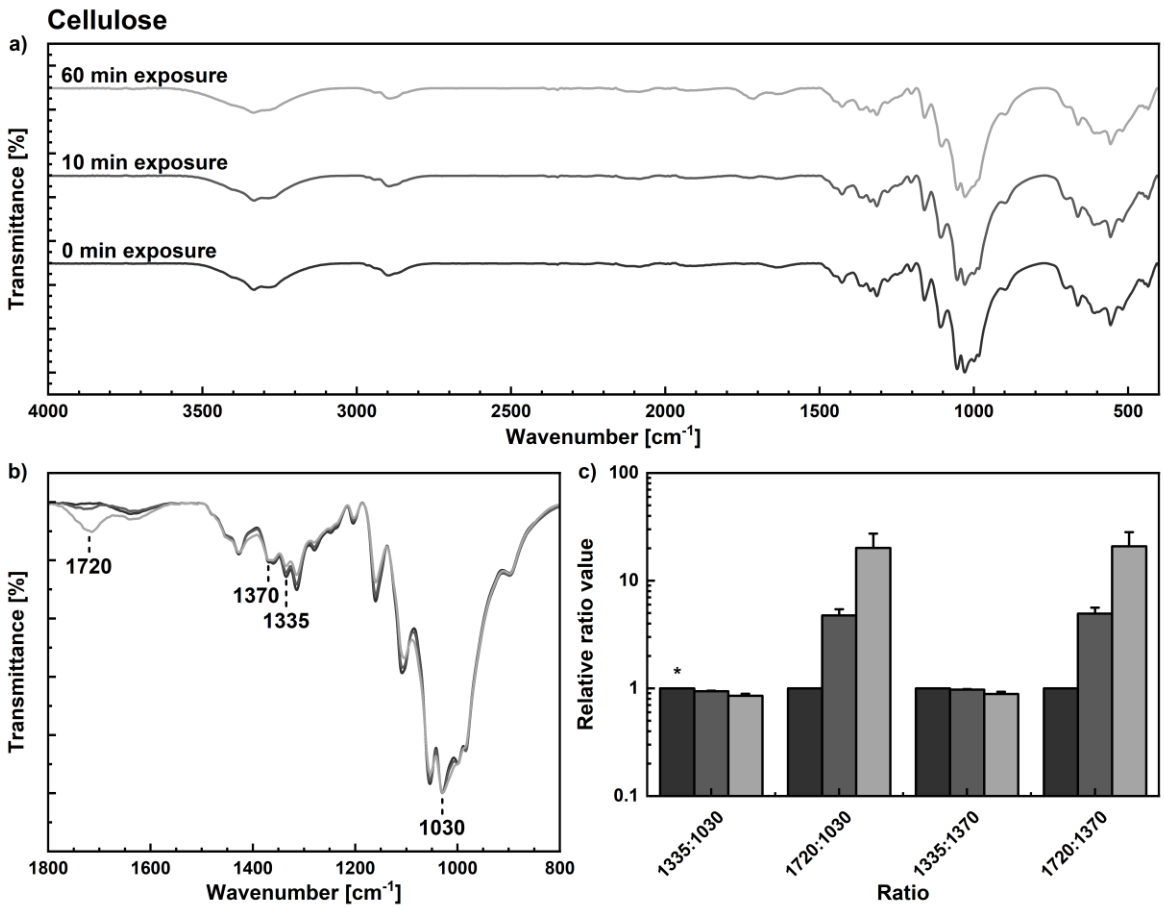

Figure S27. a) Average normalized FT-IR spectra for cellulose samples between 400-4000 cm^{-1}; **b)** Average FT-IR spectra for cellulose samples between 1800-800 cm^{-1}, highlighting regions with changes in band transmittance upon exposure to UV-ozone; **c)** Change in FT-IR band ratios upon exposure to UV-ozone (1030 cm^{-1}: stretching of C-O, 1335 cm^{-1}: vibration of OH, 1370 cm^{-1}: vibration of CH, 1720 cm^{-1}: stretching of C=O; * $p \leq 0.05$ compared to ratio after 60 min UV-ozone exposure) (0 min UV-ozone exposure: dark grey, 10 min UV-ozone exposure: grey, 60 min UV ozone exposure: light grey; N = 2, n = 3; Error: ±S.E.).

