Supplement for:

Chromophores and chemical composition of brown carbon characterized at an urban kerbside by excitation-emission spectroscopy and mass spectrometry

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1 Nitroaromatic compound calibration

After the field campaign, the calibration of 4-nitrophenol, 4-nitrocatechol, 2-Methyl-4-nitrophenol, and 2-Methyl-4-nitrocatechol was utilized to characterize the sensitivity factor of NACs. Each NACs was dissolved into methanol to about 10 ng/μL as a standard NACs solution. The different volume (1, 2, and 5 μL) of the standard NACs solution was deposited on a PTFE filter using an accurate syringe. The deposited filter was heated by FIGAERO-iodide-CIMS carried by ultra-high purity nitrogen following a thermal desorption. The filters were then desorbed in the same way as for the field sampling. Every volume of the standard solution was repeated three times. The average sensitivity factor of 4 NACs was 1.7 ± 0.06 (Fig. S2).

2 Total potential brown carbon molecules

We observed typically about 2000 mass peaks corresponding to different oxygenated organic compounds in particles by using FIGAERO-CIMS. Individual compounds were assigned to the mass peaks by fitting, $C_cH_hO_oN_n$, different numbers of atoms: c carbon, h hydrogen, o oxygen, and n nitrogen (Lopez-Hilfiker et al., 2014). A double bond equivalent (DBE) can be calculated as follows (Daumit et al., 2013):

$$DBE = \frac{n - h}{2} + c + 1$$

Lin et al. (2018) assigned potential brown carbon compounds in the plot of DBE vs the number of carbon atoms per molecule. They employed high-resolution mass spectrometry to analyze biomass burning organic aerosol. We used this method to find potential BrC molecules, as shown in Fig. S14.

3 Pearson's Correlation of PARAFAC components with the potential BrC molecules

PARAFAC component intensities were normalized to the sum of component fluorescence intensities for a given sample. And the mass concentrations of each potential BrC molecule were normalized to the total mass concentration of the 321 potential BrC molecules for a given sample. Pearson's correlations were derived between each potential BrC molecule and PARAFAC data across 8 samples. Molecules correlated to PARAFAC component intensities with Pearson's r ≥ 0.621 (1-sided t-test) were assigned to each PARAFAC component (Table S10).

Table S1. Instruments were installed in the measurement container.

Measured parameter	Instrument	Data period	
		Summer 2019	Winter 2020
Ambient temperature	WS700 (Lufft GmbH)	7-29 July	27 February - 26 March
Container temperature	WS700 (Lufft GmbH)	7-29 July	27 February - 26 March
Relative humidity	WS700 (Lufft GmbH)	7-29 July	27 February -26 March
Pressure	WS700 (Lufft GmbH)	7-29 July	27 February -26 March
Wind speed	WS700 (Lufft GmbH)	7-29 July	27 February - 26 March
Wind direction	WS700 (Lufft GmbH)	7-29 July	27 February - 26 March
Precipitation	WS700 (Lufft GmbH)	7-29 July	27 February - 26 March
Global radiation	WS700 (Lufft GmbH)	7-29 July	27 February - 26 March
O_3	O341M (Environment SA)	7-29 July	27 February - 26 March
NO_2	AS32M (Environment SA)	7-29 July	27 February - 26 March
Particle optical diameter (0.18-18 µm)	OPC FIDAS200 (Palas GmbH)	7-29 July	27 February - 26 March
Black carbon (BC)	AE51 Aethalometer (Aethlabs Inc.)	7-29 July	27 February - 26 March
Black carbon (BC)	MA200 Aethalometer (Aethlabs Inc.)	-	27 February - 26 March
Particle compounds	AMS (Aerodyne Research Inc.)	7-29 July	27 February - 26 March
Light absorption and emission excitation spectroscopy (offline analysis of filters extracts)	Aqualog (Horiba Inc.)	7-29 July	27 February - 26 March
Particle-phase oxygenate organic molecules (offline analysis of filters)	FIGAERO-CIMS (Aerodyne Research Inc.)	7-29 July	27 February - 26 March

Table S2. Instruments installed on top of a physic building at KIT (~65 m above ground level)

Measured parameter	Instrument	Data period	
		Summer2019	Winter 2020
Wind speed	WS700 (LufftGmbH)	7-29 July	27 February-26 March
Wind direction	WS700 (LufftGmbH)	7-29 July	27 February-26 March

Table S3. A list of Teflon filters sampled for FIGAERO-CIMS analysis at Durlacher Tor, Karlsruhe

Filter No.	Starting time	Ending time	Duration (min)	Sampling flow (L min^{-1})	Volume (L)	Time
4	03/17/202008:35	03/17/202010:35	120	5.2	624	Morning
5	03/17/202010:42	03/17/202014:14	212	5.2	1102	Noon
6	03/17/202020:59	03/17/202022:50	111	5.2	577	Night
7	03/18/202008:50	03/18/202011:20	150	5.2	780	Morning
8	03/18/202012:36	03/18/202016:30	234	5.2	1217	Noon
9	03/18/202021:35	03/18/202023:10	95	5.2	494	Night
10	03/19/202008:40	03/19/202011:20	160	5.2	832	Morning
11	03/19/202011:30	03/19/202016:05	275	5.2	1430	Noon
12	03/19/202020:00	03/19/202022:04	124	5.2	645	Night
13	03/20/202009:05	03/20/202011:30	145	5.2	754	Morning
14	03/20/202012:00	03/20/202014:20	140	5.2	728	Noon

Table S4. A list of quartz filters sampled for Aqualog analysis at Durlacher Tor, Karlsruhe

Sample IDs.	Starting time	Ending time	Duration(h)	Sampling flow (m^3h^{-1})	Volume (m^3)	Times
2019 Summer						
1	07/07/2019 12:30	07/08/2019 12:00	23.5	2.3	54	One day
2	07/08/2019 12:30	07/09/2019 12:00	23.5	2.3	54	One day
3	07/10/2019 12:30	07/11/2019 12:00	23.5	2.3	54	One day
4	07/12/2019 12:30	07/13/2019 12:00	23.5	2.3	54	One day
5	07/14/2019 12:30	07/15/2019 12:00	23.5	2.3	54	One day
6	07/15/2019 12:30	07/16/2019 12:00	23.5	2.3	54	One day
7	07/16/2019 12:30	07/17/2019 12:00	23.5	2.3	54	One day
8	07/17/2019 12:30	07/18/2019 12:00	23.5	2.3	54	One day
9	07/18/2019 12:30	07/19/2019 12:00	23.5	2.3	54	One day
10	07/19/2019 12:30	07/20/2019 12:00	23.5	2.3	54	One day
11	07/20/2019 12:30	07/21/2019 12:00	23.5	2.3	54	One day
12	07/21/2019 12:30	07/22/2019 12:00	23.5	2.3	54	One day
13	07/23/2019 12:30	07/24/2019 12:00	23.5	2.3	54	One day
2020Winter						
14	02/27/2020 09:30	02/28/2020 09:00	23.5	2.3	54	One day
15	02/28/2020 09:30	02/29/2020 09:00	23.5	2.3	54	One day
16	02/29/2020 09:30	03/01/2020 09:00	23.5	2.3	54	One day
17	03/01/2020 09:30	03/02/2020 09:00	23.5	2.3	54	One day
18	03/02/2020 09:30	03/03/2020 09:00	23.5	2.3	54	One day
19	03/03/2020 09:30	03/04/2020 09:00	23.5	2.3	54	One day
20	03/04/2020 09:30	03/05/2020 09:00	23.5	2.3	54	One day
21	03/05/2020 09:30	03/06/2020 09:00	23.5	2.3	54	One day
22	03/06/2020 09:30	03/07/2020 09:00	23.5	2.3	54	One day
23	03/07/2020 09:30	03/08/2020 09:00	23.5	2.3	54	One day
24	03/09/2020 09:30	03/10/2020 09:00	23.5	2.3	54	One day
25	03/10/2020 09:30	03/11/2020 09:00	23.5	2.3	54	One day
26	03/11/2020 09:30	03/12/2020 09:00	23.5	2.3	54	One day
27	03/12/2020 09:30	03/13/2020 09:00	23.5	2.3	54	One day
28	03/13/2020 09:30	03/14/2020 09:00	23.5	2.3	54	One day
29	03/14/2020 09:30	03/15/2020 09:00	23.5	2.3	54	One day
30	03/15/2020 09:30	03/16/2020 09:00	23.5	2.3	54	One day
31	03/16/2020 09:30	03/17/2020 09:00	23.5	2.3	54	One day
32	03/17/2020 09:30	03/18/2020 09:00	23.5	2.3	54	One day
33	03/18/2020 09:30	03/18/2020 12:10	2.7	2.3	6	Morning
34	03/18/2020 12:12	03/18/2020 18:25	6.2	2.3	14	Afternoon
35	03/18/2020 18:30	03/19/2020 08:42	14.1	2.3	60	Night
36	03/19/2020 08:45	03/19/2020 11:33	2.8	2.3	6	Morning
37	03/19/2020 11:33	03/19/2020 19:40	8.1	2.3	19	Afternoon
38	03/19/2020 19:43	03/20/2020 09:05	13.4	2.3	31	Night

39	03/20/2020 09:10	03/20/2020 12:00	2.8	2.3	7	Morning
40	03/20/2020 12:03	03/20/2020 18:22	6.3	2.3	15	Afternoon
41	03/20/2020 18:30	03/21/2020 09:00	14.5	2.3	33	Night
42	03/21/2020 09:30	03/22/2020 09:00	23.5	2.3	54	One day
43	03/22/2020 09:30	03/23/2020 09:00	23.5	2.3	54	One day
44	03/23/2020 09:30	03/24/2020 09:00	23.5	2.3	54	One day
45	03/24/2020 09:30	03/25/2020 09:00	23.5	2.3	54	One day
46	03/25/2020 09:30	03/26/2020 09:00	23.5	2.3	54	One day
47	03/26/2020 09:30	03/27/2020 09:00	23.5	2.3	54	One day

Table S5. Results of the PARAFAC model

Parameters	Fitting of observed concentrations and predicted concentrations	Split-half analysis
Values	0.98	0.98

Table S6. Comparison of aerosol particle light absorption, mass absorption efficiency, and absorption Ångström exponent observed in Karlsruhe with other studies.

