Supporting Information for:

Emissions of Intermediate- and Semi-Volatile Organic Compounds (I/SVOCs) from Different Cumulative Mileage Diesel Vehicles under Various Ambient Temperatures

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Summary of the Supporting Information:

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SI-1. Description of all organic category names.

Alkane: n-alkane and i-alkane. Alcohol: aliphatic alcohol. Phenol: organics containing one benzene ring and a hydrocarbon group directly attached to the benzene ring. Carbonyls: aliphatic ketone and aliphatic aldehyde. Acid: aliphatic acid. Oxy-PAH & Oxy-benzene: organic compounds containing benzene rings and oxygen-containing groups, except for phenols whose hydroxyl group is directly connected to one benzene ring. PAH_2rings: PAH with 2 benzene rings. PAH_3rings: PAH with 3 benzene rings. PAH_4rings: PAH with 4 benzene rings. Alkene: organics containing carbon double bond(s) without any other function groups. Cycloalkane: organics containing a saturated carbon ring without any other function groups.

SI-2. Description of the steps for qualitatively identifying organic compounds using mass spectrometry principles.

Taking alkanes as an example, compounds containing hydrocarbon chains give rise to a series of ions separated by 14 Da (-CH2-), as shown in Fig. SI1. As a result, the top ions to identify alkanes would be m/z = 43, m/z = 57, m/z = 71, and m/z = 84. Due to the stability of chemical groups, generally, the abundance of m/z = 57 is highest, followed by m/z = 43 and m/z = 71. When incorporating these rules into the data treatment software (Canvas, version 2.5, J&X Technologies), a few steps need to be taken, as shown in Fig. SI2. Four built-in features can be deployed. ABUND (X) returns the normalized abundance of the input ion mass; HASMASS (X) returns the value to indicate if the input ion exists; ORDER (X) returns the order of the input ion mass; MASS (X) returns the mass of the input ion's order. Additionally, the function allows two logical operators, "And" and "Or". Then, the cluster of alkanes can be extracted by the following rules:

((MASS(1)=43 && (MASS(2)=57 || MASS(2)=71 || MASS(2)=41)) || (MASS(1)=57 && (MASS(2)=43 || MASS(2)=71 || MASS(2)=41)))

where "&&" and "||" refer to the logical operators "And" and "Or", respectively. Paste the rules in Ion Extractor Editor and the cluster of alkanes can be filtered, as shown in Fig. SI3.

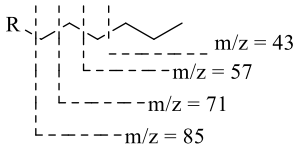

Figure SI1. The common fragmentation patterns of n-alkanes.

Open Canvas → Open Browser → File → Load Data (load a sample) → Speciation → Find All Peaks → Mass Spectrum → Extraction Rules

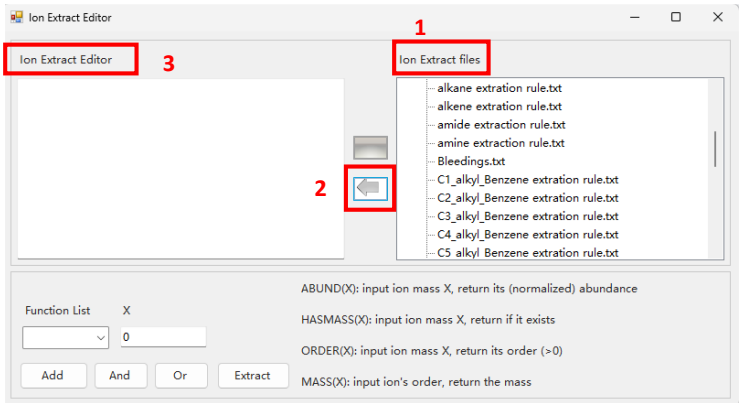

Figure SI2. The steps to enable the ion extract function built in Canvas.