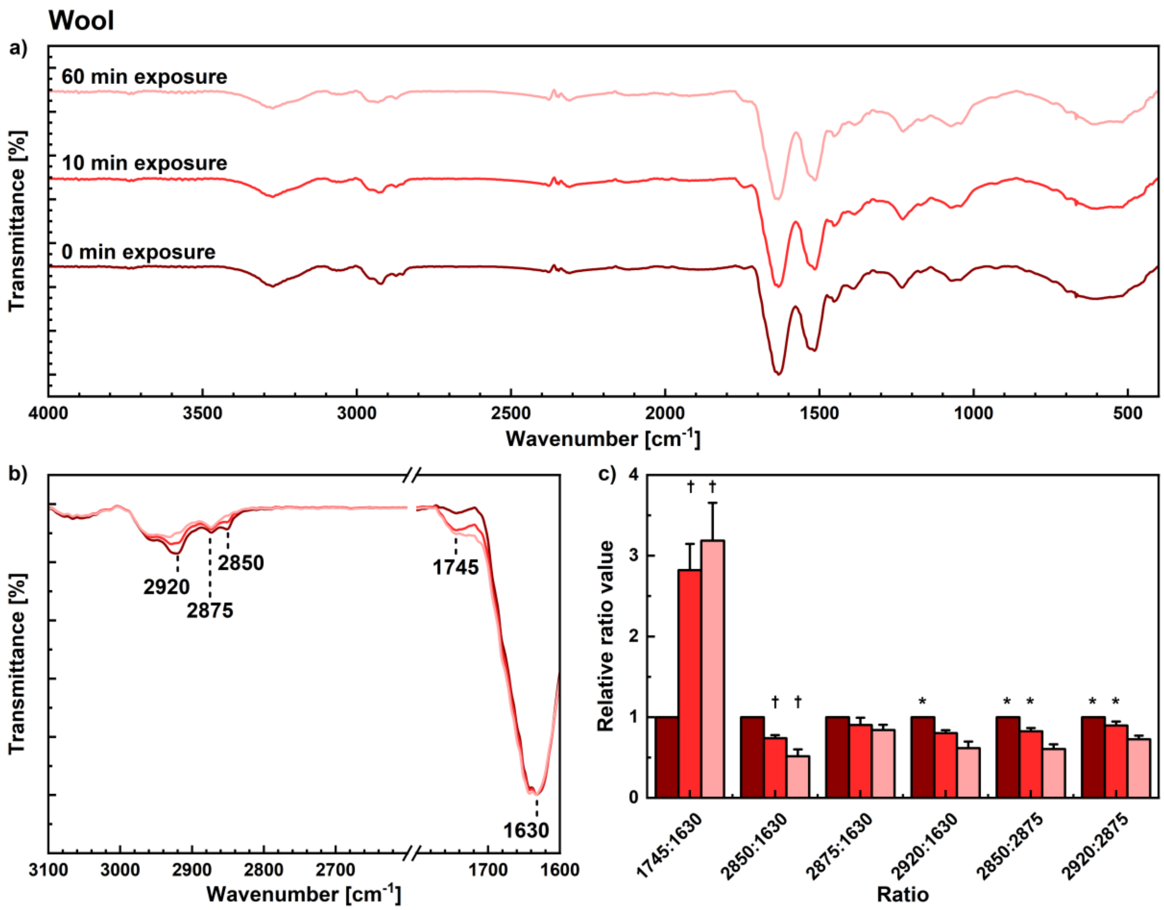

Figure S28. a) Average normalized FT-IR spectra for wool samples between 400-4000 cm^{-1}; **b)** Average FT-IR spectra for wool samples between 3100-2600 cm^{-1} and 1800-1600 cm^{-1}, highlighting regions with changes in band transmittance upon exposure to UV-ozone; **c)** Change in FT-IR band ratios upon exposure to UV-ozone (1630 cm^{-1}: amide I stretching, 1745 cm^{-1}: stretching of C=O, 2850 cm^{-1}: stretching of crystalline CH_2, 2875 cm^{-1}: stretching of amorphous CH_2, 2920 cm^{-1}: stretching of crystalline CH_2; * $p \leq 0.05$ compared to ratio after 60 min UV-ozone exposure, † $p \leq 0.05$ compared to ratio after 0 min UV-ozone exposure) (0 min UV-ozone exposure: dark green-cyan, 10 min UV-ozone exposure: green-cyan, 60 min UV ozone exposure: light green-cyan; N = 3, n = 3; Error: ±S.E.).

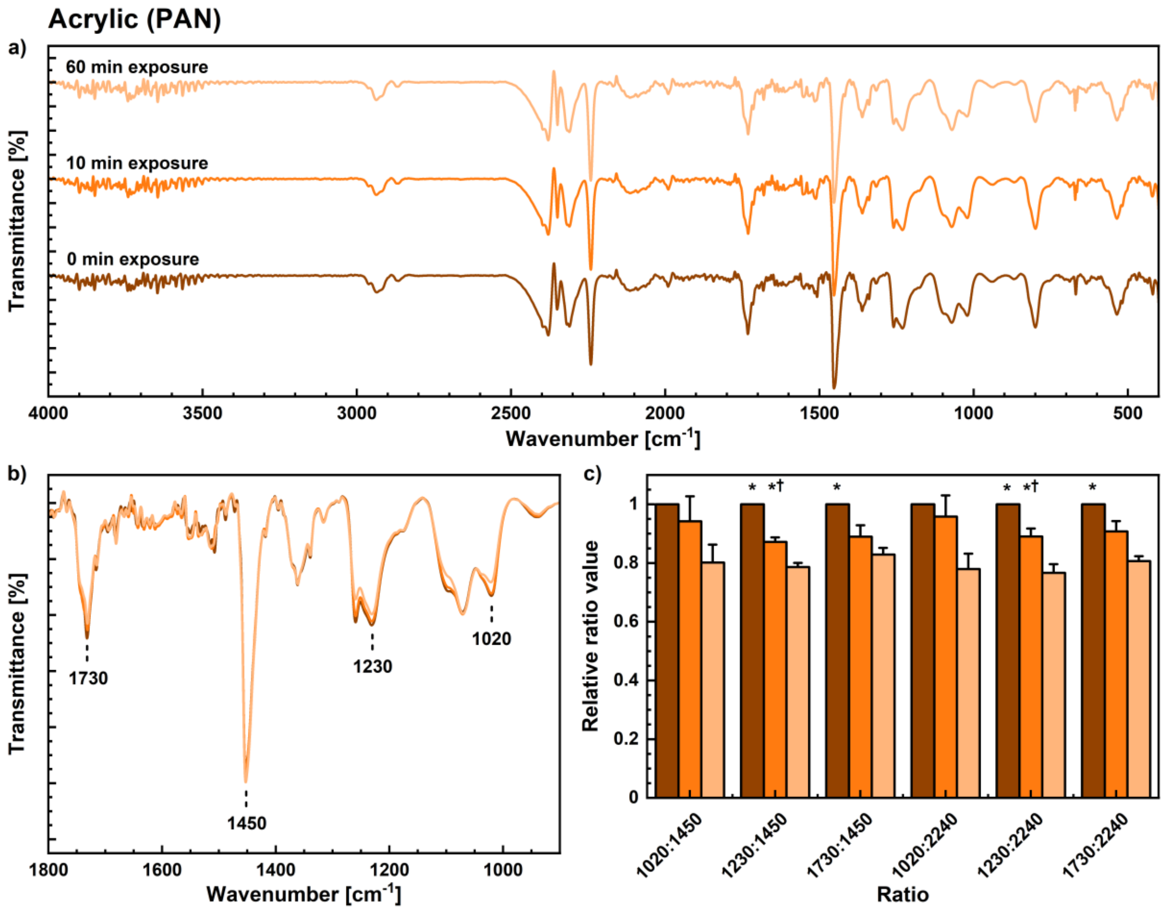

Figure S29. a) Average normalized FT-IR spectra for acrylic samples between 400-4000 cm^{-1}; **b)** Average FT-IR spectra for acrylic samples between 1800-900 cm^{-1} highlighting region with changes in band transmittance upon exposure to UV-ozone; **c)** Change in FT-IR band ratios with exposure to UV-ozone (1020 cm^{-1}:stretching of C-O (copolymer), 1230 cm^{-1}: stretching of C-O (copolymer), 1730 cm^{-1}: stretching of C=O (copolymer) 1450 cm^{-1}: bending of CH_2, 2240 cm^{-1}:stretching of C≡N (PAN); * $p \leq 0.05$ compared to ratio after 60 min UV-ozone exposure, † $p \leq 0.05$ compared to ratio after 0 min UV-ozone exposure) (0 min UV-ozone exposure: dark orange, 10 min UV-ozone exposure: orange, 60 min UV ozone exposure: light orange; N = 3, n = 3; Error: ±S.E.).

