Supporting information

A quantum chemical assessment on the sensing ability of porphyrins and phthalocyanines towards volatile organic compounds using density functional theory investigations

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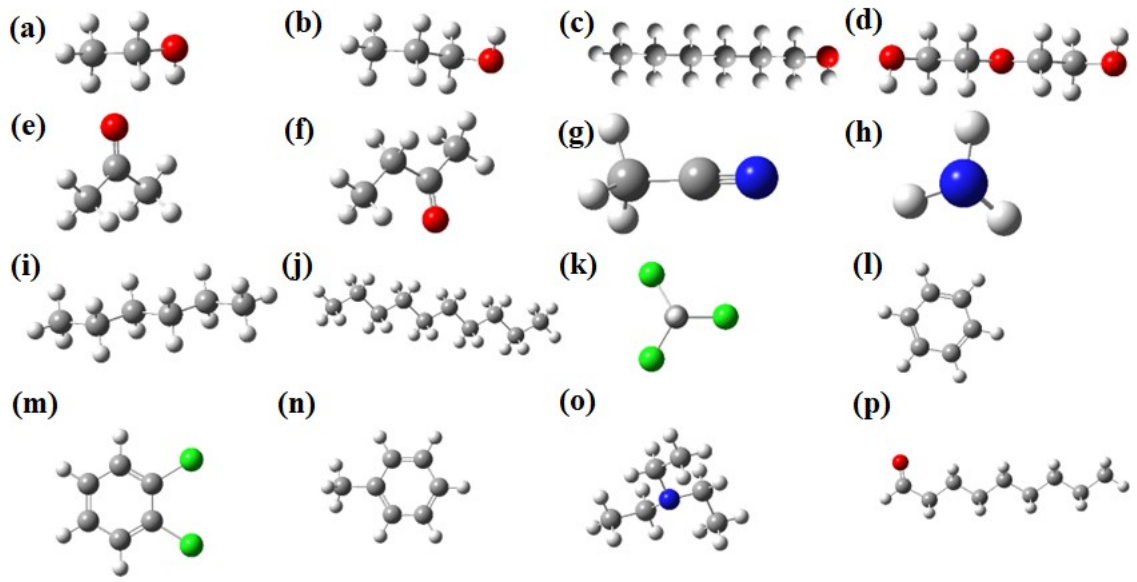
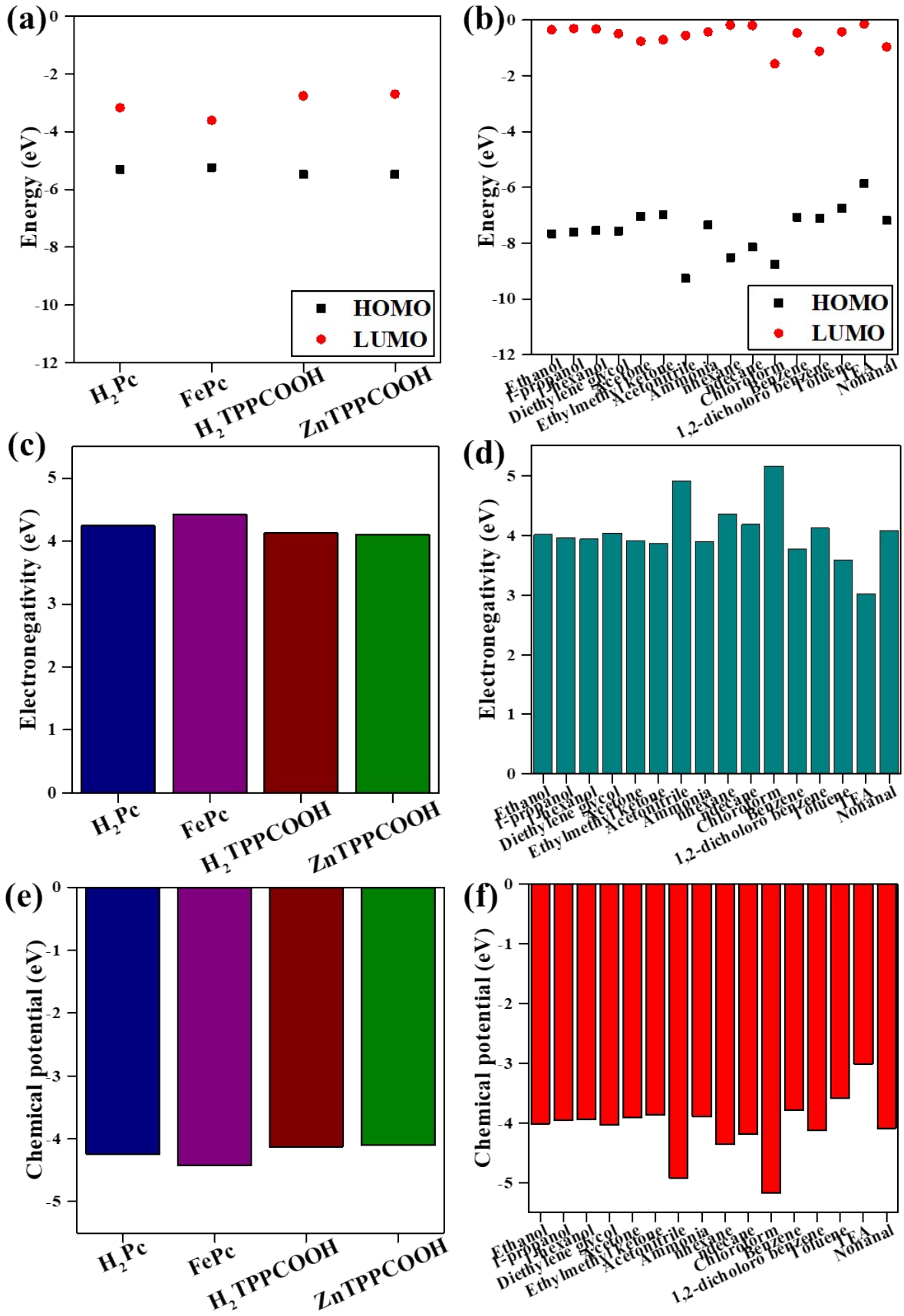