Sampling sites	Seasons	Abs (Mm^{-1})	MAE ($m^2\ g^{-1}$)	AAE	Remarks	References
Melpitz (rural)*, Germany	Summer	1.2 ± 0.3	0.3 ± 0.05	-	The Abs and MAE of BrC at 370 nm; the AAE of BrC in Athen at 470 – 950 nm	(Teich et al., 2017)
Melpitz (rural)*, Germany	Winter	6.6 ± 3.5	1.4 ± 0.5	-		(Teich et al., 2017)
Leipizig (urban)*, Germany	Winter	6.8 ± 3.9	1.5 ± 0.3	-		(Teich et al., 2017)
Waldstein (forest)*, Germany	Summer	0.9 ± 0.1	0.3 ± 0.03	-		(Teich et al., 2017)
Magadino (rural)**, Switzerland	Winter	5.6 ± 3.7	0.9	3.8	The Abs and MAE of BrC at 365 nm; the AAE of BrC at 300 – 400 nm	(Moschos et al., 2018)
Zurich (urban)**, Switzerland	Summer	1.0 ± 0.7	0.3	5.1		(Moschos et al., 2018)
Zurich (urban)**, Switzerland	Winter	2.2 ± 1.6	0.9	4.5		(Moschos et al., 2018)
Karlsruhe (urban), Germany	Autumn	-	12.9 ± 2.8	2.6 ± 0.8	The MAE of refractory black carbon (rBC) at 445 nm; the AAE of rBC at 445 – 532nm	(Linke et al., 2016)
Karlsruhe# (urban), Germany	Summer	1.6 ± 0.5	0.5 ± 0.2	5.3 ± 1.2	The Abs and MAE of BrC at 365 nm; the AAE of BrC at 300-400 nm	This study
Karlsruhe# (urban), Germany	Winter	2.8 ± 1.9	1.1 ± 0.3	4.7 ± 0.3		This study

*: alkaline solvent extraction; **: water extraction; #: methanol extraction

Table S7. Spectral characteristics of the four PARAFAC components identified in the EEM datasets of methanol extracts from aerosol particles collected during summer and winter

PARAFAC component	Excitation wavelength (nm)	Emission wavelength (nm)	Component characteristics from this study	Associated AMS-PMF factors	Associated molecular characteristics (winter)	Similar component characteristics from references
C1	< 240	363	Less-oxygenated HULIS	BBOA	High nitrogen-containing molecules, high molecular weight, and low oxidation status	Humic-like component and less oxygenated species. (Chen et al., 2016) Enriched in biomass burning aerosols (Tang et al., 2020)
C2	248, 362	469	Highly oxygenated HULIS-1	LVOOA1 (summer)	Low nitrogen-containing molecules, low molecular weight, and high oxidation status	Highly oxygenated species and humic-like substance (Chen et al., 2016) An intermediate contribution in urban aerosol (Matos et al., 2015)
C3	< 240, 323	408	Highly oxygenated HULIS-2	LVOOA2 (summer) LVOOA (winter)	Low nitrogen-containing molecules, low molecular weight, and high oxidation status	Highly oxygenated species and humic-like substance (Chen et al., 2016) The highest contribution in urban aerosol (Matos et al., 2015)
C4	266	307	Protein-like substances	SV-OOA and LV-OOA (winter)	High nitrogen-containing molecules, low molecular weight, and low oxidation status	Protein-like and non-N-containing species. (Chen et al., 2016) More intense in vehicle exhaust particles. (Tang et al., 2020)

Table S8. Assignment of 316 potential brown carbon molecules detected in Karlsruhe, including mass, formula, double bond equivalent (DBE), the ratio of O/C, and correlation coefficients with the absorption of BrC at 365 nm.

Number	Mass (g mol^{-1})	Formula	O/C	H/C	DBE	Correlation coefficient
1	527	C22H25O14N1	0.6	1.1	11	.841**
2	492	C18H20O16	0.9	1.1	9	.790**
3	412	C18H20O11	0.6	1.1	9	.925**
4	366	C17H18O9	0.5	1.1	9	.959**
5	465	C16H19O15N1	0.9	1.2	8	.855**
6	433	C16H19O13N1	0.8	1.2	8	.928**
7	400	C16H16O12	0.8	1.0	9	.758*
8	368	C16H16O10	0.6	1.0	9	.921**
9	398	C16H14O12	0.8	0.9	10	.890**
10	403	C15H17O12N1	0.8	1.1	8	.905**
11	436	C15H16O15	1.0	1.1	8	.768*
12	372	C15H16O11	0.7	1.1	8	.635*
13	356	C15H16O10	0.7	1.1	8	.979**
14	324	C15H16O8	0.5	1.1	8	.846**
15	434	C15H14O15	1.0	0.9	9	0.317
16	370	C15H14O11	0.7	0.9	9	.884**
17	354	C15H14O10	0.7	0.9	9	.906**
18	368	C15H12O11	0.7	0.8	10	0.601
19	408	C14H16O14	1.0	1.1	7	.622*
20	392	C14H16O13	0.9	1.1	7	0.616
21	376	C14H16O12	0.9	1.1	7	.811**
22	360	C14H16O11	0.8	1.1	7	.886**
23	328	C14H16O9	0.6	1.1	7	.721*
24	374	C14H14O12	0.9	1.0	8	.800**
25	358	C14H14O11	0.8	1.0	8	.901**
26	326	C14H14O9	0.6	1.0	8	.849**
27	372	C14H12O12	0.9	0.9	9	.664*
28	324	C14H12O9	0.6	0.9	9	.943**
29	370	C14H10O12	0.9	0.7	10	0.541
30	393	C13H15O13N1	1.0	1.2	7	.934**
31	345	C13H15O10N1	0.8	1.2	7	.968**
32	394	C13H14O14	1.1	1.1	7	.933**
33	346	C13H14O11	0.8	1.1	7	.759*
34	330	C13H14O10	0.8	1.1	7	.803**
35	282	C13H14O7	0.5	1.1	7	.876**
36	391	C13H13O13N1	1.0	1.0	8	.937**
37	328	C13H12O10	0.8	0.9	8	.810**
38	326	C13H10O10	0.8	0.8	9	.755*
39	365	C12H15O12N1	1.0	1.3	6	.971**
40	333	C12H15O10N1	0.8	1.3	6	.954**

41	301	C12H15O8N1	0.7	1.3	6	.960**
42	285	C12H15O7N1	0.6	1.3	6	.807**
43	382	C12H14O14	1.2	1.2	6	0.470
44	350	C12H14O12	1.0	1.2	6	.928**
45	334	C12H14O11	0.9	1.2	6	.665*
46	318	C12H14O10	0.8	1.2	6	.769*
47	302	C12H14O9	0.8	1.2	6	.882**
48	286	C12H14O8	0.7	1.2	6	.908**
49	380	C12H12O14	1.2	1.0	7	.714*
50	348	C12H12O12	1.0	1.0	7	.782*
51	332	C12H12O11	0.9	1.0	7	.874**
52	300	C12H12O9	0.8	1.0	7	.896**
53	319	C11H13O10N1	0.9	1.2	6	.961**
54	303	C11H13O9N1	0.8	1.2	6	.978**
55	287	C11H13O8N1	0.7	1.2	6	.917**
56	320	C11H12O11	1.0	1.1	6	.846**
57	288	C11H12O9	0.8	1.1	6	0.291
58	272	C11H12O8	0.7	1.1	6	.896**
59	256	C11H12O7	0.6	1.1	6	.745*
60	349	C11H11O12N1	1.1	1.0	7	.774*
61	301	C11H11O9N1	0.8	1.0	7	.912**
62	285	C11H11O8N1	0.7	1.0	7	.846**
63	318	C11H10O11	1.0	0.9	7	.823**
64	286	C11H10O9	0.8	0.9	7	.857**
65	347	C11H9O12N1	1.1	0.8	8	.857**
66	284	C11H8O9	0.8	0.7	8	.913**
67	282	C11H6O9	0.8	0.5	9	0.611
68	355	C10H13O13N1	1.3	1.3	5	.817**
69	323	C10H13O11N1	1.1	1.3	5	.915**
70	307	C10H13O10N1	1.0	1.3	5	.898**
71	291	C10H13O9N1	0.9	1.3	5	.930**
72	275	C10H13O8N1	0.8	1.3	5	.884**
73	259	C10H13O7N1	0.7	1.3	5	.878**
74	243	C10H13O6N1	0.6	1.3	5	.909**
75	227	C10H13O5N1	0.5	1.3	5	0.313
76	211	C10H13O4N1	0.4	1.3	5	.728*
77	340	C10H12O13	1.3	1.2	5	.728*
78	308	C10H12O11	1.1	1.2	5	-0.453
79	292	C10H12O10	1.0	1.2	5	0.051
80	276	C10H12O9	0.9	1.2	5	.756*
81	260	C10H12O8	0.8	1.2	5	.868**
82	244	C10H12O7	0.7	1.2	5	.826**
83	228	C10H12O6	0.6	1.2	5	.786*
84	196	C10H12O4	0.4	1.2	5	.814**

85	180	C10H12O3	0.3	1.2	5	.813**
86	353	C10H11O13N1	1.3	1.1	6	.926**
87	305	C10H11O10N1	1.0	1.1	6	.901**
88	273	C10H11O8N1	0.8	1.1	6	.943**
89	257	C10H11O7N1	0.7	1.1	6	.981**
90	306	C10H10O11	1.1	1.0	6	.816**
91	290	C10H10O10	1.0	1.0	6	.900**
92	274	C10H10O9	0.9	1.0	6	.688*
93	258	C10H10O8	0.8	1.0	6	.886**
94	242	C10H10O7	0.7	1.0	6	.771*
95	304	C10H8O11	1.1	0.8	7	.836**
96	288	C10H8O10	1.0	0.8	7	.890**
97	256	C10H8O8	0.8	0.8	7	.888**
98	309	C9H11O11N1	1.2	1.2	5	.928**
99	293	C9H11O10N1	1.1	1.2	5	.912**
100	277	C9H11O9N1	1.0	1.2	5	.948**
101	261	C9H11O8N1	0.9	1.2	5	.920**
102	245	C9H11O7N1	0.8	1.2	5	.906**
103	229	C9H11O6N1	0.7	1.2	5	.934**
104	213	C9H11O5N1	0.6	1.2	5	.909**
105	310	C9H10O12	1.3	1.1	5	0.605
106	294	C9H10O11	1.2	1.1	5	0.570
107	278	C9H10O10	1.1	1.1	5	.657*
108	262	C9H10O9	1.0	1.1	5	0.356
109	246	C9H10O8	0.9	1.1	5	.672*
110	230	C9H10O7	0.8	1.1	5	.831**
111	214	C9H10O6	0.7	1.1	5	.762*
112	198	C9H10O5	0.6	1.1	5	0.417
113	182	C9H10O4	0.4	1.1	5	.832**
114	307	C9H9O11N1	1.2	1.0	6	.966**
115	259	C9H9O8N1	0.9	1.0	6	.960**
116	211	C9H9O5N1	0.6	1.0	6	.892**
117	308	C9H8O12	1.3	0.9	6	0.481
118	292	C9H8O11	1.2	0.9	6	.811**
119	260	C9H8O9	1.0	0.9	6	.680*
120	228	C9H8O7	0.8	0.9	6	.853**
121	313	C8H11O12N1	1.5	1.4	4	.804**
122	297	C8H11O11N1	1.4	1.4	4	.897**
123	281	C8H11O10N1	1.3	1.4	4	.883**
124	265	C8H11O9N1	1.1	1.4	4	.868**
125	249	C8H11O8N1	1.0	1.4	4	.706*
126	233	C8H11O7N1	0.9	1.4	4	0.233
127	217	C8H11O6N1	0.8	1.4	4	.832**
128	201	C8H11O5N1	0.6	1.4	4	.706*

