Supplementary Information

Systematic approach for wettability prediction using molecular dynamics simulations

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S1 Standard deviation and block averaging over longer simulation time

To assess the required simulation times to equilibrate a simulation box and to obtain accurate and reproducible solubility parameters, we performed MD simulations with a duration of 1 ns on randomly selected molecules from the following categories:

- Small molecules: Decane, Triethylsilane, Ethanol, Nonane

- Polymers: PET, POM, PVA

- The largest surfactant: Tergitol

Fig. S1 shows the evolution of the solubility parameter with simulation time block-averaged every 20 ps. The MD simulation starts with an energy minimized configuration, and therefore the solubility parameter rises slightly in the beginning. Only minor variations are observed after about 100 ps, indicating that most systems are at, or close to, equilibrium. Standard deviations of the 20 ps block averages over the interval from 200 ps to 1 ns are included in Table S1. This indicates that an equilibration phase of 180 ps and a sampling duration of 20 ps are acceptable, for the small molecules and polymer fragments considered here, to obtain a reasonable estimate of the solubility parameter. This is consistent with other studies [1–3] where 200 ps was enough to compute the solubility parameter. With this short equilibration and sampling durations, the proposed approach balances accuracy and speed, and thereby enables one to quickly screen a lot of liquids in terms of their wettability.
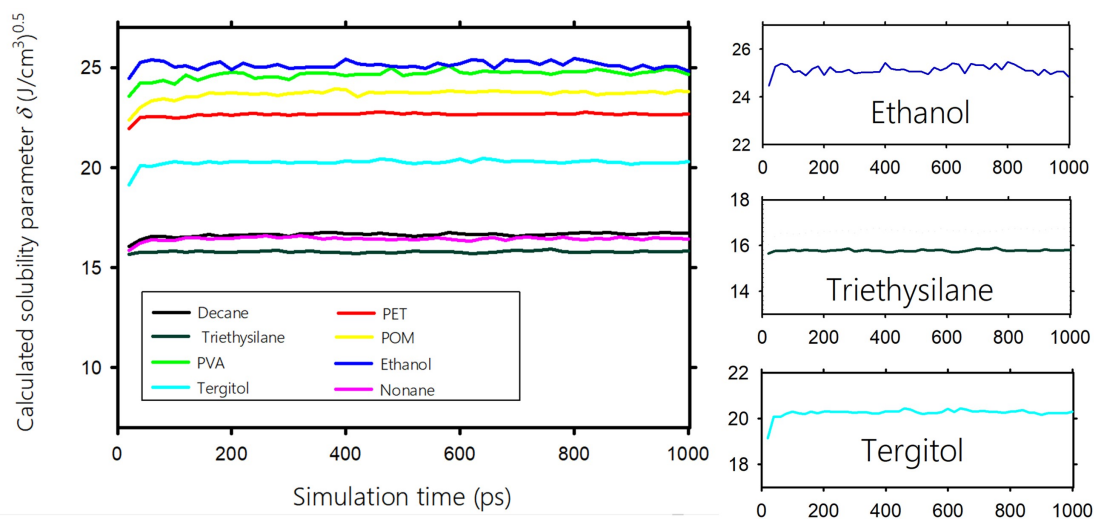

Fig. S1 Solubility parameter of eight molecules plotted against simulation time and block averaged every 20 ps.

To make sure our results are reproducible, we repeated the preparation procedure described in section 2.2 with 5 different initial configurations for each of these randomly selected molecules. Table S1 shows the results and obtained standard deviations. For the large molecules and polymers the deviation has a maximum range of 0.23 $(J/cm^3)^{0.5}$, and for small molecules, it is below 0.17 $(J/cm^3)^{0.5}$.