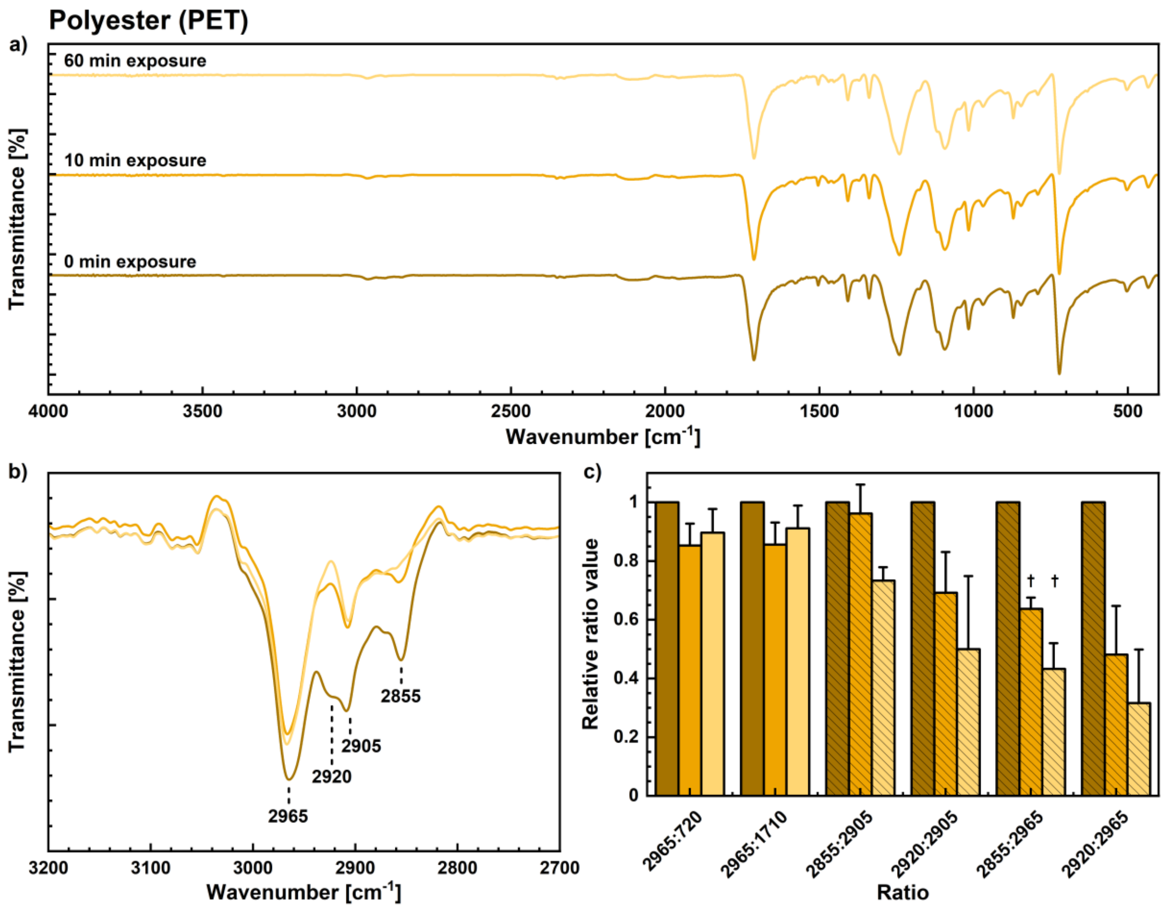

Figure S30. a) Average normalized FT-IR spectra for PET samples between 400-4000 cm^{-1}; **b)** Average FT-IR spectra for polyester samples between 3200-2700 cm^{-1}, highlighting changes in polymer crystallinity upon exposure to UV-ozone; **c)** Change in FT-IR band ratios upon exposure to UV-ozone (720 cm^{-1}: benzene ring stretching, 1710 cm^{-1}: stretching of C=O, 2855 cm^{-1}: stretching of trans (crystalline) CH_2, 2905 cm^{-1}: stretching of CH_2, 2920 cm^{-1}: stretching of CH_2, 2965 cm^{-1}: stretching of cis (amorphous) CH_2; patternless bars: all four samples, bars with diagonal pattern: P6/30 and PES1000 only) (0 min UV-ozone exposure: dark yellow, 10 min UV-ozone exposure: yellow, 60 min UV ozone exposure: light yellow; N = 4, n = 3; Error: ±S.E.).

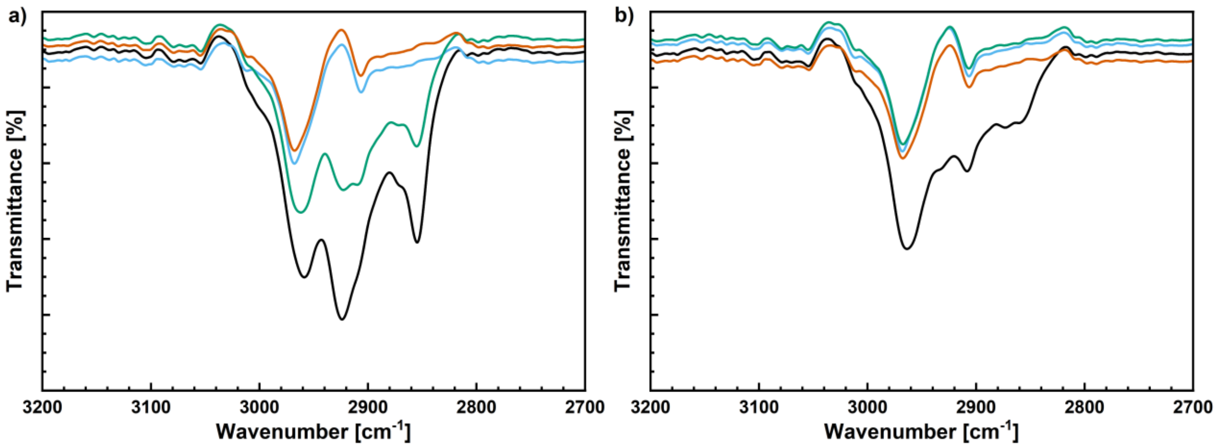

Figure S31. FT-IR spectra for individual polyester samples between 3200-2700 cm-1 at **a)** 0 min UV-ozone exposure and **b)** 60 min UV-ozone exposure. Bands at c. 2920 and c. 2855 cm^{-1} are associated with crystalline CH_2 whilst the band at c. 2965 cm^{-1} is associated with amorphous CH_2 (black line: P6/30, blue line: PE60, green line: PES1000, orange line: ZZ).

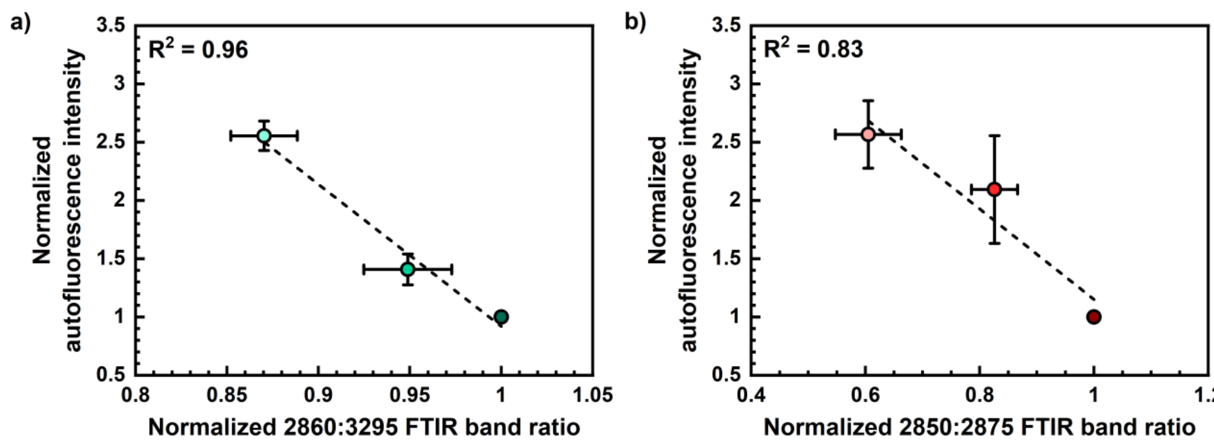

Figure S32. Normalized plots correlating increase in fluorescence intensity with FT-IR detection of polymer degradation, via decrease in band absorbance for crystalline CH_2 groups, due to photooxidation for **a)** nylon and **b)** wool samples. Error: ±S.E.