129	185	C8H11O4N1	0.5	1.4	4	0.394
130	169	C8H11O3N1	0.4	1.4	4	-0.127
131	266	C8H10O10	1.3	1.3	4	0.578
132	250	C8H10O9	1.1	1.3	4	.909**
133	234	C8H10O8	1.0	1.3	4	0.488
134	218	C8H10O7	0.9	1.3	4	.716*
135	202	C8H10O6	0.8	1.3	4	.645*
136	186	C8H10O5	0.6	1.3	4	-0.024
137	170	C8H10O4	0.5	1.3	4	0.103
138	154	C8H10O3	0.4	1.3	4	0.475
139	295	C8H9O11N1	1.4	1.1	5	.926**
140	279	C8H9O10N1	1.3	1.1	5	0.405
141	263	C8H9O9N1	1.1	1.1	5	-.629*
142	247	C8H9O8N1	1.0	1.1	5	-0.040
143	231	C8H9O7N1	0.9	1.1	5	.960**
144	215	C8H9O6N1	0.8	1.1	5	.889**
145	199	C8H9O5N1	0.6	1.1	5	0.587
146	183	C8H9O4N1	0.5	1.1	5	.857**
147	280	C8H8O11	1.4	1.0	5	.732*
148	264	C8H8O10	1.3	1.0	5	.710*
149	248	C8H8O9	1.1	1.0	5	.859**
150	232	C8H8O8	1.0	1.0	5	0.573
151	216	C8H8O7	0.9	1.0	5	0.554
152	200	C8H8O6	0.8	1.0	5	.691*
153	184	C8H8O5	0.6	1.0	5	0.358
154	168	C8H8O4	0.5	1.0	5	0.418
155	229	C8H7O7N1	0.9	0.9	6	.922**
156	213	C8H7O6N1	0.8	0.9	6	.941**
157	262	C8H6O10	1.3	0.8	6	.642*
158	230	C8H6O8	1.0	0.8	6	0.342
159	182	C8H6O5	0.6	0.8	6	0.111
160	267	C7H9O10N1	1.4	1.3	4	.866**
161	251	C7H9O9N1	1.3	1.3	4	.874**
162	235	C7H9O8N1	1.1	1.3	4	.751*
163	219	C7H9O7N1	1.0	1.3	4	.725*
164	203	C7H9O6N1	0.9	1.3	4	.817**
165	187	C7H9O5N1	0.7	1.3	4	0.486
166	171	C7H9O4N1	0.6	1.3	4	0.208
167	155	C7H9O3N1	0.4	1.3	4	.842**
168	123	C7H9O1N1	0.1	1.3	4	0.581
169	268	C7H8O11	1.6	1.1	4	.639*
170	252	C7H8O10	1.4	1.1	4	0.556
171	236	C7H8O9	1.3	1.1	4	.663*
172	220	C7H8O8	1.1	1.1	4	0.444

173	204	C7H8O7	1.0	1.1	4	0.437
174	188	C7H8O6	0.9	1.1	4	0.554
175	172	C7H8O5	0.7	1.1	4	0.377
176	156	C7H8O4	0.6	1.1	4	0.397
177	140	C7H8O3	0.4	1.1	4	.671*
178	249	C7H7O9N1	1.3	1.0	5	0.517
179	233	C7H7O8N1	1.1	1.0	5	-0.601
180	217	C7H7O7N1	1.0	1.0	5	.873**
181	201	C7H7O6N1	0.9	1.0	5	.748*
182	185	C7H7O5N1	0.7	1.0	5	.919**
183	266	C7H6O11	1.6	0.9	5	0.591
184	250	C7H6O10	1.4	0.9	5	0.189
185	218	C7H6O8	1.1	0.9	5	0.216
186	202	C7H6O7	1.0	0.9	5	0.230
187	186	C7H6O6	0.9	0.9	5	.716*
188	170	C7H6O5	0.7	0.9	5	0.407
189	154	C7H6O4	0.6	0.9	5	0.161
190	271	C6H9O11N1	1.8	1.5	3	.976**
191	255	C6H9O10N1	1.7	1.5	3	.916**
192	239	C6H9O9N1	1.5	1.5	3	.850**
193	223	C6H9O8N1	1.3	1.5	3	.831**
194	207	C6H9O7N1	1.2	1.5	3	.868**
195	191	C6H9O6N1	1.0	1.5	3	.753*
196	175	C6H9O5N1	0.8	1.5	3	.738*
197	159	C6H9O4N1	0.7	1.5	3	0.323
198	143	C6H9O3N1	0.5	1.5	3	0.084
199	127	C6H9O2N1	0.3	1.5	3	0.398
200	240	C6H8O10	1.7	1.3	3	0.533
201	224	C6H8O9	1.5	1.3	3	.770*
202	208	C6H8O8	1.3	1.3	3	0.429
203	192	C6H8O7	1.2	1.3	3	0.537
204	176	C6H8O6	1.0	1.3	3	0.549
205	160	C6H8O5	0.8	1.3	3	0.553
206	144	C6H8O4	0.7	1.3	3	-0.176
207	128	C6H8O3	0.5	1.3	3	0.250
208	112	C6H8O2	0.3	1.3	3	0.419
209	269	C6H7O11N1	1.8	1.2	4	.791**
210	253	C6H7O10N1	1.7	1.2	4	.802**
211	237	C6H7O9N1	1.5	1.2	4	.885**
212	221	C6H7O8N1	1.3	1.2	4	.955**
213	205	C6H7O7N1	1.2	1.2	4	.641*
214	189	C6H7O6N1	1.0	1.2	4	.799**
215	173	C6H7O5N1	0.8	1.2	4	0.426
216	157	C6H7O4N1	0.7	1.2	4	0.193

217	141	C6H7O3N1	0.5	1.2	4	-0.041
218	238	C6H6O10	1.7	1.0	4	.654*
219	222	C6H6O9	1.5	1.0	4	0.138
220	206	C6H6O8	1.3	1.0	4	0.011
221	190	C6H6O7	1.2	1.0	4	0.382
222	174	C6H6O6	1.0	1.0	4	0.285
223	158	C6H6O5	0.8	1.0	4	0.384
224	142	C6H6O4	0.7	1.0	4	0.028
225	126	C6H6O3	0.5	1.0	4	0.295
226	110	C6H6O2	0.3	1.0	4	0.108
227	235	C6H5O9N1	1.5	0.8	5	.761*
228	203	C6H5O7N1	1.2	0.8	5	0.265
229	187	C6H5O6N1	1.0	0.8	5	.646*
230	123	C6H5O2N1	0.3	0.8	5	0.238
231	91	C6H5N1	0.0	0.8	5	0.222
232	220	C6H4O9	1.5	0.7	5	0.589
233	204	C6H4O8	1.3	0.7	5	.684*
234	188	C6H4O7	1.2	0.7	5	0.203
235	172	C6H4O6	1.0	0.7	5	0.463
236	156	C6H4O5	0.8	0.7	5	0.372
237	140	C6H4O4	0.7	0.7	5	.715*
238	241	C5H7O10N1	2.0	1.4	3	0.273
239	225	C5H7O9N1	1.8	1.4	3	.752*
240	209	C5H7O8N1	1.6	1.4	3	.914**
241	193	C5H7O7N1	1.4	1.4	3	0.519
242	177	C5H7O6N1	1.2	1.4	3	.784*
243	161	C5H7O5N1	1.0	1.4	3	0.566
244	145	C5H7O4N1	0.8	1.4	3	0.282
245	129	C5H7O3N1	0.6	1.4	3	0.589
246	113	C5H7O2N1	0.4	1.4	3	0.039
247	210	C5H6O9	1.8	1.2	3	0.572
248	194	C5H6O8	1.6	1.2	3	0.414
249	178	C5H6O7	1.4	1.2	3	0.543
250	162	C5H6O6	1.2	1.2	3	0.347
251	146	C5H6O5	1.0	1.2	3	0.448
252	130	C5H6O4	0.8	1.2	3	0.014
253	114	C5H6O3	0.6	1.2	3	0.086
254	223	C5H5O9N1	1.8	1.0	4	.782*
255	207	C5H5O8N1	1.6	1.0	4	.694*
256	191	C5H5O7N1	1.4	1.0	4	-0.175
257	175	C5H5O6N1	1.2	1.0	4	0.151
258	159	C5H5O5N1	1.0	1.0	4	0.501
259	143	C5H5O4N1	0.8	1.0	4	0.135
260	127	C5H5O3N1	0.6	1.0	4	-0.341

261	111	C5H5O2N1	0.4	1.0	4	-0.123
262	208	C5H4O9	1.8	0.8	4	0.102
263	192	C5H4O8	1.6	0.8	4	-0.128
264	176	C5H4O7	1.4	0.8	4	0.566
265	144	C5H4O5	1.0	0.8	4	0.187
266	128	C5H4O4	0.8	0.8	4	-0.049
267	112	C5H4O3	0.6	0.8	4	0.360
268	80	C5H4O1	0.2	0.8	4	-0.295
269	197	C4H7O8N1	2.0	1.8	2	.914**
270	181	C4H7O7N1	1.8	1.8	2	.865**
271	165	C4H7O6N1	1.5	1.8	2	.630*
272	149	C4H7O5N1	1.3	1.8	2	0.605
273	133	C4H7O4N1	1.0	1.8	2	0.439
274	117	C4H7O3N1	0.8	1.8	2	0.083
275	85	C4H7O1N1	0.3	1.8	2	0.520
276	182	C4H6O8	2.0	1.5	2	0.329
277	166	C4H6O7	1.8	1.5	2	-0.004
278	150	C4H6O6	1.5	1.5	2	0.553
279	134	C4H6O5	1.3	1.5	2	0.534
280	118	C4H6O4	1.0	1.5	2	0.044
281	102	C4H6O3	0.8	1.5	2	0.002
282	86	C4H6O2	0.5	1.5	2	-0.238
283	70	C4H6O1	0.3	1.5	2	-0.469
284	211	C4H5O9N1	2.3	1.3	3	.664*
285	195	C4H5O8N1	2.0	1.3	3	-.687*
286	179	C4H5O7N1	1.8	1.3	3	.853**
287	163	C4H5O6N1	1.5	1.3	3	0.271
288	147	C4H5O5N1	1.3	1.3	3	0.259
289	131	C4H5O4N1	1.0	1.3	3	0.252
290	99	C4H5O2N1	0.5	1.3	3	-0.171
291	196	C4H4O9	2.3	1.0	3	0.341
292	180	C4H4O8	2.0	1.0	3	0.271
293	164	C4H4O7	1.8	1.0	3	0.267
294	148	C4H4O6	1.5	1.0	3	0.287
295	132	C4H4O5	1.3	1.0	3	0.460
296	116	C4H4O4	1.0	1.0	3	-0.033
297	84	C4H4O2	0.5	1.0	3	0.509
298	68	C4H4O1	0.3	1.0	3	-0.469
299	199	C3H5O9N1	3.0	1.7	2	.733*
300	183	C3H5O8N1	2.7	1.7	2	.706*
301	167	C3H5O7N1	2.3	1.7	2	-0.182
302	151	C3H5O6N1	2.0	1.7	2	.754*
303	135	C3H5O5N1	1.7	1.7	2	.701*
304	119	C3H5O4N1	1.3	1.7	2	0.542

305	103	C3H5O3N1	1.0	1.7	2	-0.015
306	87	C3H5O2N1	0.7	1.7	2	-0.112
307	168	C3H4O8	2.7	1.3	2	0.456
308	152	C3H4O7	2.3	1.3	2	0.009
309	136	C3H4O6	2.0	1.3	2	0.270
310	120	C3H4O5	1.7	1.3	2	0.480
311	104	C3H4O4	1.3	1.3	2	0.138
312	88	C3H4O3	1.0	1.3	2	0.339
313	72	C3H4O2	0.7	1.3	2	-0.298
314	92	C2H4O4	2.0	2.0	1	0.177
315	76	C2H4O3	1.5	2.0	1	-0.217
316	60	C2H4O2	1.0	2.0	1	0.025

Pearson’s correlation coefficient (1-sided t test), **: $p < 0.01$, *: $p < 0.05$

Table S9. Mass absorption coefficients (MAC) (m^2g^{-1}) were determined for different nitro-aromatic compounds by (Xie et al., 2020).