Table S1 Standards deviations for eight molecules over the five different initial configurations. All values in $(J/cm^3)^{0.5}$

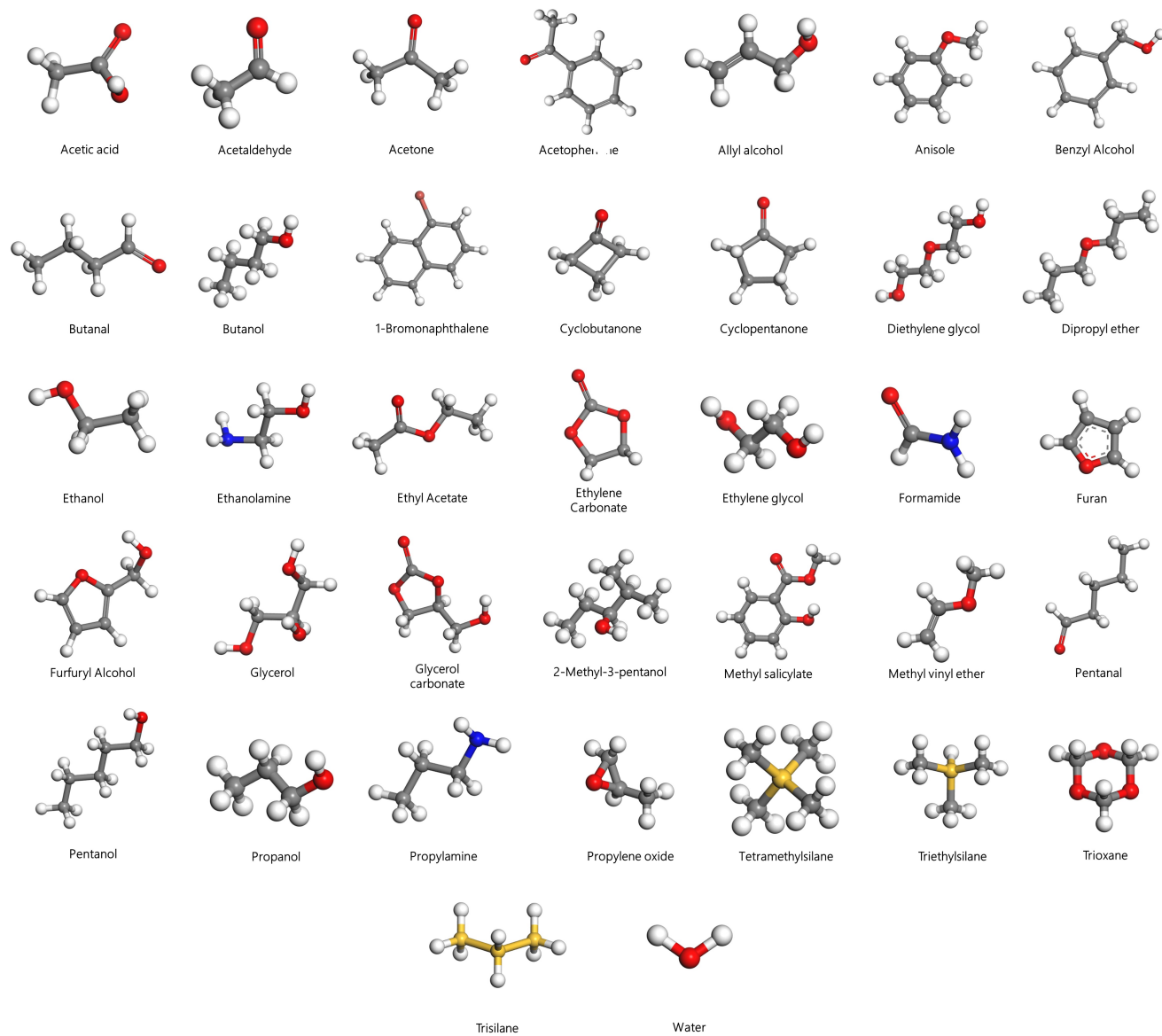|	Solubility parameter					Standard deviations	
	Config. 1	Config. 2	Config. 3	Config. 4	Config. 5	5 Configs.	0.2 to 1 ns
Decane	16.58	16.46	16.45	16.51	16.64	0.07	0.06
Ethanol	24.67	24.70	24.56	24.91	24.72	0.17	0.19
Nonane	16.90	16.51	16.68	16.72	16.46	0.15	0.15
PET	23.08	22.62	22.92	22.81	22.49	0.21	0.10
POM	24.26	23.88	24.08	23.69	23.72	0.22	0.11
PVA	24.42	24.74	24.42	24.83	24.66	0.17	0.21
Tergitol	20.70	20.62	20.72	21.07	20.36	0.23	0.19
Triethylsilane	15.72	15.82	15.88	15.95	15.88	0.08	0.05