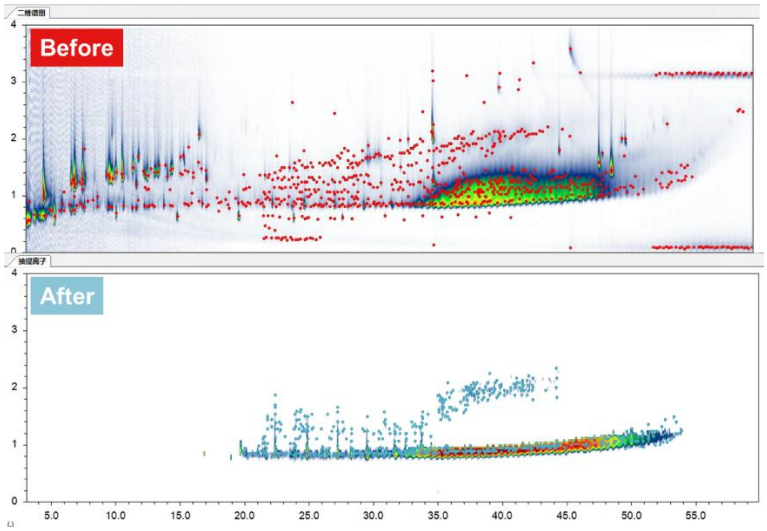

Figure SI3. Comprehensive two-dimensional chromatograms before and after screening alkanes. Each red and blue point represents a chromatographic peak.

Table S1. Sets of test cycles.

No.	Vehicle ID	Ambient Temperature	Cold- or Hot-start Cycle	Repetitions
1	D1	23°C	Cold-start cycle	2
2	D1	23°C	Hot-start cycle	2
3	D2	23°C	Cold-start cycle	2
4	D2	23°C	Hot-start cycle	2
5	D2	0°C	Hot-start cycle	2
6	D3	23°C	Cold-start cycle	3
7	D3	23°C	Hot-start cycle	3
8	D4	23°C	Cold-start cycle	3
9	D4	23°C	Hot-start cycle	3
10	D4	0°C	Hot-start cycle	2

Table S2. The list of 120 external standard curves used in this study.

No.	Groups	Name	Molecular Formula	Cas No.	R^2
1	Alkane	Heptane	C7H16	142-82-5	0.973
2	Alkane	Octane	C8H18	111-65-9	0.984
3	Alkane	Nonane	C9H20	111-84-2	0.996
4	Alkane	Decane	C10H22	124-18-5	0.995
5	Alkane	Undecane	C11H24	1120-21-4	0.992
6	Alkane	Dodecane	C12H26	112-40-3	0.973
7	Alkane	Tridecane	C13H28	629-50-5	0.975
8	Alkane	Tetradecane	C14H30	629-59-4	0.985
9	Alkane	Pentadecane	C15H32	629-62-9	0.987
10	Alkane	Hexadecane	C16H34	544-76-3	0.988
11	Alkane	heptadecane	C17H36	629-78-7	0.975
12	Alkane	Octadecane	C18H38	593-45-3	0.969