Fig S1. Optimised structures of VOCs: **(a)** Ethanol, **(b)** 1-propanol, **(c)** 1-hexanol, **(d)** Diethyl glycol, **(e)** Acetone, **(f)** Ethylmethyl ketone, **(g)** Acetonitrile, **(h)** Ammonia, **(i)** n-hexane, **(j)** n-decane, **(k)** Chloroform, **(l)** Benzene, **(m)**1,2-dicholoro benzene, **(n)** Toluene, **(o)** TEA, **(p)** Nonanal.


(a)
Energy (eV)
HOMO
LUMO
H2Pc
FePc
H2TPPCOOH
ZnTPPCOOH
(b)
Energy (eV)
HOMO
LUMO
Ethanol
1-propanol
Hexanol
Diethylene glycol
Acetone
Ethylmethylketone
Acetonitrile
Ammonia
hexane
decane
Chloroform
Benzene
1,2-dicholoro benzene
Toluene
TEA
Nonanal
(c)
Electronegativity (eV)
H2Pc
FePc
H2TPPCOOH
ZnTPPCOOH
(d)
Electronegativity (eV)
Ethanol
1-propanol
Hexanol
Diethylene glycol
Acetone
Ethylmethylketone
Acetonitrile
Ammonia
hexane
decane
Chloroform
Benzene
1,2-dicholoro benzene
Toluene
TEA
Nonanal
(e)
Chemical potential (eV)
H2Pc
FePc
H2TPPCOOH
ZnTPPCOOH
(f)
Chemical potential (eV)
Ethanol
1-propanol
Hexanol
Diethylene glycol
Acetone
Ethylmethylketone
Acetonitrile
Ammonia
hexane
decane
Chloroform
Benzene
1,2-dicholoro benzene
Toluene
TEA
Nonanal