Abbreviations: PET: polyethylene terephthalate, POM: polyoxymethylene, and PVA: polyvinyl alcohol.

S2 Pictorial of all the employed compounds

Carbon Hydrogen Fluorine Silicon
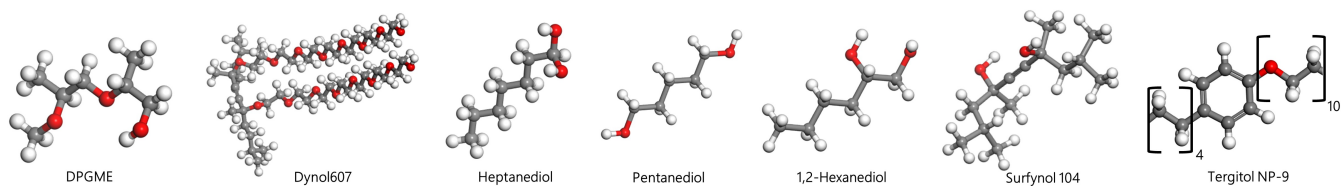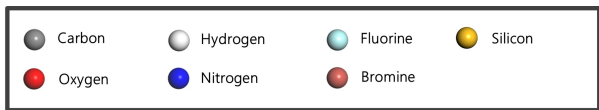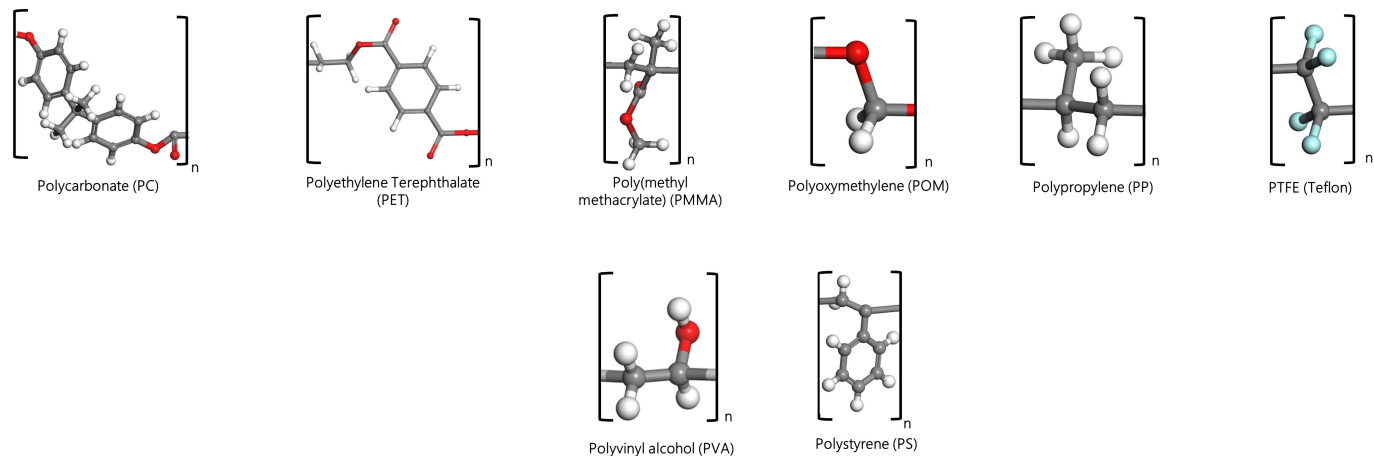
Oxygen Nitrogen Bromine