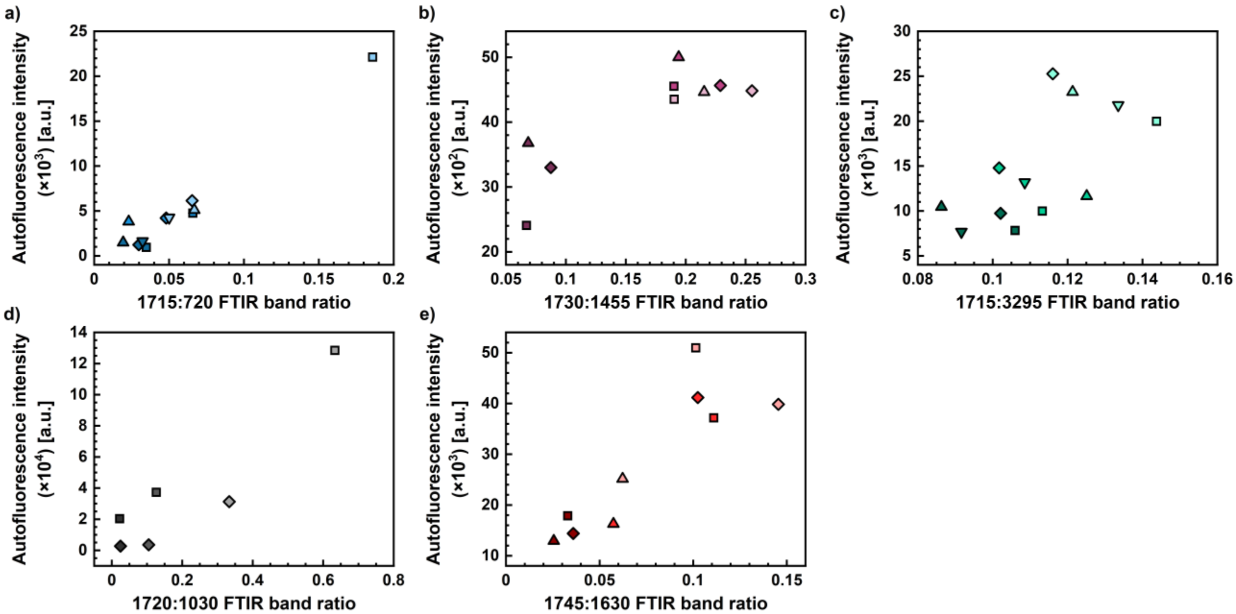

Figure S33. Correlation between increase in actual sample FT-IR band ratios and autofluorescence intensities for **a**) PE (squares: HMPE 35A, diamonds: HMPE 95A, triangles: HMPE 125A, inverted triangles: HMPE 500A; dark blue: 0 min UV-ozone exposure, blue: 10 min UV-ozone exposure, light blue: 60 min UV-ozone exposure); **b)** PP (squares:, diamonds:, triangles:; dark magenta: 0 min UV-ozone exposure, magenta: 10 min UV-ozone exposure, light magenta: 60 min UV-ozone exposure); **c)** nylon (squares: N3/10, diamonds: N3/20, triangles: N3/30, inverted triangles: WN60; dark green-cyan: 0 min UV-ozone exposure, green-cyan: 10 min UV-ozone exposure, light green-cyan: 60 min UV-ozone exposure); **d)** cellulose (square: Whatman filter paper as received, diamond: Whatman filter paper pulp; dark grey: 0 min UV-ozone exposure, grey: 10 min UV-ozone exposure, light grey: 60 min UV-ozone exposure); and **e)** wool (square: light tone, diamond: mid tone, triangle: dark tone; dark red: 0 min UV-ozone exposure, red: 10 min UV-ozone exposure, light red: 60 min UV-ozone exposure)

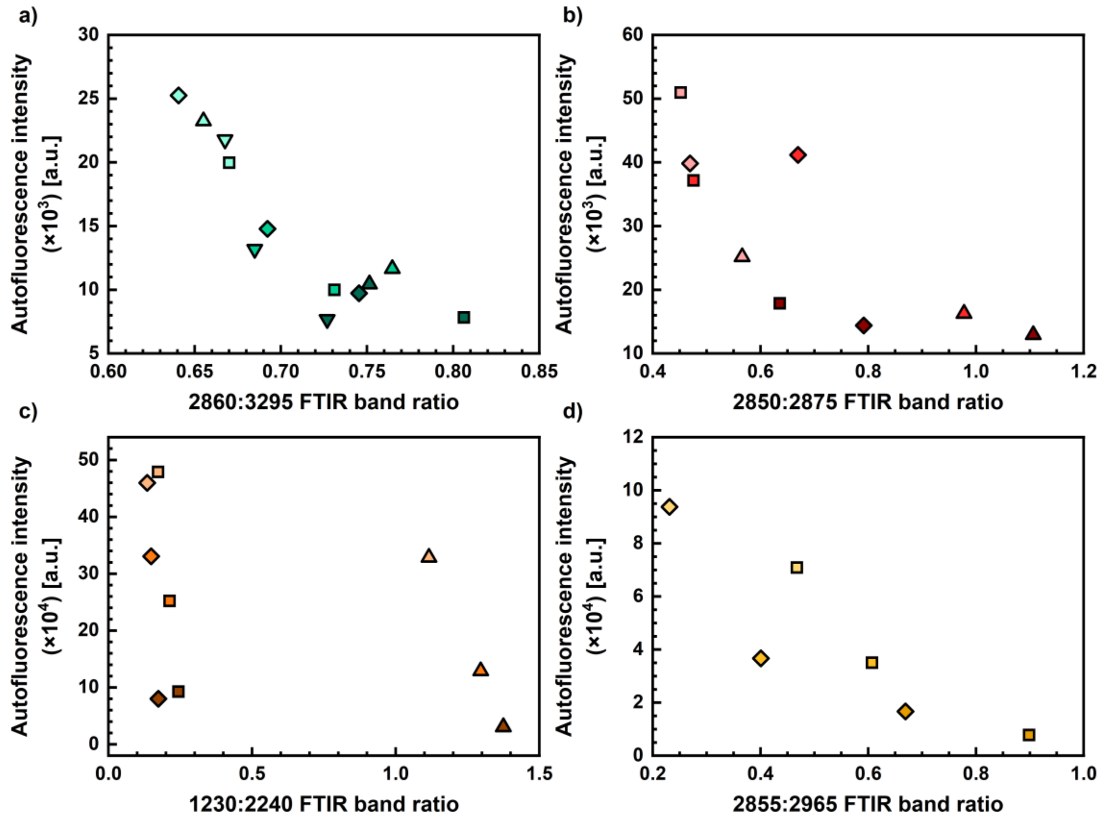

Figure S34. Correlation between decrease in actual sample FT-IR band ratios and increase in autofluorescence intensities for **a**) nylon (squares: N3/10, diamonds: N3/20, triangles: N3/30, inverted triangles: WN60; dark green-cyan: 0 min UV-ozone exposure, green-cyan: 10 min UV-ozone exposure, light green-cyan: 60 min UV-ozone exposure); **b)** wool (square: light tone, diamond: mid tone, triangle: dark tone; dark red: 0 min UV-ozone exposure, red: 10 min UV-ozone exposure, light red: 60 min UV-ozone exposure); **c)** acrylic (squares: AC3/30, diamonds: PAN60, triangles: PAN1200; dark orange: 0 min UV-ozone exposure, orange: 10 min UV-ozone exposure, light orange: 60 min UV-ozone exposure) and **d)** crystalline PET (squares: P6/30, diamonds: PES1000; dark yellow: 0 min UV-ozone exposure, yellow: 10 min UV-ozone exposure, light yellow: 60 min UV-ozone exposure)