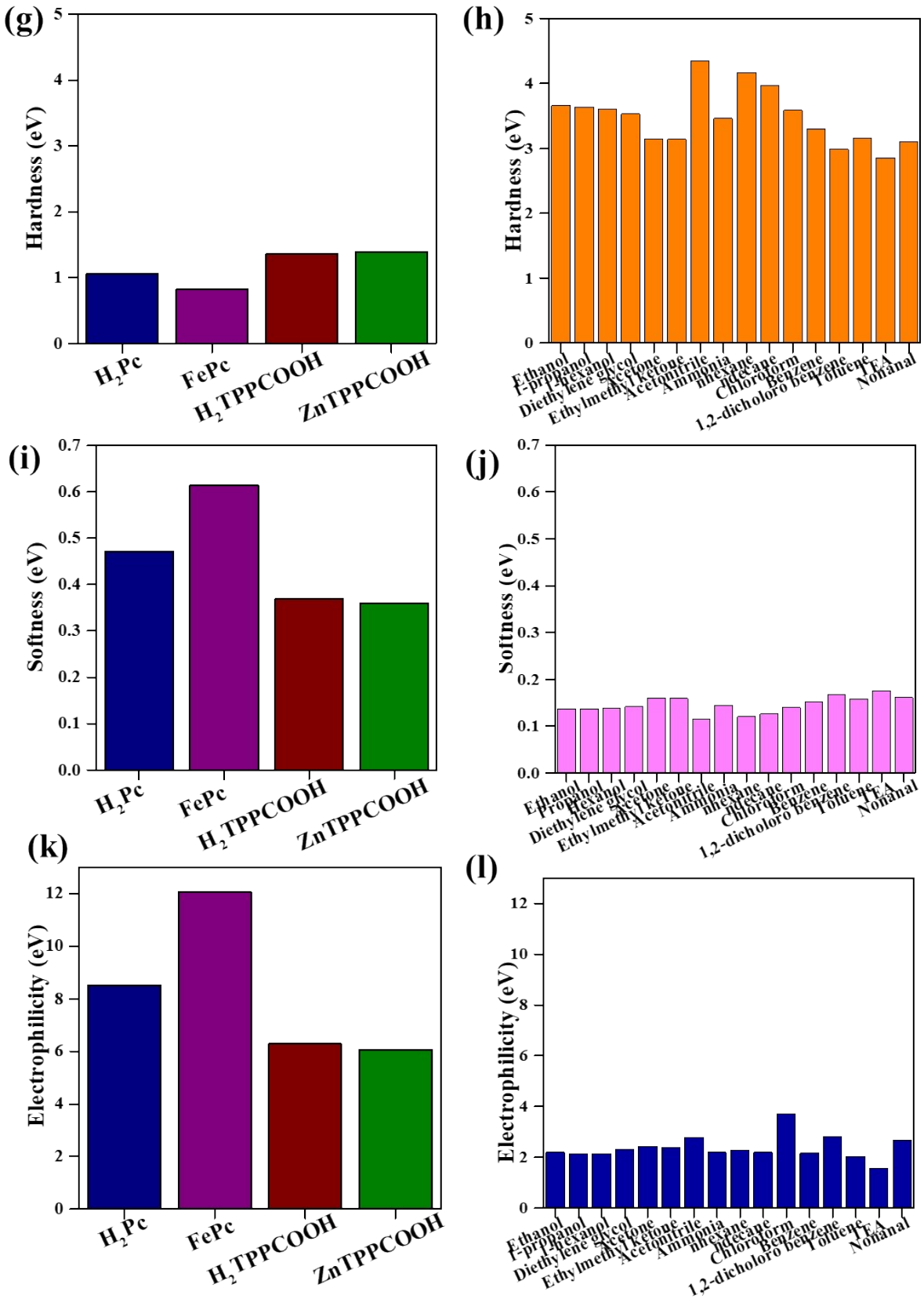


Fig S2. (a) HOMO-LUMO values of organic molecules, (b) HOMO-LUMO values of VOCs, (c) Electronegativity of organic molecules, (d) Electronegativity of VOCs, (e) Chemical potential of organic molecules, (f) Chemical potential of VOCs, (g) Hardness of organic

molecules, (h) Hardness of VOCs. (i) Softness of organic molecules, (j) softness of VOCs, (k) Electrophilicity of organic molecules, and (l) Electrophilicity of VOCs.

Dipole moment and Mulliken charge analyses

Table S1. Dipole moment of organic molecules.

Organic Molecule	Dipole moment (Debye)
H_2Pc	0.000
FePc	0.001
$H_2TPPCOOH$	6.256
ZnTPPCOOH	6.248

Table S1 shows the dipole moment of pristine organic molecules. Phthalocyanines show zero dipole moment and porphyrins have a significant dipole moment due to the presence of the functional groups. The inclusion of the central metal atom in both phthalocyanines and porphyrins results in a negligible change in the dipole moment. The effect of VOCs adsorption on the dipole moment is investigated and is summarised in Table S2.

Table S2. Dipole moment (Debye) of organic molecules+VOCs systems.