Polar and H-bonding liquids

Acetic acid Acetaldehyde Acetone Acetophenone Allyl alcohol Anisole Benzyl Alcohol

Butanal Butanol 1-Bromonaphthalene Cyclobutanone Cyclopentanone Diethylene glycol Dipropyl ether

Ethanol Ethanolamine Ethyl Acetate Ethylene Carbonate Ethylene glycol Formamide Furan

Furfuryl Alcohol Glycerol Glycerol carbonate 2-Methyl-3-pentanol Methyl salicylate Methyl vinyl ether Pentanal

Pentanol Propanol Propylamine Propylene oxide Tetramethylsilane Triethylsilane Trioxane

Trisilane Water

Surfactants

DPGME Dynol607 Heptanediol Pentanediol 1,2-Hexanediol Surfynol 104 Tergitol NP-9

Fig. S2 Molecular structure of the studied liquids, surfactants and polymers.

Carbon   Hydrogen   Fluorine   Silicon

Oxygen   Nitrogen   Bromine

Polymeric substrates

Polycarbonate (PC)

Polyethylene Terephthalate (PET)

Poly(methyl methacrylate) (PMMA)

Polyoxymethylene (POM)

Polypropylene (PP)

PTFE (Teflon)

Polyvinyl alcohol (PVA)

Polystyrene (PS)