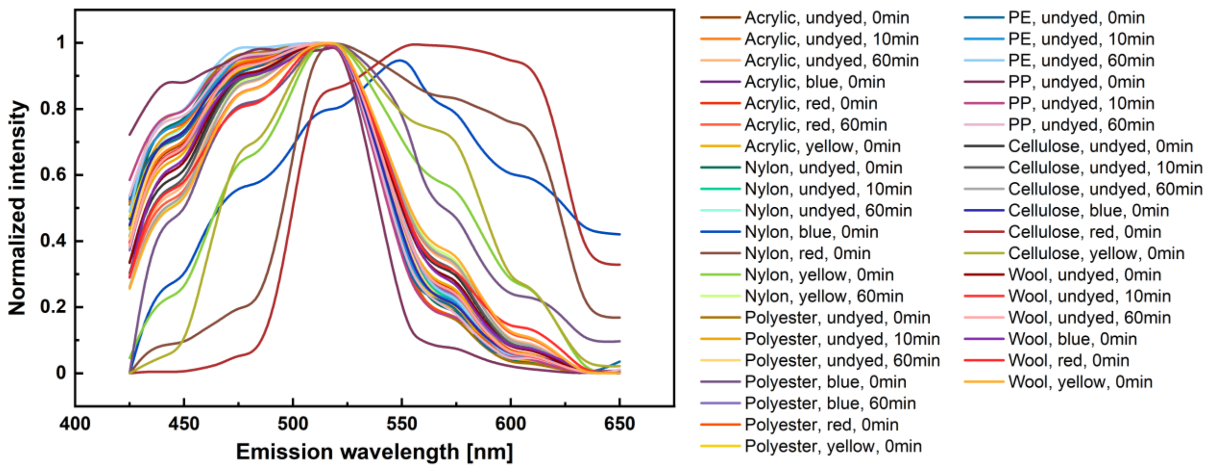

Figure S35. Normalized fluorescence spectra for all polymer samples, confirming that the majority of emission spectra are very similar to one another under excitation at 405 nm.

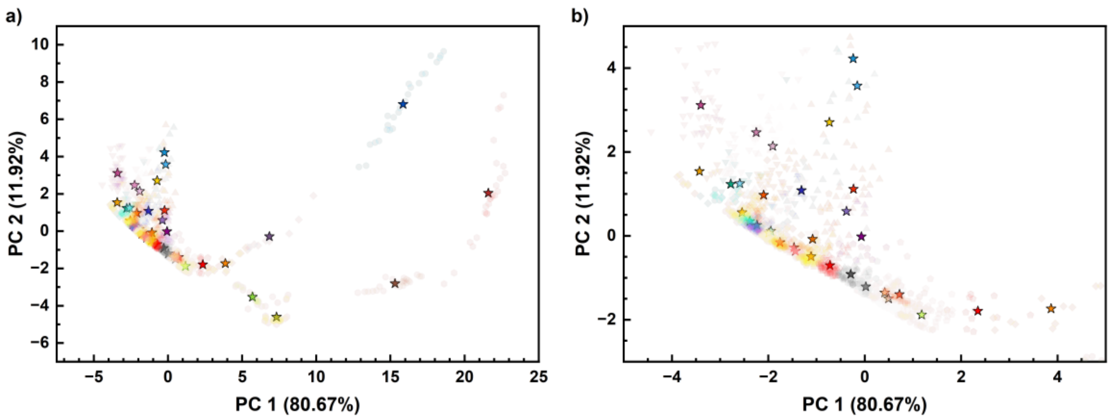

Figure S36. a) Complete principal component plot of the k-means cluster analysis for the individual normalized fluorescence channels (F) only model; **b)** section of principal component plot (stars with black edge: k-means cluster centers; shapes assigned by original polymer type: squares: acrylic, circles: nylon, diamonds: PET, triangles: PE, inverted triangles: PP, hexagons: cellulose, pentagons: wool; colour assigned by cluster membership based on key in Figure S15)

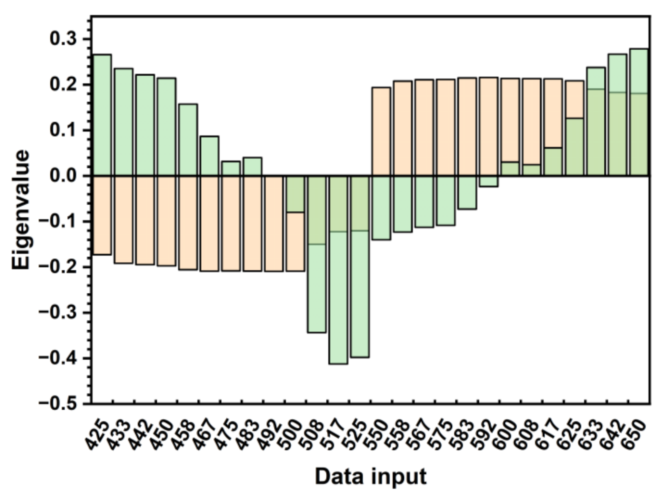

Figure S37. Eigenvalues assigned to principal component 1 (orange bars) and principal component 2 (green bars) for the individual normalized fluorescence channels (F) only model.

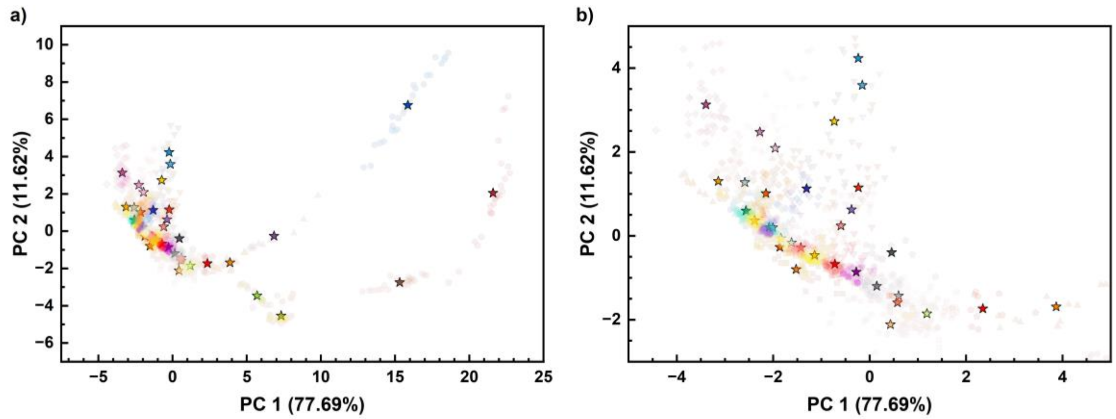

Figure S38. a) Complete principal component plot of the k-means cluster analysis for the individual normalized fluorescence channels and normalized total emission intensity (FI) model; **b)** section of principal component plot (stars with black edge: k-means cluster centers; shapes assigned by original polymer type: squares: acrylic, circles: nylon, diamonds: PET, triangles: PE, inverted triangles: PP, hexagons: cellulose, pentagons: wool; colour assigned by cluster membership based on key in Figure S15)