No.	Groups	Name	Molecular Formula	Cas No.	R^2
13	Alkane	Nonadecane	C19H40	629-92-5	0.987
14	Alkane	Eicosane	C20H42	112-95-8	0.961
15	Alkane	Heneicosane	C21H44	629-94-7	0.962
16	Alkane	Docosane	C22H46	629-97-0	0.976
17	Alkane	Tricosane	C23H48	638-67-5	0.971
18	Alkane	Tetracosane	C24H50	646-31-1	0.973
19	Alkane	Pentacosane	C25H52	629-99-2	0.995
20	Alkane	Hexacosane	C26H54	630-01-3	0.990
21	Alkane	Heptacosane	C27H56	593-49-7	0.977
22	Alkane	Octacosane	C28H58	630-02-4	0.982
23	Alkane	Nonacosane	C29H60	630-03-5	0.972
24	Alkane	Triacontane	C30H62	638-68-6	0.963
25	Alkane	Hentriacontane	C31H64	630-04-6	0.971
26	Alkane	Dotriacontane	C32H66	544-85-4	0.956
27	Alkane	Tritriacontane	C33H68	630-05-7	0.959
28	Alkane	Tetratriactoane	C34H70	14167-59-0	0.957
29	Alkane	Pentatriacontane	C35H72	630-07-9	0.989
30	Alkane	Hexatriacontane	C36H74	630-06-8	0.980
31	Alkane	Heptatriacontane	C37H76	7194-84-5	0.989
32	Alkene	Octene	C8H16	111-66-0	0.992
33	Alkene	Decene	C10H20	872-05-9	0.982
34	Alkene	Dodecene	C12H24	112-41-4	0.959
35	Alkene	Tetradecene	C14H28	1120-36-1	0.976
36	Alkene	Hexadecene	C16H32	629-73-2	0.985
37	Alkene	Octadecene	C18H36	112-88-9	0.986
38	Alkene	Eicosene	C20H40	3452-07-1	0.988
39	Alkene	Docosene	C22H44	1599-67-3	0.987
40	Alkyl-PAH	Methylnaphthalene	C11H10	90-12-0	0.997
41	Acid	Isobutyric Acid	C4H8O2	79-31-2	0.989
42	Acid	2-Methyl butyric acid	C5H10O2	116-53-0	0.986
43	Acid	Tetradecanoic acid	C11H22O2	544-63-8	0.981
44	Acid	heptadecanoic acid	C14H28O2	506-12-7	0.984
45	Acid	Undecanoic acid	C17H34O2	112-37-8	0.984
46	Alcohol	Decanol	C10H22O	112-30-1	0.982
47	Alcohol	Tridecanol	C13H28O	26248-42-0	0.987
48	Alcohol	Hexadecanol	C16H34O	36653-82-4	0.961
49	Alcohol	Nonadecanol	C19H40O	1454-84-8	0.953
50	Alcohol	Docosanol	C22H46O	661-19-8	0.994
51	Aldehyde	Valeraldehyde	C5H10O	110-62-3	0.966
52	Aldehyde	1-Pentanecarbaldehyde	C6H12O	66-25-1	0.996
53	Aldehyde	Octanal	C8H16O	124-13-0	0.995
54	Aldehyde	Decylaldehyde	C10H20O	112-31-2	0.994