Formula	Mass ($g\ mol^{-1}$)	MAC_{365} ($m^2\ g^{-1}$)
C6H5NO3	139	2.4
C7H7NO3	153	3.2
C6H5NO4	155	7.0
C7H7NO4	169	12.9
C8H9NO4	183	12.9
C7H7NO5	185	14.0
C10H7NO3	189	3.8
C9H9NO4	195	12.9
C8H7NO5	197	12.9
C8H9NO5	199	14.0
C11H9NO3	203	3.8
C10H11NO5	225	14.0
Average	-	9.5±4.7

Table S10. Correlations of fluorescent components with NACs and potential brown carbon molecules. PARAFAC components are listed from C1 to C4. Blank cells indicate no association, and cells with the value 1 indicate an association.

Formula	C1	C2	C3	C4	C1	C2	C3	C4
C22H25O14N1	.684*	-.720*	-.723*	-0.423	1			
C18H20O16	0.606	-0.413	-0.615	-0.509				
C18H20O11	.929**	-.836**	-.924**	-.687*	1			
C17H18O9	.895**	-.886**	-.959**	-0.574	1			
C16H19O15N1	.695*	-.674*	-.765*	-0.441	1			
C16H19O13N1	.816**	-.794**	-.851**	-0.546	1			
C16H16O12	0.564	-0.516	-.670*	-0.341				
C16H16O10	.902**	-.889**	-.904**	-.622*	1			
C16H14O12	.755*	-.634*	-.674*	-.631*	1			
C15H17O12N1	.852**	-.852**	-.882**	-0.563	1			
C15H16O15	0.596	-0.571	-0.527	-0.465				
C15H16O11	.688*	-0.572	-.752*	-0.488	1			
C15H16O10	.910**	-.825**	-.893**	-.677*	1			
C15H16O8	.648*	-.783*	-.785*	-0.283	1			
C15H14O15	-0.165	0.087	0.177	0.147				
C15H14O11	.752*	-.727*	-.726*	-0.544	1			
C15H14O10	.803**	-.632*	-.759*	-.666*	1			
C15H12O11	0.220	-0.148	-0.185	-0.211				
C14H16O14	0.322	-0.331	-0.294	-0.234				
C14H16O13	0.393	0.012	-0.376	-0.490				
C14H16O12	.734*	-0.535	-.784*	-0.571	1			
C14H16O11	.937**	-.752*	-.918**	-.749*	1			
C14H16O9	.772*	-0.488	-0.619	-.775*	1			
C14H14O12	.672*	-0.511	-0.573	-0.608	1			
C14H14O11	.791**	-0.540	-.713*	-.721*	1			
C14H14O9	.862**	-.809**	-.912**	-0.583	1			
C14H12O12	0.322	-0.319	-0.310	-0.229				
C14H12O9	.624*	-0.618	-0.604	-0.441	1			
C14H10O12	0.181	-0.019	-0.063	-0.285				
C13H15O13N1	.881**	-.777*	-.852**	-.676*	1			
C13H15O10N1	.876**	-.885**	-.926**	-0.562	1			
C13H14O14	.901**	-.859**	-.926**	-0.621	1			
C13H14O11	.659*	-0.573	-.674*	-0.485	1			
C13H14O10	.863**	-.630*	-.799**	-.753*	1			
C13H14O7	0.221	-0.297	-0.218	-0.113				
C13H13O13N1	.857**	-.899**	-.916**	-0.524	1			
C13H12O10	.711*	-.637*	-.714*	-0.522	1			
C13H10O10	0.614	-0.510	-0.579	-0.497				
C12H15O12N1	.917**	-.866**	-.881**	-.675*	1			
C12H15O10N1	.872**	-.770*	-.840**	-.669*	1			
C12H15O8N1	.807**	-.879**	-.801**	-0.518	1			

C12H15O7N1	.695*	-.782*	-.742*	-0.398	1
C12H14O14	-0.072	-0.135	0.040	0.177	
C12H14O12	.736*	-.688*	-.722*	-0.536	1
C12H14O11	0.600	-0.385	-0.534	-0.564	
C12H14O10	.776*	-0.574	-.764*	-.642*	1
C12H14O9	.784*	-0.618	-.780*	-.625*	1
C12H14O8	0.600	-0.558	-0.454	-0.527	
C12H12O14	0.347	-0.337	-0.369	-0.228	
C12H12O12	0.477	-0.574	-0.506	-0.256	
C12H12O11	.881**	-0.589	-.783*	-.817**	1
C12H12O9	.899**	-.745*	-.847**	-.728*	1
C11H13O10N1	.895**	-.852**	-.850**	-.663*	1
C11H13O9N1	.887**	-.852**	-.924**	-0.599	1
C11H13O8N1	.940**	-.803**	-.942**	-.712*	1
C11H12O11	0.441	-0.576	-0.375	-0.275	
C11H12O9	0.204	0.090	0.024	-0.441	
C11H12O8	.911**	-.705*	-.790**	-.808**	1
C11H12O7	0.582	-0.300	-0.449	-.632*	
C11H11O12N1	0.557	-0.536	-.658*	-0.326	
C11H11O9N1	.888**	-.720*	-.817**	-.741*	1
C11H11O8N1	.731*	-.701*	-.759*	-0.496	1
C11H10O11	0.267	-0.107	-0.034	-0.419	
C11H10O9	.874**	-0.564	-.727*	-.853**	1
C11H9O12N1	.693*	-.782*	-.740*	-0.396	1
C11H8O9	.796**	-.710*	-.749*	-0.619	1
C11H6O9	0.013	-0.062	0.034	-0.014	
C10H13O13N1	0.423	-0.508	-.635*	-0.107	
C10H13O11N1	.815**	-.733*	-.815**	-0.600	1
C10H13O10N1	.802**	-.916**	-.930**	-0.404	1
C10H13O9N1	.717*	-.690*	-.747*	-0.485	1
C10H13O8N1	.672*	-.728*	-.714*	-0.401	1
C10H13O7N1	.663*	-.731*	-.774*	-0.345	1
C10H13O6N1	.861**	-.884**	-.918**	-0.539	1
C10H13O5N1	-0.253	0.305	0.168	0.201	
C10H13O4N1	0.426	-0.179	-0.122	-0.617	
C10H12O13	0.534	-0.446	-0.578	-0.382	
C10H12O11	-0.307	0.413	0.465	0.052	
C10H12O10	0.064	0.005	0.059	-0.159	
C10H12O9	0.528	-0.304	-0.292	-.632*	
C10H12O8	0.320	-0.079	-0.170	-0.442	
C10H12O7	0.560	-0.358	-0.361	-0.617	
C10H12O6	0.225	-0.004	0.090	-0.475	
C10H12O4	.685*	-0.520	-0.566	-.632*	1
C10H12O3	0.591	-.692*	-.744*	-0.252	

C10H11O13N1	.841**	-.798**	-.905**	-0.555	1
C10H11O10N1	0.581	-0.411	-0.499	-0.539	
C10H11O8N1	.943**	-.749*	-.818**	-.825**	1
C10H11O7N1	.895**	-.852**	-.902**	-.629*	1
C10H10O11	0.489	-0.280	-0.234	-0.609	
C10H10O10	0.176	-0.292	-0.114	-0.101	
C10H10O9	0.210	0.101	0.031	-0.463	
C10H10O8	.724*	-0.416	-0.534	-.779*	1
C10H10O7	.711*	-0.265	-0.576	-.805**	1
C10H8O11	.777*	-0.501	-.680*	-.737*	1
C10H8O10	.672*	-0.515	-.687*	-0.531	1
C10H8O8	.716*	-.684*	-.714*	-0.507	1
C9H11O11N1	.677*	-.680*	-.663*	-0.470	1
C9H11O10N1	.685*	-.753*	-.699*	-0.423	1
C9H11O9N1	0.607	-0.592	-0.522	-0.477	
C9H11O8N1	.649*	-.724*	-.708*	-0.366	1
C9H11O7N1	.672*	-.718*	-.732*	-0.396	1
C9H11O6N1	.878**	-.825**	-.778*	-.692*	1
C9H11O5N1	.836**	-.789**	-.869**	-0.574	1
C9H10O12	-0.241	0.225	0.260	0.161	
C9H10O11	0.246	-0.369	-0.122	-0.185	
C9H10O10	0.194	0.202	0.098	-0.530	
C9H10O9	0.209	0.002	-0.100	-0.324	
C9H10O8	-0.105	0.241	0.361	-0.166	
C9H10O7	0.331	-0.175	-0.065	-0.480	
C9H10O6	-0.133	0.265	0.407	-0.157	
C9H10O5	0.154	0.062	-0.171	-0.206	
C9H10O4	.666*	-0.380	-.671*	-0.601	1
C9H9O11N1	.704*	-.639*	-.649*	-0.550	1
C9H9O8N1	.766*	-.809**	-.810**	-0.471	1
C9H9O5N1	.894**	-.823**	-.857**	-.672*	1
C9H8O12	-0.090	0.498	0.380	-0.340	
C9H8O11	0.400	-0.361	-0.306	-0.354	
C9H8O9	0.195	-0.045	0.024	-0.355	
C9H8O7	0.297	-0.402	-0.492	-0.021	
C8H11O12N1	0.493	-0.564	-0.616	-0.220	
C8H11O11N1	.831**	-.790**	-.837**	-0.584	1
C8H11O10N1	0.509	-0.427	-0.544	-0.369	
C8H11O9N1	0.583	-0.556	-0.564	-0.424	
C8H11O8N1	0.033	-0.133	-0.203	0.140	
C8H11O7N1	-0.041	-0.096	-0.225	0.273	
C8H11O6N1	0.601	-.814**	-.722*	-0.221	
C8H11O5N1	-0.447	0.153	0.442	0.461	
C8H11O4N1	-0.283	0.100	0.125	0.391	

C8H11O3N1	-0.295	0.192	0.223	0.301				
C8H10O10	0.099	-0.041	-0.295	0.030				
C8H10O9	.791**	-.717*	-.766*	-0.595	1			
C8H10O8	-0.257	0.320	0.151	0.212				
C8H10O7	-0.113	0.093	0.285	-0.025				
C8H10O6	-0.371	0.327	0.584	0.136				
C8H10O5	-.897**	.693*	.797**	.784*		1	1	
C8H10O4	-0.238	0.424	0.187	0.098				
C8H10O3	-0.015	0.468	0.144	-0.310				
C8H9O11N1	.642*	-0.574	-.646*	-0.471	1			
C8H9O10N1	-0.404	0.440	0.531	0.175				
C8H9O9N1	-0.517	.684*	.702*	0.144		1	1	
C8H9O8N1	-0.488	0.297	0.554	0.390				
C8H9O7N1	0.328	-0.540	-0.526	0.016				
C8H9O6N1	0.429	-0.479	-0.329	-0.332				
C8H9O5N1	0.036	0.303	0.084	-0.279				
C8H9O4N1	.926**	-.824**	-.909**	-.696*	1			
C8H8O11	0.380	-0.402	-0.297	-0.303				
C8H8O10	0.324	-0.331	-0.292	-0.238				
C8H8O9	0.141	0.060	0.091	-0.353				
C8H8O8	-0.350	0.561	0.616	-0.045				
C8H8O7	-0.369	0.554	.638*	-0.021			1	
C8H8O6	-0.394	0.566	.665*	0.003			1	
C8H8O5	-0.458	0.536	0.551	0.211				
C8H8O4	0.314	0.236	-0.120	-.628*				
C8H7O7N1	.811**	-.916**	-.920**	-0.429	1			
C8H7O6N1	.766*	-0.423	-.624*	-.795**	1			
C8H6O10	-0.192	0.488	0.463	-0.200				
C8H6O8	-0.389	0.363	0.432	0.251				
C8H6O5	-0.159	0.196	0.172	0.081				
C7H9O10N1	.670*	-0.514	-.698*	-0.520	1			
C7H9O9N1	0.567	-0.504	-.622*	-0.384				
C7H9O8N1	0.065	-0.143	-0.176	0.069				
C7H9O7N1	0.258	-0.410	-0.444	0.025				
C7H9O6N1	.654*	-.651*	-.643*	-0.456	1			
C7H9O5N1	-.781*	0.606	.702*	.676*			1	1
C7H9O4N1	-0.585	0.465	0.571	0.472				
C7H9O3N1	.907**	-.740*	-.863**	-.736*	1			
C7H9O1N1	0.246	-0.150	-0.090	-0.321				
C7H8O11	0.039	-0.063	-0.004	-0.036				
C7H8O10	-0.207	0.167	0.261	0.126				
C7H8O9	0.007	0.354	0.317	-0.405				
C7H8O8	-0.572	0.577	.777*	0.255			1	
C7H8O7	-0.453	0.445	0.615	0.208				