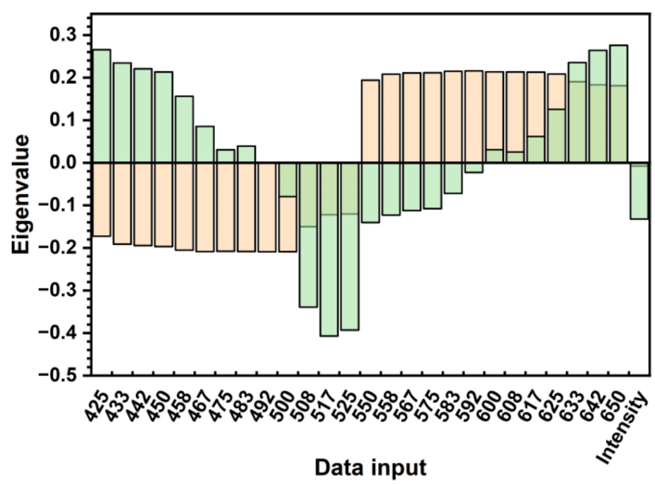

Figure S39. Eigenvalues assigned to principal component 1 (orange bars) and principal component 2 (green bars) for the individual normalized fluorescence channels and normalized total emission intensity (FI) model.

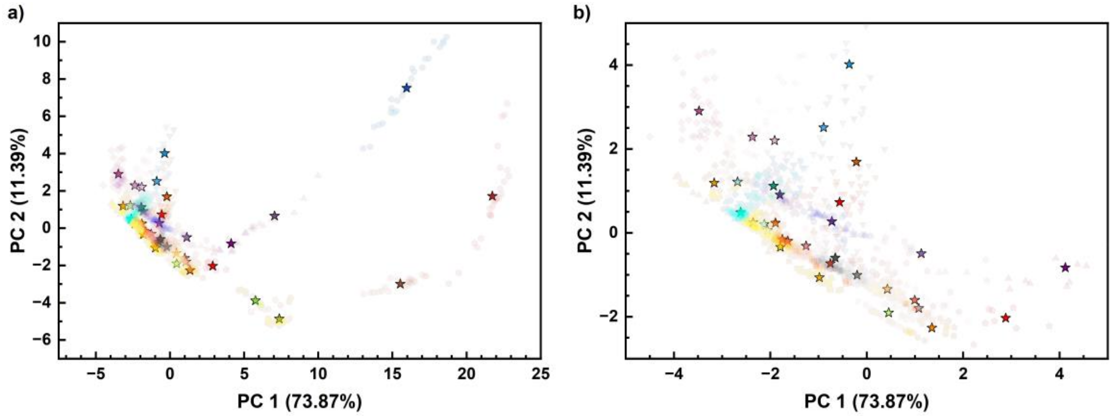

Figure S40. a) Complete principal component plot of the k-means cluster analysis for the individual normalized fluorescence channels and RGB color channels (FC) model; **b)** section of principal component plot (stars with black edge: k-means cluster centers; shapes assigned by original polymer type: squares: acrylic, circles: nylon, diamonds: PET, triangles: PE, inverted triangles: PP, hexagons: cellulose, pentagons: wool; colour assigned by cluster membership based on key in Figure S15)

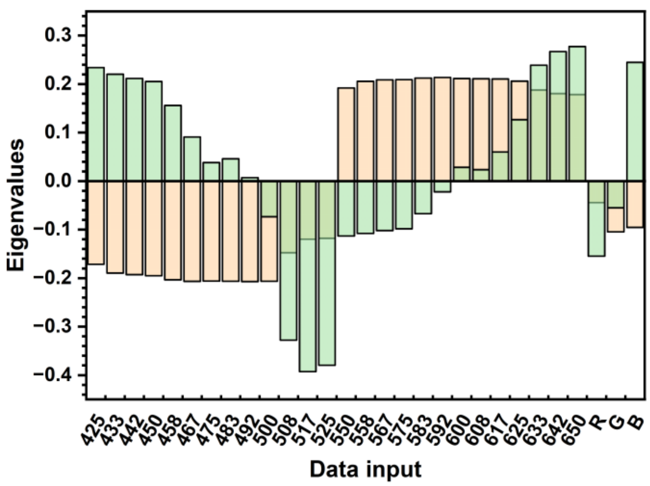

Figure S41. Eigenvalues assigned to principal component 1 (orange bars) and principal component 2 (green bars) for the individual normalized fluorescence channels and RGB color channels (FC) model.

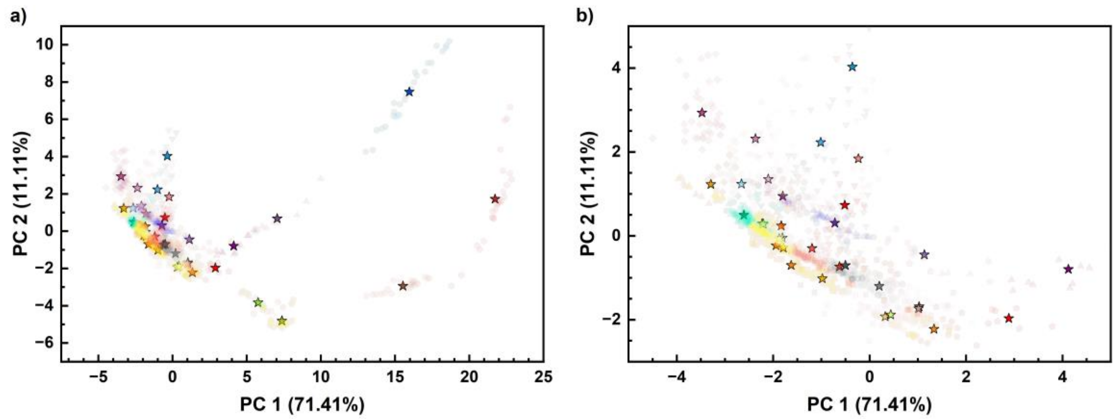

Figure S42. a) Complete principal component plot of the k-means cluster analysis for the individual normalized fluorescence channels, normalized total emission intensity and RGB color channels (FIC) model; **b)** section of principal component plot (stars with black edge: k-means cluster centers; shapes assigned by original polymer type: squares: acrylic, circles: nylon, diamonds: PET, triangles: PE, inverted triangles: PP, hexagons: cellulose, pentagons: wool; colour assigned by cluster membership based on key in Figure S15)