Hydrocarbons

Benzene

Cumene

Cycloheptene

Cyclohexene

Decane

Dimethylbutane

Dodecane

Fluorene

Heptane

Hexadecane

Hexane

Hexatriene

Mesitylene

Methylnaphthalene

Nonane

Octane

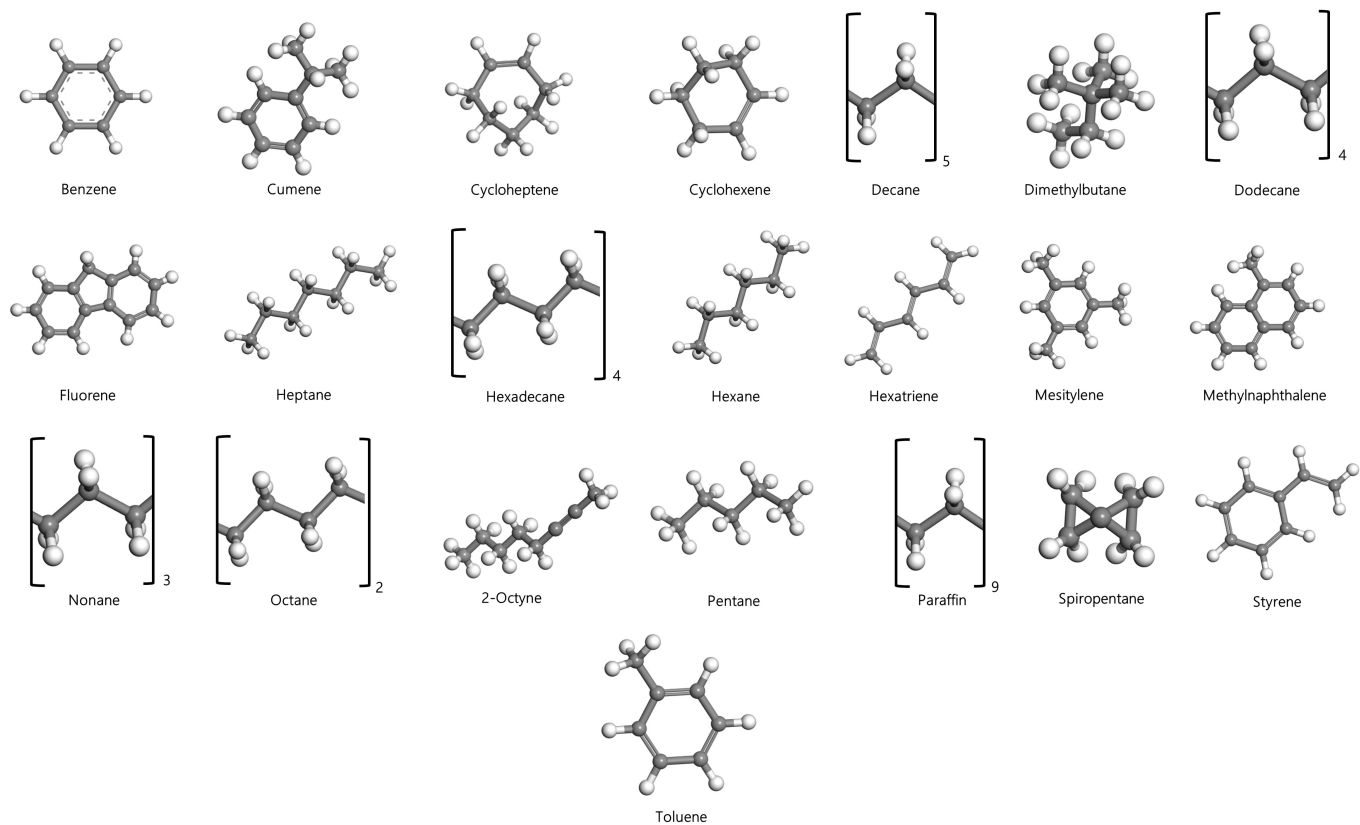2-Octyne

Pentane

Paraffin

Spiropentane

Styrene

Toluene

Fig. S2 Continued.

S3 Surface tensions calculated using a constant probe radius $r_a = 1.4$ Å

Calculated versus experimental values of surface tension obtained using equation (7) are plotted in Fig. S3, where the probe radius for the calculation of the solvent accessible area has a constant value $r_a = 1.4$ Å. Results are in good agreement with experiments, with an overall 3% deviation relative to the experimental values.
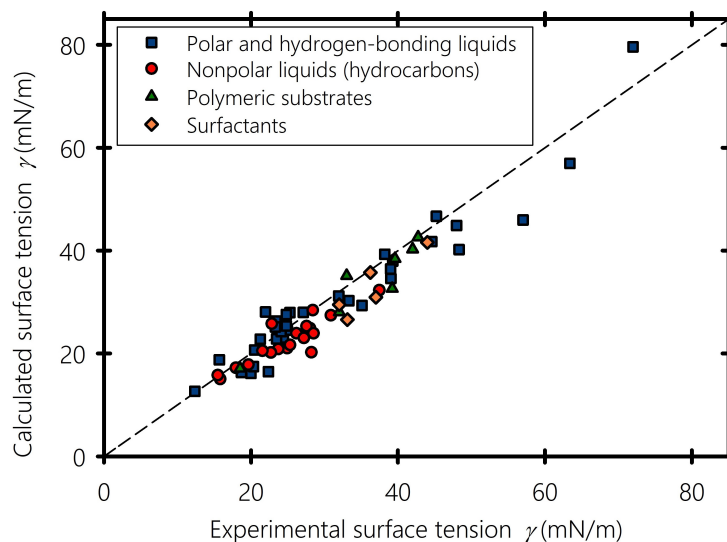

Fig. S3 Calculated versus experimental surface tension obtained using equation (7), with a constant probe radius $r_a = 1.4$ Å.