C7H8O6	-0.588	0.586	.775*	0.281			1	
C7H8O5	-.842**	.742*	.840**	.629*		1	1	1
C7H8O4	0.215	0.044	-0.181	-0.304				
C7H8O3	.691*	-0.432	-.716*	-0.591	1			
C7H7O9N1	0.112	0.035	-0.201	-0.094				
C7H7O8N1	-0.490	.639*	.645*	0.157		1	1	
C7H7O7N1	0.619	-.648*	-.627*	-0.402				
C7H7O6N1	-0.543	0.498	.632*	0.335			1	
C7H7O5N1	.956**	-.744*	-.858**	-.828**	1			
C7H7O4N1	.934**	-.749*	-.877**	-.771*	1			
C7H7O3N1	-.814**	.746*	.816**	0.589			1	
C7H6O11	-0.073	-0.202	0.123	0.160				
C7H6O10	-0.388	0.485	0.509	0.135				
C7H6O8	-0.204	0.500	0.368	-0.122				
C7H6O7	-.768*	0.479	.779*	.669*			1	1
C7H6O6	0.173	0.178	0.141	-0.505				
C7H6O5	-0.331	0.449	0.514	0.044				
C7H6O4	-0.570	.836**	0.604	0.229		1		
C6H9O11N1	.913**	-.864**	-.882**	-.669*	1			
C6H9O10N1	.831**	-0.579	-.775*	-.736*	1			
C6H9O9N1	.748*	-.625*	-.728*	-0.588	1			
C6H9O8N1	0.276	-0.453	-0.288	-0.089				
C6H9O7N1	0.466	-0.569	-0.587	-0.185				
C6H9O6N1	0.092	-0.267	-0.255	0.135				
C6H9O5N1	0.162	-0.301	-0.216	-0.002				
C6H9O4N1	-.630*	0.421	0.521	0.610				
C6H9O3N1	-0.382	0.379	0.388	0.258				
C6H9O2N1	0.171	-0.134	-0.330	-0.032				
C6H8O10	-.947**	.835**	.890**	.743*		1	1	1
C6H8O9	0.585	-0.237	-0.497	-.638*				
C6H8O8	0.165	0.248	-0.064	-0.394				
C6H8O7	-0.134	0.346	0.386	-0.184				
C6H8O6	-0.517	0.443	.690*	0.279			1	
C6H8O5	-0.555	0.479	.653*	0.356			1	
C6H8O4	-0.610	0.619	.657*	0.381			1	
C6H8O3	0.361	0.059	-0.232	-0.548				
C6H8O2	0.459	-0.012	-0.330	-.630*				
C6H7O11N1	0.405	-0.366	-0.481	-0.247				
C6H7O10N1	0.315	-0.199	-0.277	-0.301				
C6H7O9N1	.710*	-.626*	-.727*	-0.517	1			
C6H7O8N1	0.510	-0.460	-0.528	-0.363				
C6H7O7N1	-0.393	0.103	0.146	0.581				
C6H7O6N1	0.057	-0.111	0.150	-0.147				
C6H7O5N1	-.799**	.661*	.812**	0.609		1	1	

C6H7O4N1	-0.467	0.476	0.465	0.315				
C6H7O3N1	-0.425	0.538	0.454	0.212				
C6H6O10	-0.238	0.372	0.417	-0.024				
C6H6O9	-.781*	0.613	.811**	0.601			1	
C6H6O8	-.691*	.671*	.802**	0.409		1	1	
C6H6O7	-0.354	0.391	0.476	0.143				
C6H6O6	-.684*	.728*	.873**	0.320		1	1	
C6H6O5	-0.618	.653*	.687*	0.359		1	1	
C6H6O4	-0.196	0.422	0.307	-0.056				
C6H6O3	0.246	0.099	-0.147	-0.413				
C6H6O2	-0.254	0.513	0.338	-0.017				
C6H5O9N1	0.361	-0.239	-0.238	-0.390				
C6H5O7N1	-.822**	0.609	.808**	.681*			1	1
C6H5O6N1	-0.235	0.127	0.393	0.113				
C6H5O5N1	.753*	-0.594	-.722*	-0.617	1			
C6H5O4N1	.939**	-.779*	-.884**	-.761*	1			
C6H5O3N1	-0.015	0.255	-0.066	-0.061				
C6H5O2N1	0.230	0.110	-0.190	-0.360				
C6H5N1	0.046	-0.001	0.035	-0.108				
C6H4O9	-0.414	0.536	0.487	0.172				
C6H4O8	-0.245	0.307	0.387	0.042				
C6H4O7	-0.532	0.257	0.605	0.459				
C6H4O6	0.026	0.226	0.137	-0.255				
C6H4O5	-0.526	.708*	.752*	0.116			1	
C6H4O4	0.558	-0.203	-0.384	-.680*				
C5H7O10N1	-0.484	0.354	0.339	0.492				
C5H7O9N1	0.176	0.062	-0.125	-0.278				
C5H7O8N1	.946**	-.786*	-.914**	-.750*	1			
C5H7O7N1	-0.092	-0.002	-0.150	0.270				
C5H7O6N1	0.423	-0.453	-0.403	-0.285				
C5H7O5N1	-0.562	0.357	0.603	0.463				
C5H7O4N1	-0.554	0.418	0.514	0.475				
C5H7O3N1	0.364	-0.235	-0.320	-0.344				
C5H7O2N1	0.105	0.047	-0.056	-0.182				
C5H6O9	-0.135	0.285	0.286	-0.085				
C5H6O8	0.001	0.431	0.126	-0.308				
C5H6O7	-0.463	0.620	.689*	0.088			1	
C5H6O6	-.672*	0.530	.786*	0.459			1	
C5H6O5	-0.469	0.485	.636*	0.203			1	
C5H6O4	-0.424	0.476	0.424	0.263				
C5H6O3	0.102	0.232	0.039	-0.335				
C5H5O9N1	0.197	-0.271	-0.305	-0.024				
C5H5O8N1	.696*	-0.429	-0.558	-.704*	1			
C5H5O7N1	-.894**	.764*	.840**	.713*		1	1	1

C5H5O6N1	-.877**	.648*	.772*	.787*		1	1	1
C5H5O5N1	-.722*	0.615	.860**	0.458			1	
C5H5O4N1	-.691*	.669*	.759*	0.440		1	1	
C5H5O3N1	-.655*	.693*	.731*	0.377		1	1	
C5H5O2N1	-0.326	0.477	0.416	0.085				
C5H4O9	-0.337	0.358	0.480	0.126				
C5H4O8	-0.408	.647*	0.531	0.074		1		
C5H4O7	-0.178	0.305	0.130	0.086				
C5H4O5	-0.447	0.435	0.601	0.211				
C5H4O4	-0.345	0.576	0.452	0.046				
C5H4O3	0.371	-0.001	-0.296	-0.495				
C5H4O1	-.676*	0.317	0.436	.806**				1
C4H7O8N1	.781*	-0.471	-.678*	-.763*	1			
C4H7O7N1	.934**	-.719*	-.855**	-.801**	1			
C4H7O6N1	0.178	0.037	-0.233	-0.197				
C4H7O5N1	-0.613	0.463	.739*	0.414			1	
C4H7O4N1	-0.320	0.237	0.249	0.309				
C4H7O3N1	-0.254	0.330	0.255	0.133				
C4H7O1N1	-0.106	-0.001	0.212	0.059				
C4H6O8	-0.160	0.463	0.153	-0.044				
C4H6O7	-0.268	0.521	0.365	-0.013				
C4H6O6	-0.205	0.375	0.514	-0.151				
C4H6O5	-0.563	.628*	.748*	0.229		1	1	
C4H6O4	-0.183	0.378	0.262	-0.028				
C4H6O3	0.027	0.181	0.074	-0.193				
C4H6O2	-.722*	0.313	0.468	.872**				1
C4H6O1	-.717*	0.491	.677*	.632*			1	1
C4H5O9N1	0.102	0.065	-0.008	-0.219				
C4H5O8N1	-.808**	.632*	.879**	0.598		1	1	
C4H5O7N1	0.390	-0.468	-0.400	-0.219				
C4H5O6N1	-0.548	0.099	0.431	.685*				1
C4H5O5N1	-.874**	.653*	.876**	.711*		1	1	1
C4H5O4N1	-0.558	0.542	0.621	0.348				
C4H5O2N1	-0.472	0.601	0.482	0.249				
C4H4O9	-0.516	0.266	0.447	0.528				
C4H4O8	-0.420	0.259	0.396	0.386				
C4H4O7	-0.083	0.422	0.065	-0.107				
C4H4O6	-.636*	0.418	.714*	0.496			1	
C4H4O5	-0.574	0.508	.754*	0.309			1	
C4H4O4	-0.521	0.591	0.615	0.258				
C4H4O2	-0.068	0.041	0.133	0.019				
C4H4O1	-.714*	0.495	.675*	.627*			1	1
C3H5O9N1	0.329	-0.169	-0.186	-0.401				
C3H5O8N1	0.485	-0.283	-0.543	-0.398				

C3H5O7N1	-.865**	0.574	.768*	.806**		1	1
C3H5O6N1	-0.105	-0.275	-0.105	0.407			
C3H5O5N1	0.237	-0.017	-0.148	-0.334			
C3H5O4N1	-0.140	0.077	0.154	0.119			
C3H5O3N1	-0.189	0.374	0.232	0.005			
C3H5O2N1	-0.322	0.403	0.369	0.147			
C3H4O8	-.805**	.685*	.869**	0.570	1	1	
C3H4O7	-.694*	0.455	.666*	0.616		1	
C3H4O6	-0.362	0.557	0.488	0.063			
C3H4O5	-0.475	0.320	.642*	0.296		1	
C3H4O4	-0.392	0.237	0.341	0.381			
C3H4O3	0.249	0.023	-0.101	-0.408			
C3H4O2	-.650*	0.407	0.578	0.618			
C2H4O4	-0.102	0.169	0.143	0.007			
C2H4O3	-0.065	0.316	0.173	-0.157			
C2H4O2	-0.128	0.047	0.193	0.087			

Pearson's correlation coefficient (1-sided t test), **: $p < 0.01$, *: $p < 0.05$

Table S11. Average properties of molecules associated with four characteristic chromophores in winter