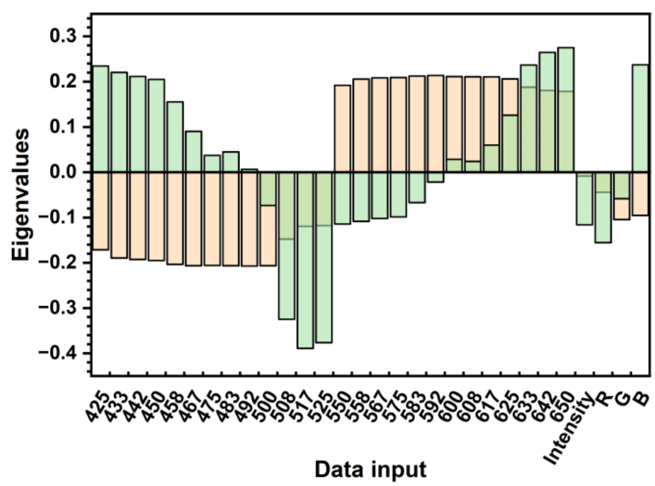

Figure S43. Eigenvalues assigned to principal component 1 (orange bars) and principal component 2 (green bars) for the individual normalized fluorescence channels, normalized total emission intensity and RGB color channels (FIC) model.

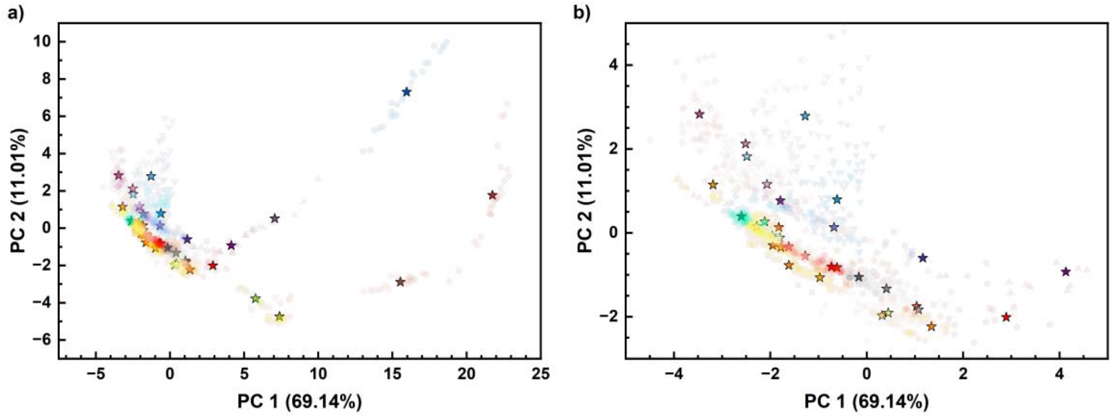

Figure S44. a) Complete principal component plot of the k-means cluster analysis for the individual normalized fluorescence channels, normalized total emission intensity, RGB color channels and shape factor (FICS) model; **b)** section of principal component plot (stars with black edge: k-means cluster centers; shapes assigned by original polymer type: squares: acrylic, circles: nylon, diamonds: PET, triangles: PE, inverted triangles: PP, hexagons: cellulose, pentagons: wool; colour assigned by cluster membership based on key in Figure S15)

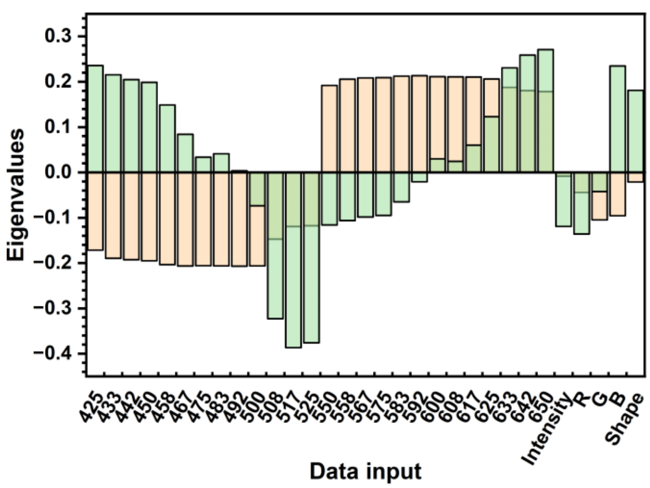

Figure S45. Eigenvalues assigned to principal component 1 (orange bars) and principal component 2 (green bars) for the individual normalized fluorescence channels, normalized total emission intensity, RGB color channels and shape factor (FICS) model.

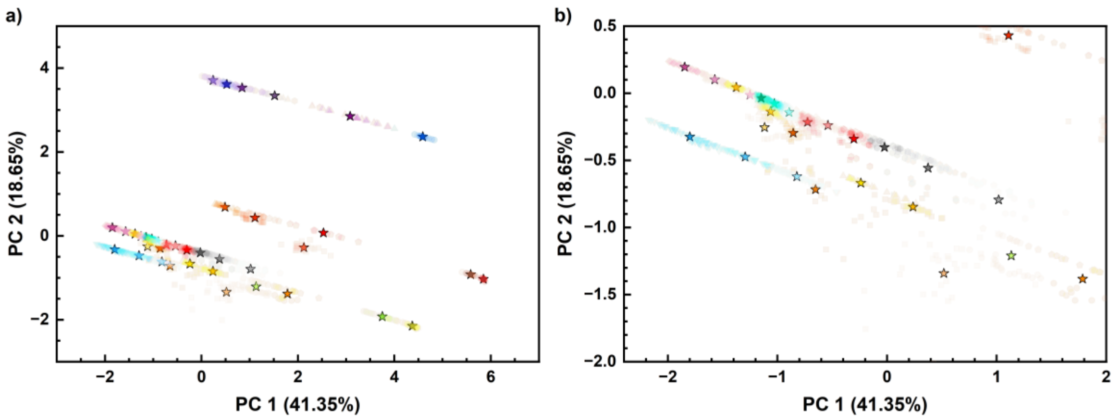

Figure S46. a) Complete principal component plot of the k-means cluster analysis for the reduced set of individual normalized fluorescence channels, normalized total emission intensity, RGB color channels and shape factor (rFICS) model; **b)** section of principal component plot (stars with black edge: k-means cluster centers; shapes assigned by original polymer type: squares: acrylic, circles: nylon, diamonds: PET, triangles: PE, inverted triangles: PP, hexagons: cellulose, pentagons: wool; colour assigned by cluster membership based on key in Figure S15)

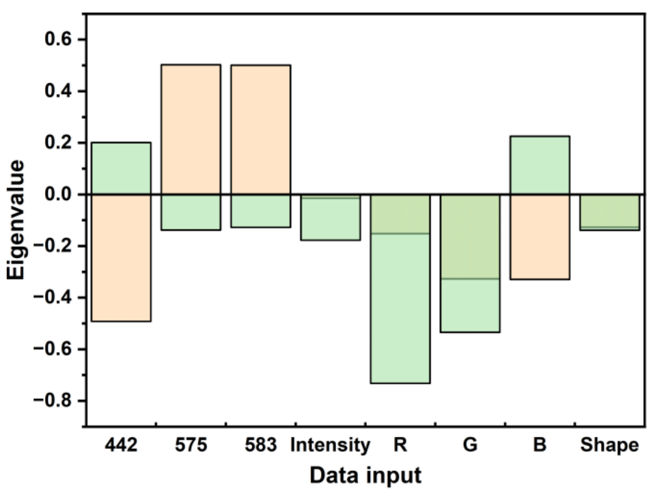

Figure S47. Eigenvalues assigned to principal component 1 (orange bars) and principal component 2 (green bars) for the reduced set of individual normalized fluorescence channels, normalized total emission intensity, RGB color channels and shape factor (rFICS) model.