No.	Groups	Name	Molecular Formula	Cas No.	R^2
55	Aldehyde	Dodecanal	C12H24O	112-54-9	0.957
56	Aldehyde	Tetradecanal	C14H28O	124-25-4	0.978
57	Aldehyde	Hexadecanal	C16H32O	629-80-1	0.955
58	Aldehyde	Octadecanone	C18H36O	638-66-4	0.968
59	Aldehyde	Icosanal	C20H40O	2400-66-0	0.959
60	Aldehyde	Docosanal	C22H44O	57402-36-5	0.952
61	Alkyl-PAH	Ethylnaphthalene	C12H12	1127-76-0	0.971
62	Amide	Acetamide	C2H5NO	60-35-5	1.000
63	Amide	Propanamide	C3H7NO	79-05-0	0.960
64	Amide	N,N-Dibutylformamide	C9H19NO	761-65-9	0.952
65	Amine	Triethylamine	C6H15N	121-44-8	0.986
66	Amine	Aniline	C6H7N	62-53-3	0.981
67	Amine	2-Aminoaniline	C6H8N2	95-54-5	0.997
68	Amine	Dibutylamine	C8H19N	111-92-2	0.990
69	Amine	1-Naphthalenamine	C10H9N	134-32-7	0.962
70	Amine	4-Biphenylamine	C12H11N	92-67-1	0.994
71	Aromatic	Ethylbenzene	C8H10	100-41-4	0.996
72	Aromatic	p-xylene	C8H10	106-42-3	0.993
73	Aromatic	o-xylene	C8H10	95-47-6	0.993
74	Aromatic	Isopropylbenzene	C9H12	98-82-8	0.995
75	Aromatic	4-Ethyltoluene	C9H12	622-96-8	0.982
76	Aromatic	1,3,5-trimethylbenzene	C9H12	108-67-8	0.993
77	Aromatic	p-Cymene	C10H14	99-87-6	0.966
78	Aromatic	butyl-benzene	C10H14	104-51-8	0.993
79	Aromatic	pentyl-benzene	C11H16	538-68-1	0.974
80	Aromatic	hexyl-benzene	C12H18	1077-16-3	0.973
81	Cycloalkane	Ethyl-cyclohexane	C8H16	1678-91-7	0.950
82	Cycloalkane	Butyl-cyclohexane	C10H20	1678-93-9	0.986
83	Cycloalkane	Hexyl-cyclohexane	C12H24	4292-75-5	0.968
84	Cycloalkane	Octyl-cyclohexane	C14H28	1795-15-9	0.950
85	Cycloalkane	Decyl-cyclohexane	C16H32	1795-16-0	0.955
86	Cycloalkane	Dodeyl-cyclohexane	C18H36	1795-17-1	0.974
87	Cycloalkane	Tetradecyl-cyclohexane	C20H40	1795-18-2	0.969
88	Cycloalkane	Hexadecyl-cyclohexane	C22H44	6812-38-0	0.979
89	Ester	Butyl acetate	C6H12O2	123-86-4	0.979
90	Ester	Isoamyl Acetate	C7H14O2	123-92-2	0.995
91	Ester	Amyl Acetate	C7H14O2	628-63-7	0.973
92	Furan	Furan	C4H4O	110-00-9	0.961
93	Ketone	2-Pentanone	C5H10O2	107-87-9	0.990
94	Ketone	3-Heptanone	C7H14O	106-35-4	0.995
95	Ketone	2-Nonanone	C9H18O	821-55-6	0.984
96	Ketone	2-Dodecanone	C12H24O	6175-49-1	0.972

No.	Groups	Name	Molecular Formula	Cas No.	R^2
97	Ketone	Pentadecanone	C15H30O	2345-28-0	0.986
98	Oxy-PAH	1,4-naphthoquinone	C10H6O2	130-15-4	0.994
99	Oxy-PAH	1-naphthaldehyde	C11H8O	66-77-3	0.982
100	Oxy-PAH	9,10-anthraquinone	C14H8O2	84-65-1	0.992
101	Oxy-PAH	benzo[a]anthracene-7,12-dione	C18H10O2	2498-66-0	0.983
102	PAH	Indene	C9H8	95-13-6	0.990
103	PAH	Naphthalene	C10H8	91-20-3	0.997
104	PAH	Acenaphthylene	C12H8	208-96-8	0.996
105	PAH	Acenaphthene	C12H10	83-32-9	0.989
106	PAH	Fluorene	C13H10	86-73-7	0.997
107	PAH	Phenanthrene	C14H10	85-01-8	0.994
108	PAH	Anthracene	C14H10	120-12-7	0.992
109	PAH	Pyrene	C16H10	129-00-0	0.992
110	PAH	Benz[a]anthracene	C18H12	56-55-3	0.973
111	PAH	Chrysene	C18H12	218-01-9	0.973
112	PAH	Benzo[b]fluoranthene	C20H12	205-99-2	0.961
113	PAH	Benzo[k]fluoranthene	C20H12	207-08-9	0.983
114	PAH	Benzo[a]pyrene	C20H12	50-32-8	0.967
115	PAH	Indeno[1,2,3-cd]fluoranthene	C22H12	193-39-5	0.991
116	Pinene	(+)-alpha-Pinene	C10H16	7785-70-8	0.950
117	Pinene	β-Pinene	C10H16	18172-67-3	0.991
118	Polyphenyls	Biphenyl	C12H10	92-52-4	0.952
119	Polyphenyls	p-terphenyl	C18H14	92-94-4	0.967
120	Polyphenyls	p-quaterphenyl	C24H18	135-70-6	0.987

Table S3. Average THC, NOx, and CO EFs for LMV and HMV, respectively.