Average properties	Molecular mass [g mol^{-1}]	O/C ratio	Mass fraction of potential BrC [%]	Mass fraction of nitrogen-containing molecules *[%]
LO-HULIS (C1)	265 ± 2	0.8 ± 0.01	17 ± 4	62 ± 1
HO-HULIS-1 (C2)	170 ± 1	0.9 ± 0.01	14 ± 2	9 ± 0.3
HO-HULIS-2 (C3)	166 ± 1	1.0 ± 0.02	34 ± 4	9 ± 0.3
Protein like (C4)	163 ± 8	0.8 ± 0.03	5 ± 1	32 ± 2

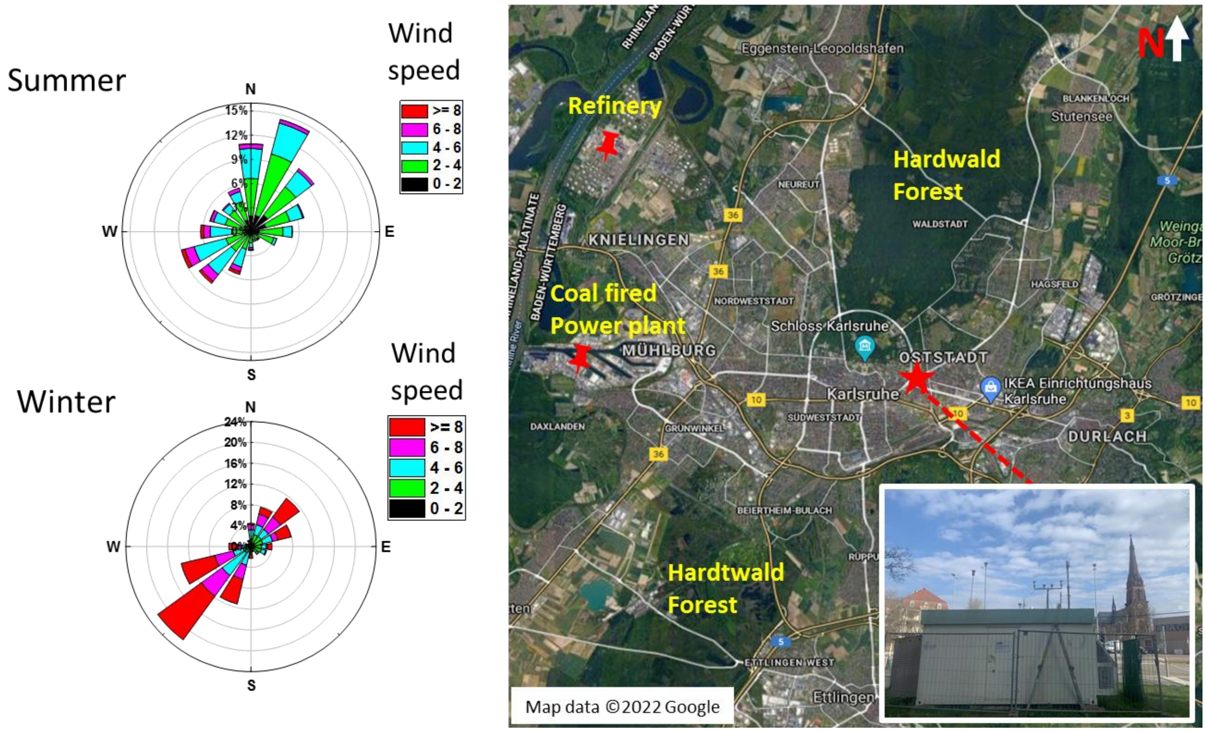


Figure S1. Wind roses (left) pattern, and measurement location map and container picture (right) pattern. Background map courtesy of © Google Maps.

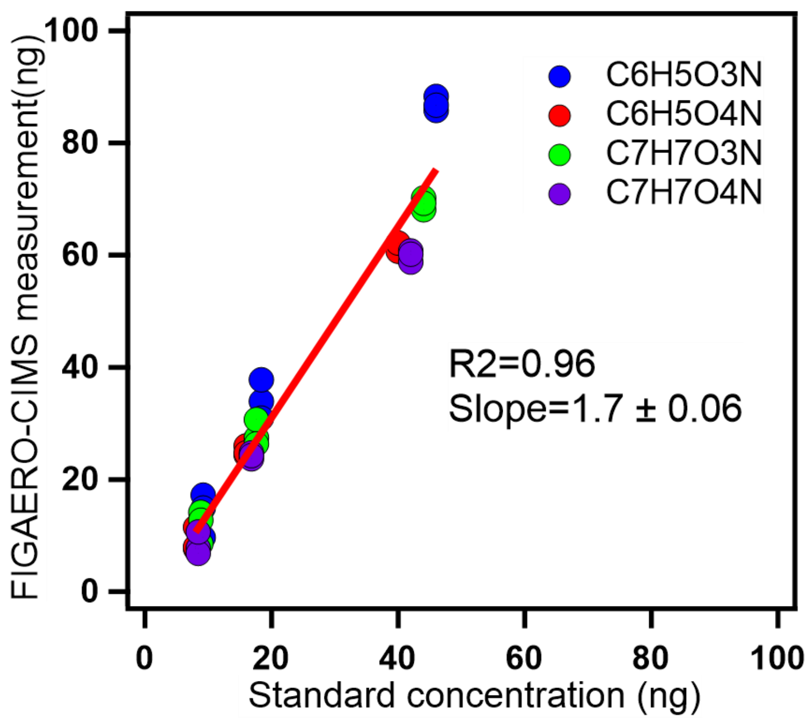


Figure S2. A calibration of FIGAERO-CIMS with NACs. Blue: C6H5O3N; Red: C6H5O4N; Green: C7H7O3N; Purple: C7H7O4N.

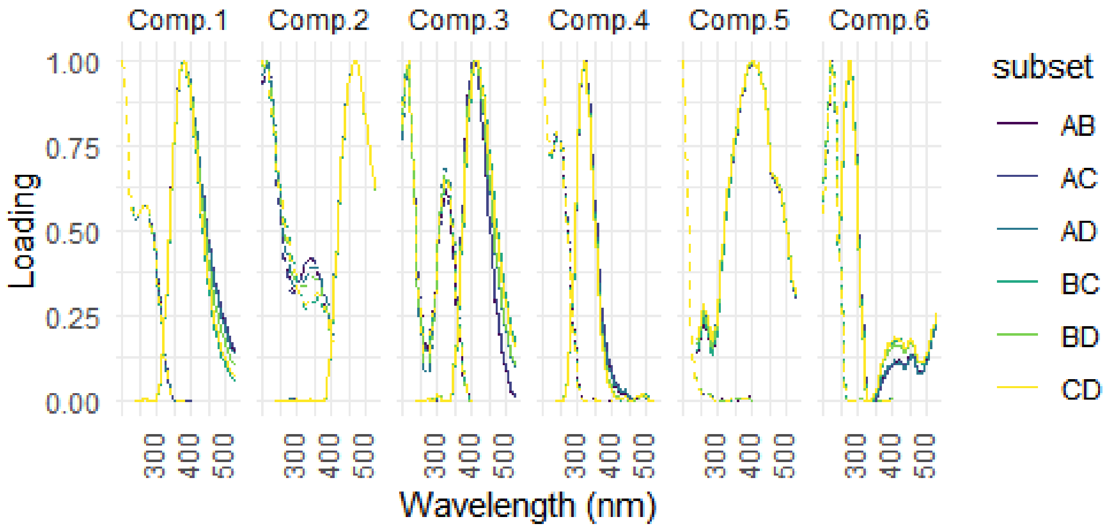
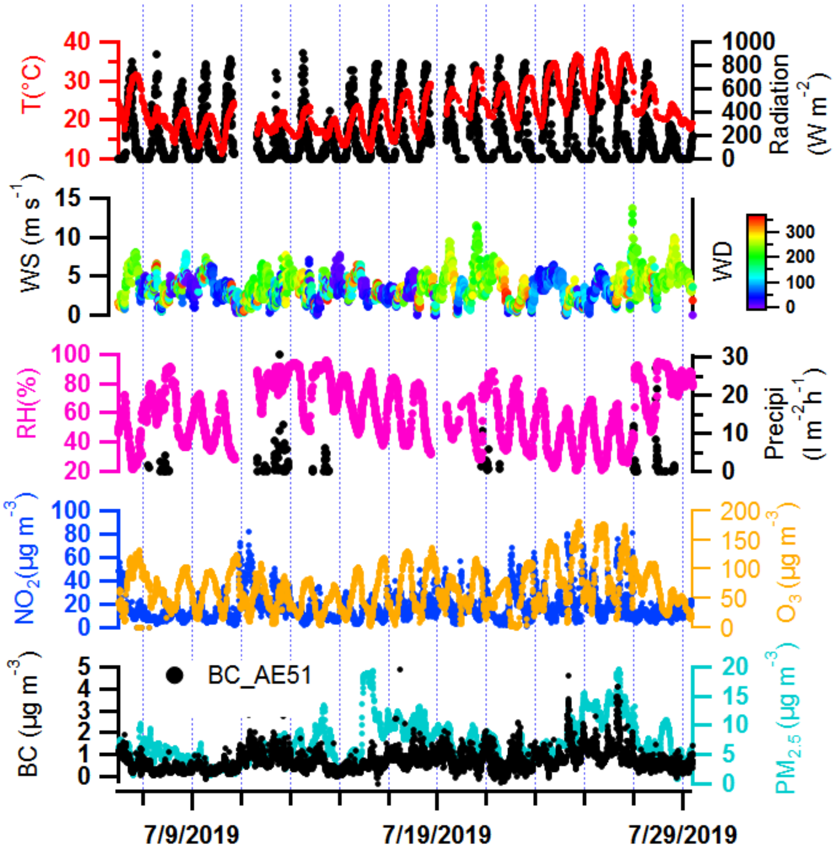
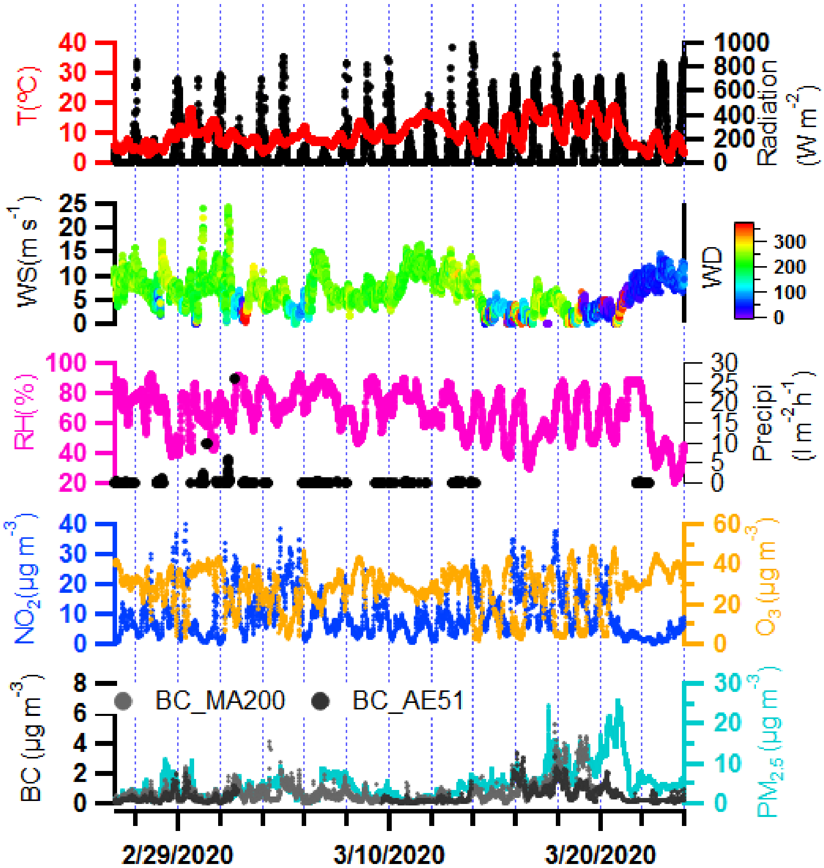


Figure S3. Split analysis of 6 component PARAFAC model with the split style '$S_4C_6T_3$' for all EEMs. The data are split into four subsets (A, B, C, and D) and recombined to compare one-half of the data to the other in different combinations (AB-CD, AD-BC, AC-DB) (Pucher et al., 2019).