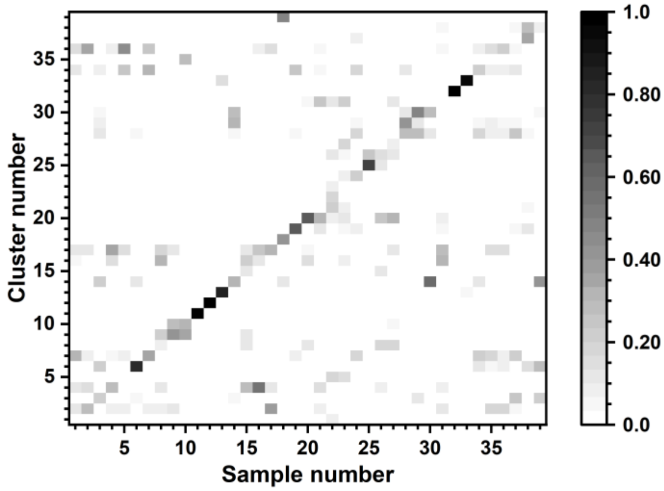

Figure S48. Heat map indicating the fraction of each polymer sample assigned to each k-means cluster for the individual normalized fluorescence channels (F) only model. Scale bar: fraction of each sample assigned to a given cluster number.

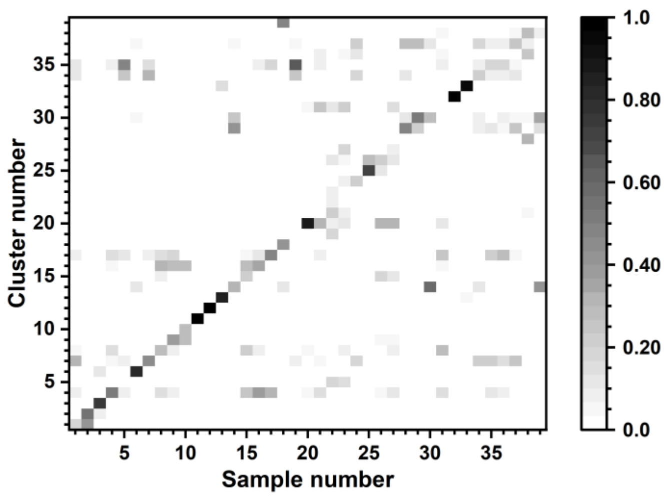

Figure S49. Heat map indicating the fraction of each polymer sample assigned to each k-means cluster for the individual normalized fluorescence channels and normalized total emission intensity (FI) model. Scale bar: fraction of each sample assigned to a given cluster number.

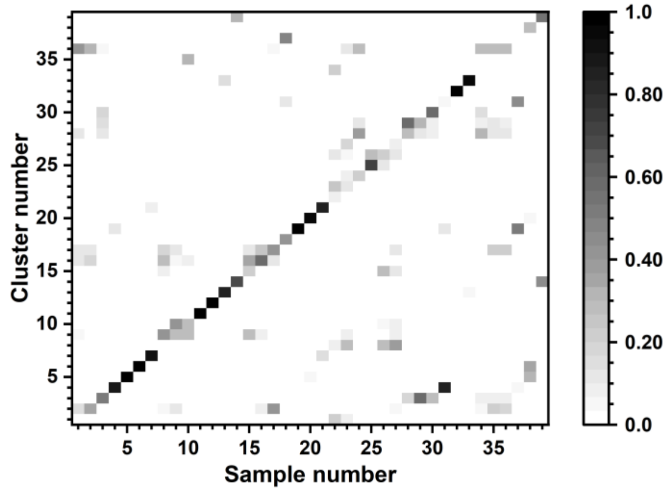

Figure S50. Heat map indicating the fraction of each polymer sample assigned to each k-means cluster for the individual normalized fluorescence channels and RGB color channels (FC) model. Scale bar: fraction of each sample assigned to a given cluster number.

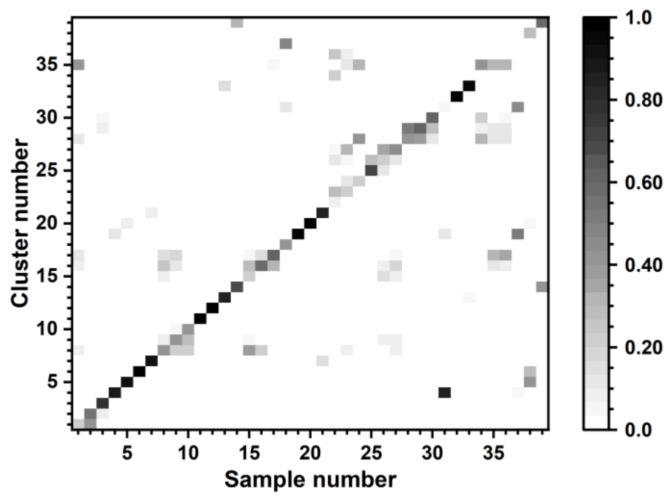

Figure S51. Heat map indicating the fraction of each polymer sample assigned to each k-means cluster for the individual normalized fluorescence channels, normalized total emission intensity and RGB color channels (FIC) model. Scale bar: fraction of each sample assigned to a given cluster number.

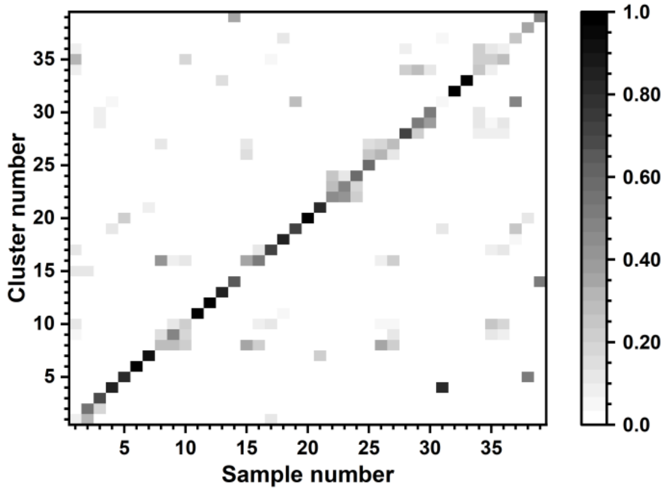

Figure S52. Heat map indicating the fraction of each polymer sample assigned to each k-means cluster for the reduced set of individual normalized fluorescence channels, normalized total emission intensity, RGB color channels and shape factor (rFICS) model. Scale bar: fraction of each sample assigned to a given cluster number.