VOCs	H_2Pc	FePc	$H_2TPPCOOH$	ZnTPPCOOH
Ethanol	2.10	3.28	6.63	8.13
1-propanol	2.00	3.37	7.05	7.37
1-hexanol	2.05	3.67	6.41	7.64
Diethylene glycol	2.83	2.38	8.57	7.73
Acetone	2.76	4.77	6.63	9.50
Ethyl methyl ketone	3.66	4.69	6.97	8.13
Acetonitrile	4.16	5.54	8.58	10.00
Ammonia	1.57	3.15	7.25	7.84
n-hexane	0.14	1.53	6.98	6.23
n-decane	0.17	1.57	6.18	6.31
Chloroform	2.31	0.76	9.27	6.17
Benzene	0.53	1.79	6.10	6.15
1,2-dichlorobenzene	3.56	1.79	3.28	4.80
Toluene	0.58	2.26	5.52	6.33
TEA	0.46	1.55	7.30	6.68
Nonanal	2.44	4.61	6.55	8.85

The change in dipole moment observed during adsorption is due to charge transfer between organic molecules and VOCs.[1] In all the cases, organic molecules with acetonitrile

have the highest dipole moment. The adsorption of acetonitrile on ZnTPPCOOH has the highest dipole (10 Debye) moment whereas the adsorption of n-hexane on H_2Pc has the lowest dipole moment (0.14 Debye). It can be concluded that porphyrin systems have the highest dipole moment than phthalocyanines. Mulliken charge analysis illustrates this point. It determines the partial atomic charges of molecules in a system.[2] Charge transfer from organic molecules to VOCs can be seen in this Table S3. Charge transfer mechanism such as physisorption (low charge transfer) and chemisorption (high charge transfer) were used to confirm the magnitude of gas interaction.[3] In all circumstances, organic molecules with metal ions exhibit a greater ability to transfer charge. As a result, metal-organic molecules exhibit higher charge transfer than metal-free organic molecules.

Table S3. Mulliken charge (e) on organic molecules after adsorption of VOCs.

VOCs	H_2Pc	FePc	$H_2TPPCOOH$	ZnTPPCOOH
Ethanol	-0.02	-0.48	-0.02	-0.21
1-propanol	-0.03	-0.55	-0.02	-0.15
1-hexanol	0.09	-0.31	-0.01	-0.03
Diethyl glycol	0.01	-0.39	0.02	-0.15
Acetone	0.02	-0.55	-0.02	-0.20
Ethyl methyl ketone	0.07	-0.52	-0.02	-0.19
Acetonitrile	0.08	-0.59	0.00	-0.34
Ammonia	0.01	-0.58	0.03	-0.33
n-hexane	0.12	-0.27	-0.03	0.06
n-decane	0.07	-0.24	-0.02	0.08
Chloroform	0.07	-0.48	0.01	0.00
Benzene	0.03	-0.24	0.09	-0.03
1,2-dichloroben zene	0.06	-0.41	-0.08	0.07
Toluene	0.07	-0.20	0.09	-0.03
TEA	0.08	-0.15	-0.04	0.11
Nonanal	0.11	-0.51	0.03	0.14

Table S4. Sensitivity of organic molecules toward VOCs.

VOCs	H_2Pc	FePc	$H_2TPPCOOH$	ZnTPPCOOH
Ethanol	56.04	100.00	22.83	471.21
1-propanol	56.04	100.00	9.46	489.65
1-hexanol	50.36	100.00	17.33	324.60

Diethylene glycol	59.38	100.00	26.96	403.02
Acetone	24.91	100.00	19.49	433.20
Ethyl methyl ketone	11.17	100.00	100.00	525.03
Acetonitrile	26.24	100.00	23.24	531.68
Ammonia	22.95	100.00	14.66	689.06
n-hexane	0.00	100.00	0.50	23.60
n-decane	0.53	100.00	4.12	34.53
Chloroform	26.24	100.00	21.69	23.60
Benzene	2.68	100.00	12.84	10.59
1,2-dichlorobenzene	7.70	100.00	2.06	36.68
Toluene	6.00	100.00	10.97	14.16
TEA	0.00	100.00	515.37	15.99
Nonanal	26.91	100.00	19.07	5.66

Table S5. Selectivity of organic molecules toward VOCs.