S4 Surface tension and solubility parameters obtained by the Y-MB method

Solubility parameter obtained using the Yamamoto-Molecular Break (Y-MB) group contribution method[4,5] are provided in Table S3 for all molecules studied in the main text. Comparing with Table 1, we notice that δ_h values predicted by Y-MB are often higher than those computed from MD. One explanation is that Y-MB overestimates the hydrogen-bonding contribution of the solubility parameter, as pointed out by Levin et al.[6] Re-fitting Equation (7) with the solubility parameters obtained by Y-MB gave $b = 0.4577$ and $\alpha = 0.5448$. These were used to plot the experimental versus calculated surface tensions in Fig. S4. Surface tensions obtained using solubility parameter values from Y-MB method agrees well with experiments for the case of hydrocarbons and some liquids such as glycerol, Furan and cyclobutanone. For the other liquids and polymers, the calculated surface tension shows higher deviations comparing to experiments.
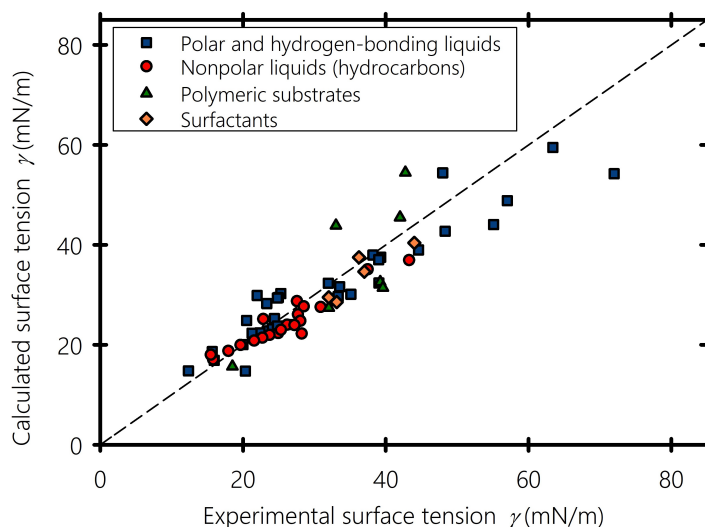

Fig. S4 Calculated versus experimental surface tensions obtained using our equation (7), where the Y-MB method is used to calculate the solubility parameters. The values $\alpha = 0.5448$ and $b = 0.4577$ where obtained by re-fitting Equation 7.

Table S2 Experimental and computed solubility parameters in $(J/cm^3)^{0.5}$ obtained using Y-MD method, along with the experimental and calculated surface tensions (mN/m) at 298.15 K, obtained using equation (7).