Vehicle	Test Cycle	THC ($mg \cdot km^{-1}$)	NOx ($mg \cdot km^{-1}$)	CO ($mg \cdot km^{-1}$)
LMV (D2)	Hot_23°C	35	6951	600
	Hot_0°C	38	8048	657
HMV (D4)	Hot_23°C	289	2629	359
	Hot_0°C	302	3555	404

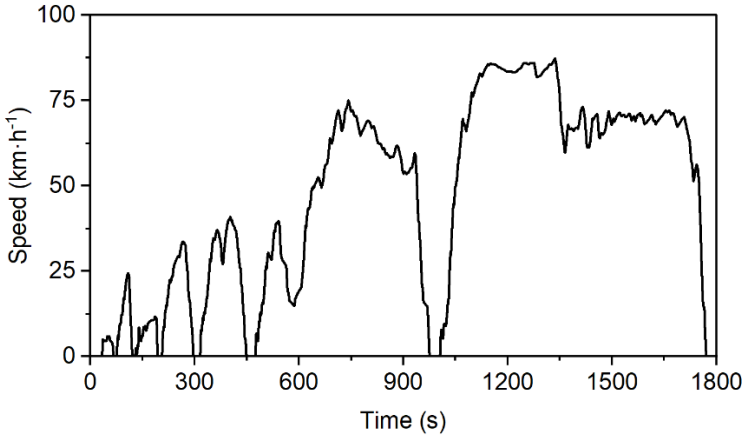

Figure S1. CHTC-TT test cycle for tractor trailers. The cycle lasts 1800 s, with the first 473 s as phase 1 and the last 1327 s as phase 2. The total driving distance is about 23 km, and the maximum speed is 88 km·h^{-1}.

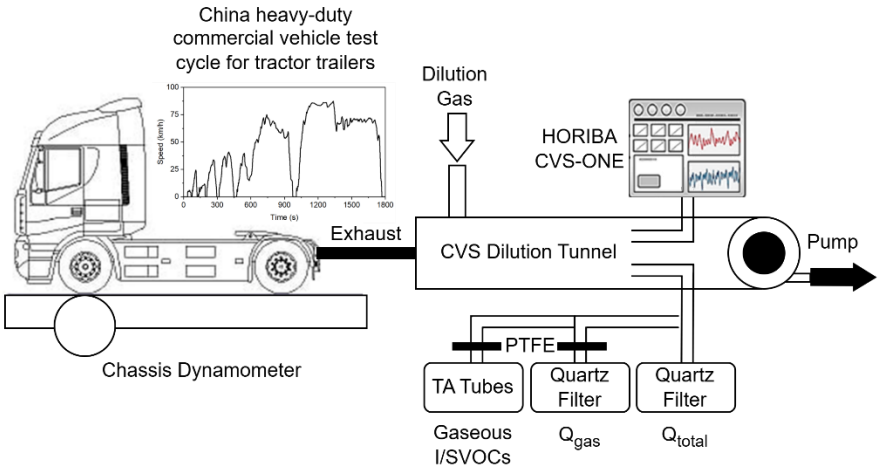

Figure S2. A schematic of the sampling systems.