VOCs	H_2Pc	FePc	H_2TPPCOOH	ZnTPPCOOH
Ethanol	0.149	0.063	0.028	0.117
1-propanol	0.149	0.063	0.012	0.121
1-hexanol	0.134	0.063	0.021	0.081
Diethylene glycol	0.157	0.063	0.033	0.100
Acetone	0.066	0.063	0.024	0.107
Ethyl methyl ketone	0.030	0.063	0.122	0.130
Acetonitrile	0.070	0.063	0.028	0.132
Ammonia	0.061	0.063	0.018	0.171
n-hexane	0.000	0.063	0.001	0.006
n-decane	0.001	0.063	0.005	0.009
Chloroform	0.070	0.063	0.026	0.006
Benzene	0.007	0.063	0.016	0.003
1,2-dichlorobenzene	0.020	0.063	0.003	0.009
Toluene	0.016	0.063	0.013	0.004

TEA	0.000	0.063	0.628	0.004
Nonanal	0.071	0.063	0.023	0.001

Table S6. Recovery time (sec) of VOCs on each organic molecule at room temperature 298K.

VOCs	H_2Pc	FePc	H_2TPPCOOH	ZnTPPCOOH
Ethanol	9.71E-09	2.02E+04	6.46E-07	1.39E-06
1-propanol	7.81E-09	4.34E+03	9.87E-10	1.54E-06
1-hexanol	3.54E-09	3.00E+04	7.05E-07	1.38E-06
Diethylene glycol	1.55E-08	2.54E+03	1.73E-08	6.43E-07
Acetone	1.44E-11	2.71E+03	1.69E-06	1.27E-07
Ethylmethyl ketone	5.26E-12	4.74E+03	3.02E-07	1.35E-07
Acetonitrile	2.58E-11	2.73E+08	7.07E-08	2.00E-08
Ammonia	4.31E-11	1.16E+12	1.32E-05	3.21E-04
n-hexane	1.80E-12	4.12E-10	2.38E-12	1.73E-12
n-decane	1.26E-12	4.43E-10	1.47E-12	1.97E-12
Chloroform	1.16E-10	1.00E-05	3.48E-09	3.01E-10
Benzene	2.94E-12	2.10E-09	7.81E-11	3.75E-12
1,2-dicholoro benzene	8.34E-12	6.72E-06	1.19E-10	3.32E-11
Toluene	2.44E-12	8.41E-09	1.61E-10	3.47E-12
TEA	1.48E-12	3.50E-10	4.52E-12	1.95E-12
Nonanal	1.92E-11	8.47E+04	4.21E-07	8.06E-11

Table S7. Recovery time (sec) of VOCs on each organic molecule at a high temperature of 498K.

VOCs	H_2Pc	FePc	H_2TPPCOOH	ZnTPPCOOH
Ethanol	2.43E-10	5.72E-03	3.00E-09	4.75E-09
1-propanol	2.14E-10	2.28E-03	6.19E-11	5.03E-09
1-hexanol	1.33E-10	7.24E-03	3.16E-09	4.72E-09

Diethylene glycol	3.22E-10	1.65E-03	3.44E-10	2.99E-09
Acetone	4.93E-12	1.72E-03	5.33E-09	1.13E-09
Ethylmethyl ketone	2.70E-12	2.40E-03	1.90E-09	1.18E-09
Acetonitrile	7.00E-12	1.69E+00	7.98E-10	3.74E-10
Ammonia	9.50E-12	2.52E+02	1.83E-08	1.23E-07
n-hexane	1.42E-12	3.67E-11	1.68E-12	1.39E-12
n-decane	1.15E-12	3.83E-11	1.26E-12	1.50E-12
Chloroform	1.72E-11	1.55E-08	1.32E-10	3.04E-11
Benzene	1.91E-12	9.72E-11	1.36E-11	2.21E-12
1,2-dicholoro benzene	3.56E-12	1.22E-08	1.75E-11	8.13E-12
Toluene	1.70E-12	2.23E-10	2.09E-11	2.10E-12
TEA	1.27E-12	3.33E-11	2.47E-12	1.49E-12
Nonanal	5.85E-12	1.35E-02	2.32E-09	1.38E-11

References

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[2] R. Sarkar, T.K. Kundu, Density functional theory studies on PVDF/ionic liquid composite systems, J. Chem. Sci. 130 (2018). https://doi.org/10.1007/s12039-018-1522-4.

[3] Z. Zhao, Y. Yong, Q. Zhou, Y. Kuang, X. Li, Gas-Sensing Properties of the SiC Monolayer and Bilayer: A Density Functional Theory Study, ACS Omega. 5 (2020) 12364–12373. https://doi.org/10.1021/acsomega.0c01084.