	Y-MB				Exp.	Calculated
	δ	δ_d	δ_p	δ_h	γ^{**}	γ using Eq. 7[‡]
Polar and H-bonding liquids						
Acetic acid	21.4	15.2	6.6	13.6	27.1	24.0
Acetaldehyde	21.7	15.8	12.0	8.8	20.5	24.8
Acetone	19.3	15.7	9.1	6.5	23.5−25.2[▽]	22.8
Acetophenone	20.4	18.7	6.8	4.5	38.9−39.1[▽]	32.4
Allyl alcohol	23.8	16.2	8.0	15.5	25.3	30.3
Anisole	19.7	18.3	4.9	5.6	35.1	30.1
Benzyl alcohol	23.5	19.0	6.0	12.5	39.3	37.5
1-Bromonaphthalene	21.5	20.3	4.7	5.1	44.6	38.9
Butanal	18.9	15.7	8.5	6.1	24.3[◇]	23.3
Butanol	22.6	15.8	6.4	14.8	24.9−25.7[▽]	29.4
Cyclobutanone	22.7	18.4	11.8	6.1	31.9	32.3
Cyclopentanone	20.6	18.0	8.6	5.1	33.3	29.7
Diethylene glycol	29.1	17.4	11.0	20.6	45.2	44.1
Dipropyl ether	15.9	15.1	3.5	3.5	20.0	20.0
Ethanol	25.0	15.6	9.3	17.2	22.0	29.8
Ethanolamine	29.6	17.8	10.3	21.3	48.3	42.7
Ethylene carbonate	18.0	22.4	9.3	1.3		40.7
Ethyl acetate	18.5	15.7	6.3	7.5	23.4	22.8
Ethylene glycol	35.3	17.8	13.5	27.4	48.0	54.4
Formamide	34.5	17.7	21.5	20.5	57.0	48.8
Furan	18.3	16.7	4.9	5.8	24.1	23.2
Furfuryl alcohol	25.1	18.6	8.7	14.5	38.2	38.0
Glycerol	35.7	18.3	12.7	27.8	63.4	59.5
Glycerol carbonate	32.0	18.5	21.8	14.5		52.2
2-Methyl-3-pentanol	18.9	15.6	4.6	9.6	24.4	25.2
Methyl salicylate	22.9	18.7	8.7	10.2	39.0	37.0
Methyl vinyl ether	16.7	14.9	5.6	5.2	15.7	18.6
Pentanal	18.5	15.8	7.6	5.8	24.8−25.4[▽]	23.8
Pentanol	21.7	16.0	5.8	13.6	25.4−26.7[▽]	29.3
Propanol	22.6	15.7	7.3	14.6	23.3	28.2
Propylamine	18.5	15.7	5.2	8.3	21.7−22.4[▽]	22.4
Propylene oxide	18.9	15.8	7.5	7.0	24.5	22.3
Tetramethylsilane	13.2	12.9	1.7	2.0	12.3	14.8
Triethylsilane	13.4	13.1	1.9	1.9	20.3	14.7
Trioxane	23.0	17.8	10.8	9.7		31.6
Trisilane	13.7	13.7	1.2	0.1	18.7[◇]	16.9
Water	47.9	0.0	38.8	24.5	72.0	54.2
Surfactants						
DPGME	20.1	16.2	6.4	9.9		28.5
Dynol607	17.2	15.7	4.7	5.4		29.5
Heptanediol	23.4	16.5	6.9	15.1	37.0	34.6
1,2-Hexanediol	25.2	16.7	7.1	17.5	36.2	37.5
Pentanediol	26.9	17.0	8.9	18.9	44.0	40.4
Surfynol 104	18.3	16.4	3.7	7.2	33.1	28.5
Tergitol NP-9	19.0	16.3	7.7	5.9	32.0	29.5
Polymeric substrates						
PC	21.3	18.9	5.1	8.4	42.7	54.5
PET	23.1	19.6	11.7	3.6	40.0−43.0[▽]	45.5
PMMA	16.9	16.2	1.6	4.7	39.2	32.6

Abbreviation: PC: polycarbonate, PET: polyethylene terephthalate, PMMA: polymethyl methacrylate, POM: polyoxymethylene, and DPGME: di(propylene glycol) methyl ether.

[◇] Surface tensions at 293.15 K.

[**] Experimental surface tension values are obtained from Refs. 7–13.

[▽] Dispersed experimental values in the literature.

[‡] Equation (7) with a probe radius that depends on the atom types of the molecules.

Table S2 Continued.

	Y-MB				Exp.	Calculated
	δ	δ_d	δ_p	δ_h	γ^{**}	γ using Eq. 7[‡]
Polymeric substrates						
POM	20.5	16.8	9.8	6.4	38.0−39.6[▽]	31.4
PP	16.3	16.2	0.5	1.9	29.6−32.0[▽]	27.4
PS	18.8	18.7	0.6	2.1	33.0−36.0[▽]	43.9
PTFE	12.5	12.5	0.5	0.2	18.5	15.7
PVA	34.4	19.3	10.4	26.5	37.0	73.2
Hydrocarbons						
Benzene	16.6	16.6	0.1	0.1	28.2	22.3
Cumene	17.4	17.1	1.8	2.3	27.7	26.1
Cycloheptene	17.3	16.8	2.2	3.4	28.0[◇]	24.78
Cyclohexene	17.3	16.8	2.1	3.5	26.2	24.0
Decane	15.6	15.6	0.1	0.1	23.7	22.0
Dimethylbutane	14.2	14.1	0.1	0.1	15.8	17.1
Dodecane	15.8	15.8	0.1	0.1	25.3	23.0
Fluorene	20.4	20.0	2.8	2.8	43.3	36.9
Heptane	15.2	15.2	0.1	0.1	19.6	19.9
Hexadecane	15.9	15.9	0.1	0.1	27.2	23.9
Hexane	14.9	14.9	0.1	0.1	17.9	18.7
Hexatriene	16.7	16.0	2.5	4.3		21.8
Mesitylene	18.4	17.9	2.9	3.1	27.5	28.7
Methylnaphthalene	20.1	19.5	3.1	4.1	37.5	35.1
Nonane	15.5	15.5	0.1	0.1	22.7	21.4
Octane	15.4	15.4	0.1	0.1	21.5	20.8
2-Octyne	16.5	15.9	3.4	2.9	23.9	22.3
Pentane	14.8	14.8	0.1	0.1	15.5	18.0
Paraffin oil	15.9	15.9	0.1	0.1	27.7−28.9[▽]	24.2
Spiropentane	17.8	17.8	0.1	0.1	22.8	25.1
Styrene	18.3	17.8	2.5	3.5	30.9[◇]	27.6
Toluene	18.5	18.0	2.6	3.3	28.5	27.7