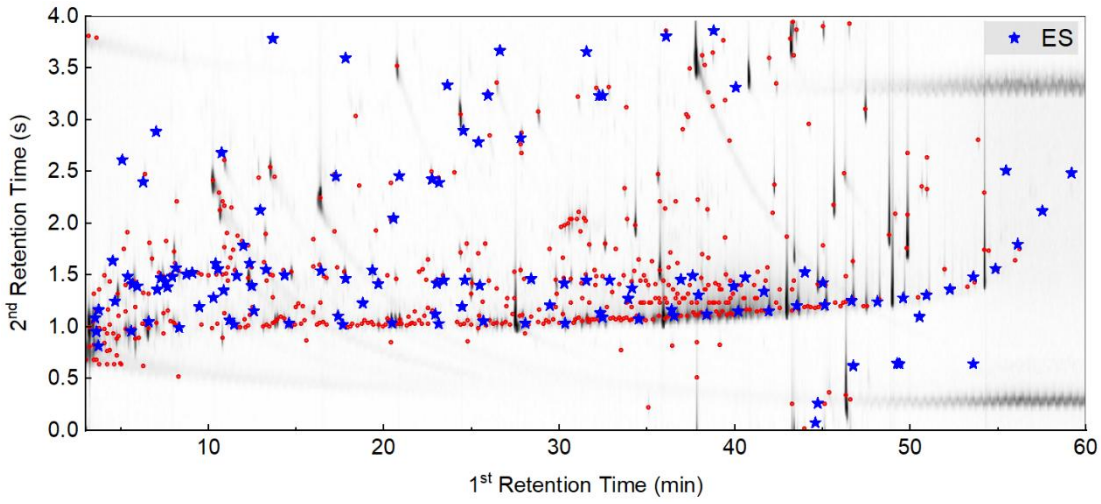

Figure S3. Actual GC×GC chromatogram and sample chromatographic peaks (the red dots). The blue stars represent all ES used in this study including n-alkanes, PAHs, carbonyls, etc. All their

detailed information was listed in Table S1.

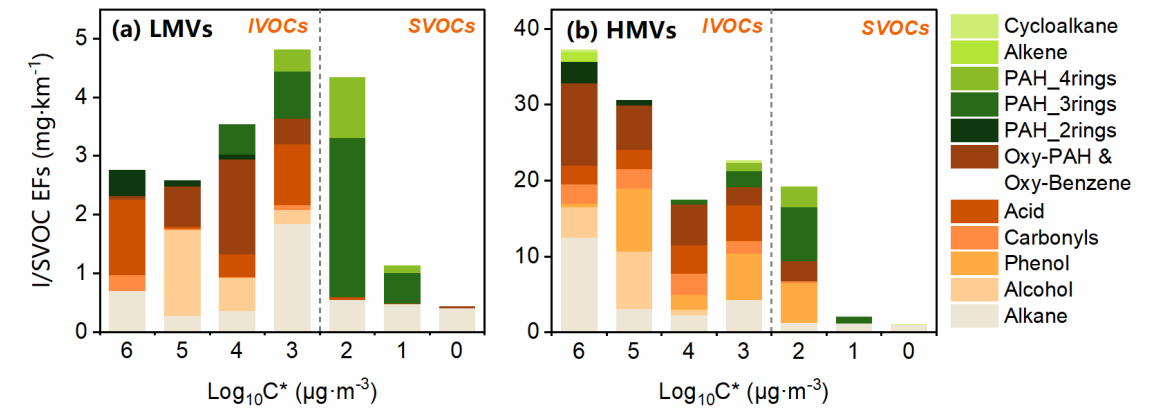

Figure S4. The average volatility distribution of I/SVOCs from the (a) LMVs and (b) HMVs. Different colored bars represent different organic groups.