90 **Figure S4. Overview of the meteorological parameters: temperature (T), radiation, wind speed (WS), wind direction (WD), relative humidity (RH), precipitation (Precipi), trace gases (NO_2 and O_3), black carbon (BC), and $PM_{2.5}$ in summer.**



95 **Figure S5. Overview of the meteorological parameters: temperature (T), radiation, windspeeds (WS), wind direction (WD), relative humidity (RH), precipitation (Precipi), trace gases (NO_2 and O_3), black carbon (BC), and $PM_{2.5}$ in winter.**

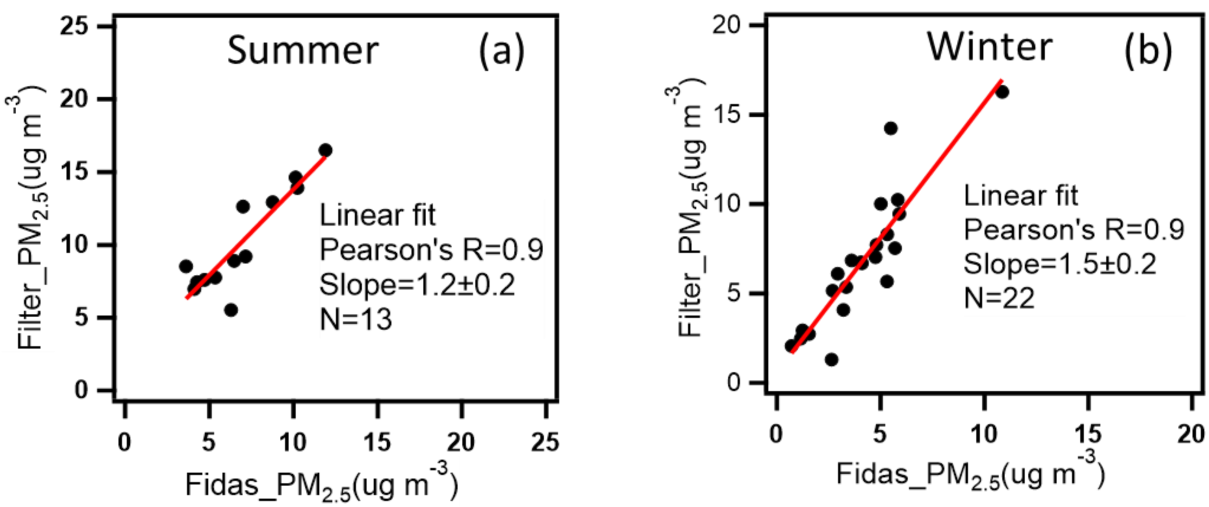


Figure S6. Linear correlation of $PM_{2.5}$ mass concentrations from gravimetric analysis of filter and Fidas-OPC in summer (a) and winter (b).

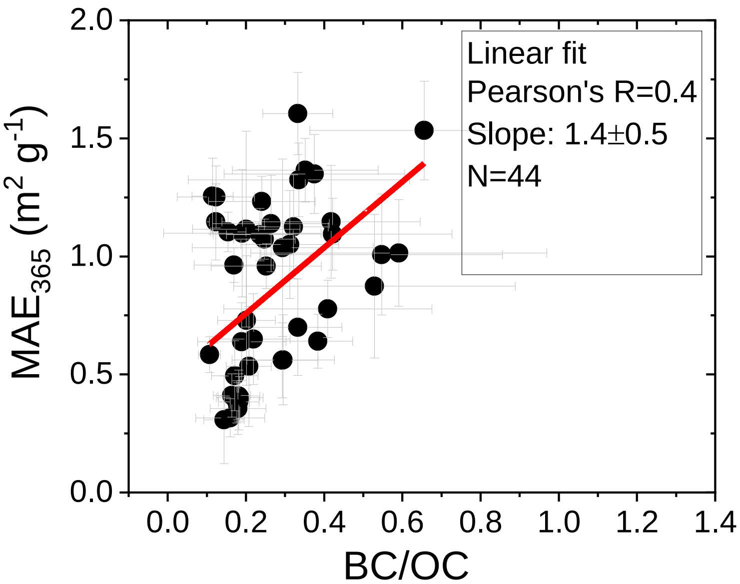


Figure S7. Linear correlation between the MAE_{365} and the BC/OC ratio.

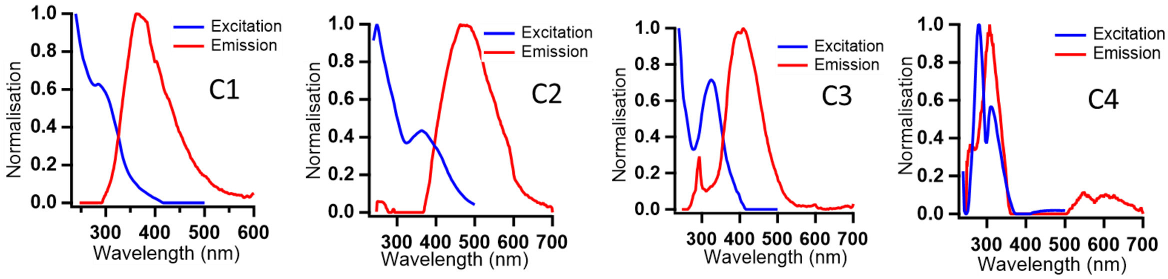


Figure S8. Normalization of spectral loading of C1, C2, C3, and C4.

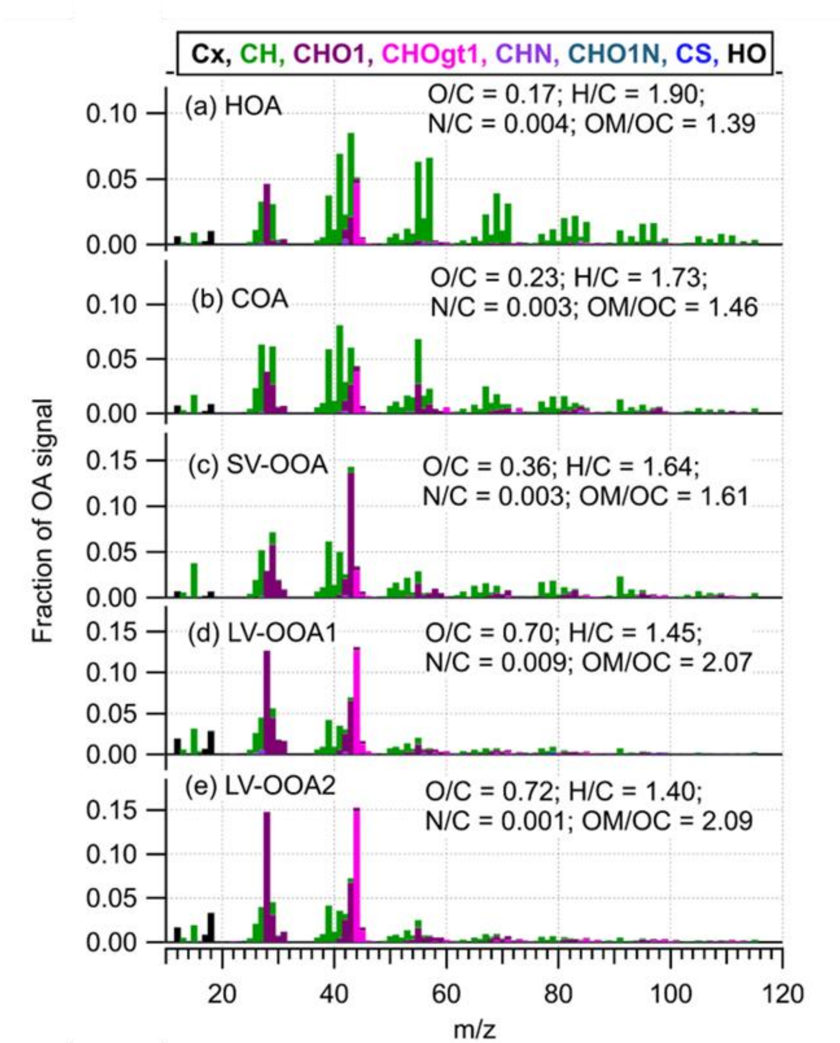


Figure S9. Mass spectra of five PMF-resolved organic aerosol (OA) factors at Durlacher Tor, Karlsruhe in summer 2019. HOA = hydrocarbon-like OA; COA = cooking-related OA; SV-OOA = semi-volatile oxidized OA and LV-OOA = low-volatile oxygenated OA (LV-OOA1 and LV-OOA2).

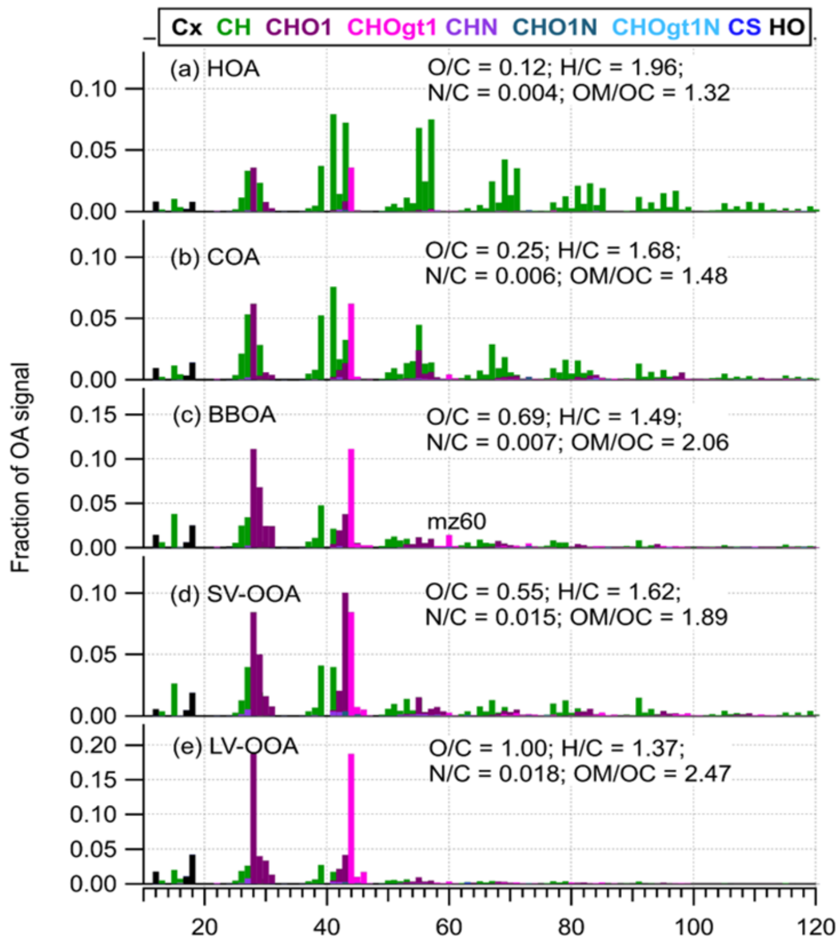


Figure S10. Mass spectra of five PMF-resolved organic aerosol (OA) factors at Durlacher Tor, Karlsruhe in winter 2020. HOA = hydrocarbon-like OA; COA = cooking-related OA; BBOA = biomass burning-related OA; SV-OOA = semi-volatile oxygenated OA; LV-OOA = low-volatile oxygenated OA.