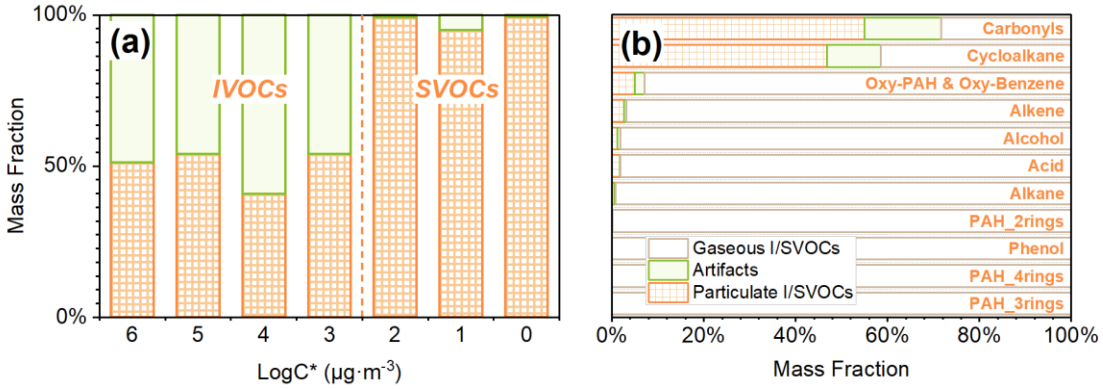

Figure S5.(a) The mass fraction of artifacts and particulate I/SVOCs divided by C* captured by quartz. (b) Gas-particle partition and artifacts of various organic compound groups.

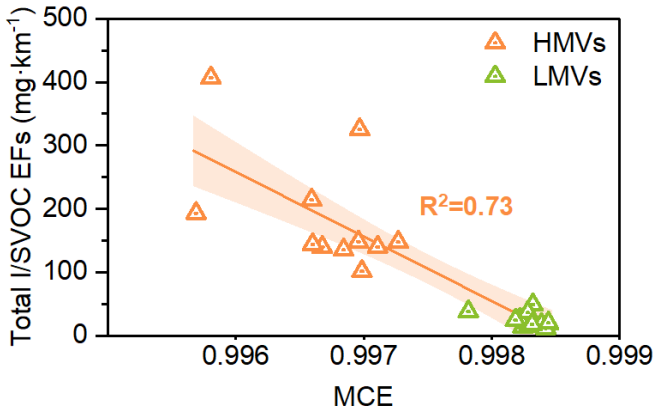

Figure S6. The linear correlation between total I/SVOC EFs and MCE.

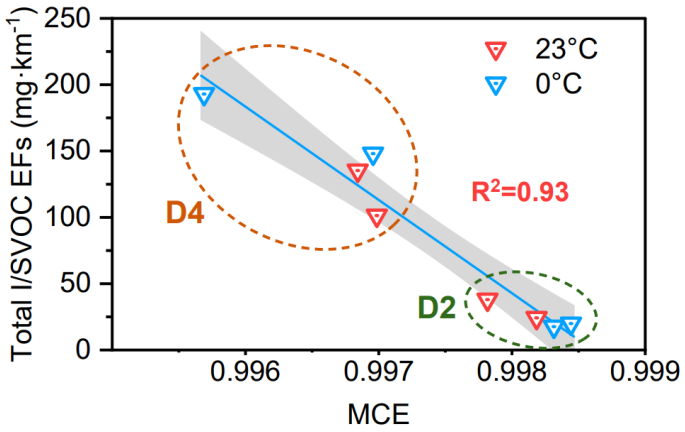

Figure S7. The linear correlation between hot-start cycle I/SVOC EFs and MCE of LMV (D2) and HMV (D4) at different ambient temperatures.

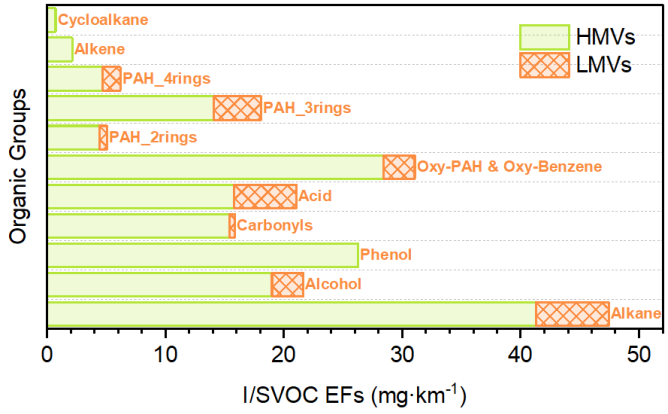

Figure S8. The average organic group distribution of HMVs and LMVs.