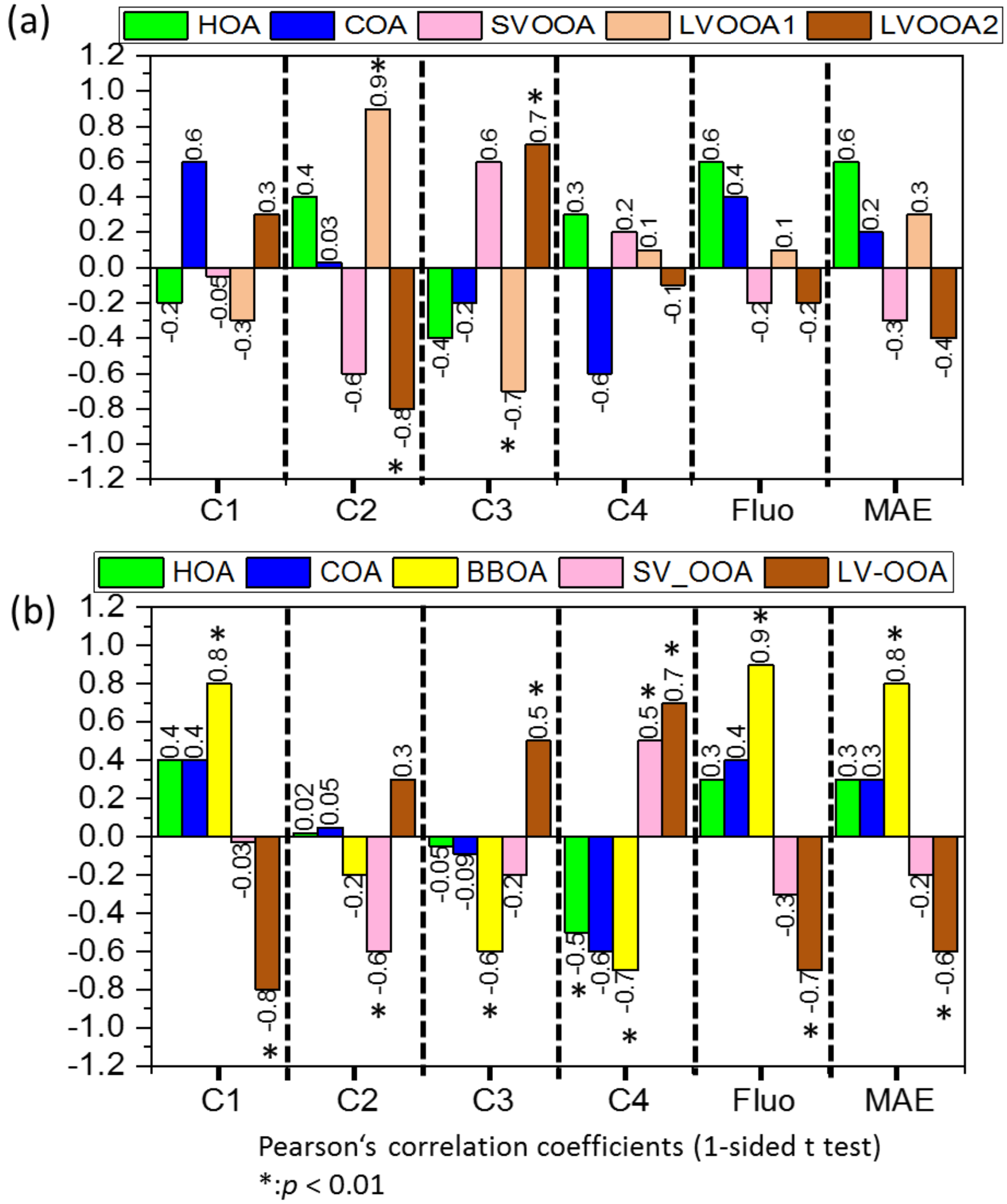


Figure S11. Pearson's correlation coefficients and significance levels (*p*,1-sided t test) of chromophore components and AMS-PMF factors. a: summer (n = 11), b: winter (n = 30).

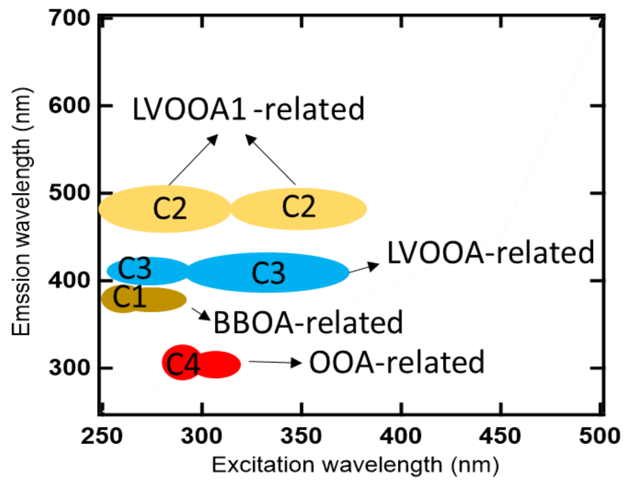


Figure S12. Diagram of the association of the EEM profiles with AMS-PMF factors.

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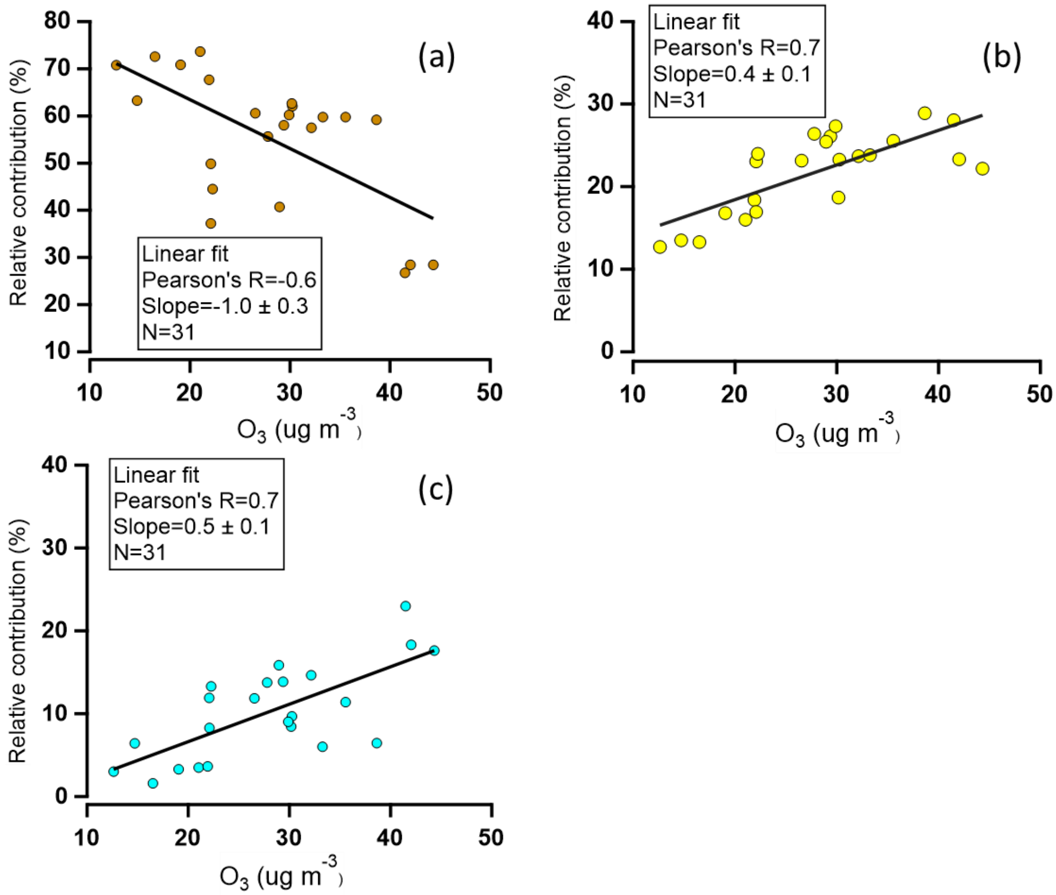

Figure S13. The linear correlations between chromophore components with O_3, LO-HULIS (a), HO-HULIS-1 (b), and HO-HULIS-2 (c).

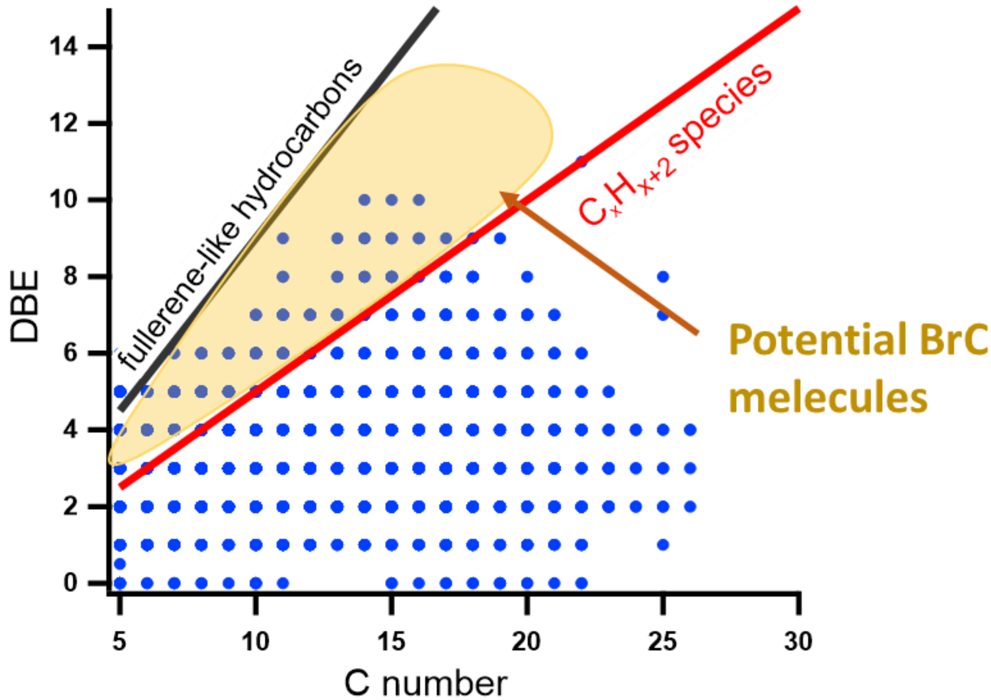

Figure S14. The plot of the double bond equivalent (DBE) vs a number of carbon atoms according to our measurements following the procedure described by Lin et al. (2018). The lines indicate DBE reference values of linear conjugated polyenes C_xH_{x+2} (red solid line) and fullerene-like hydrocarbons with DBE=0.9*c (black solid line). Data points inside the yellow shaded area are potential BrC molecules. (cf. Lin et al. 2018).

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