Abbreviation: PP: polypropylene, PTFE: polytetrafluoroethylene, PS: polystyrene, and PVA: polyvinyl alcohol.

[◇] Surface tensions at 293.15 K.

[**] Experimental surface tension values are obtained from Refs. 7–13.

[▽] Dispersed experimental values in the literature.

[‡] Equation (7) with a probe radius that depends on the atom types of the molecules.

S5 Tabulated summary of contact angles

Table S3 summarizes contact angles of various liquids on polymeric substrates in degrees (°). Experimental values are gathered from literature, calculated values are obtained using equation (10).

Table S3 Experimental and computed contact angles in degrees (°).

	PMMA		PTFE		PP		PC		PET		POM		PVA		PS	
	$\theta_{exp.}$	$\theta_{calc.}$	$\theta_{exp.}$	$\theta_{calc.}$	$\theta_{exp.}$	$\theta_{calc.}$	$\theta_{exp.}$	$\theta_{calc.}$	$\theta_{exp.}$	$\theta_{calc.}$	$\theta_{exp.}$	$\theta_{calc.}$	$\theta_{exp.}$	$\theta_{calc.}$	$\theta_{exp.}$	$\theta_{calc.}$
Water	76	79.7	111	116.8	101	108.2	91	83.0	79.9	80.83	72.1	75.9	73.4	70.4	88.0	100.8
Glycerol	71	68.8	104	112.4	92	105.9	80	73.8	68.1	70.7	69.7	64.1	60.3	56.6	77.0	94.7
Ethylene glycol	55	53.0	92	101.8	67	93.3	63	54.9	50.8	52.8	54.6	46.8	32.1	37.7	62.7	80.3
Formamide	56	56.8	99	105.3	84	97.6	69	61.6	60.0	58.5	55.5	51.4	32.3	43.2	66.0	84.8
Bromonaphthalene	31	50.7	76	77.1	49	60.9	12	12.3		32.5		49.4		56.2		42.3
Heptane	0	0	24	26.8	0	0	0	0		0		0		0		0
Octane	0	0	29	35.6	0	0	0	0		0		0		9.7		0
Nonane	0	0	35	38.8	0	0	0	0		0		0		18.7		0
Decane	0	0	39	41.5	0	0	0	0		0		0		23.4		0
Dodecane	0	0	44	44.2	0	0	0	0		0		0		27.3		0
Hexadecane	0	10.7	48	48.3	0	0	0	0		0		5.6		33.9		0
Paraffin	25	30.8	62	54	23	18.7	0	0		0		29.6		45.0		0

Abbreviations: PMMA: polymethyl methacrylate, PTFE: polytetrafluoroethylene, PP: polypropylene, PC: polycarbonate, PET: polyethylene terephthalate, POM: polyoxymethylene, PS: polystyrene, and PVA: polyvinyl alcohol.

Experimental contact angle values are gathered from Refs. 10,14,15, where the sessile drop method and the one-liquid contact angle method were used.

S6 Labeled Figures of the surface tension and contact angle

Figures S5 and S6 show labeled versions of Figures 6 (b) and 7, specifying the various liquids.
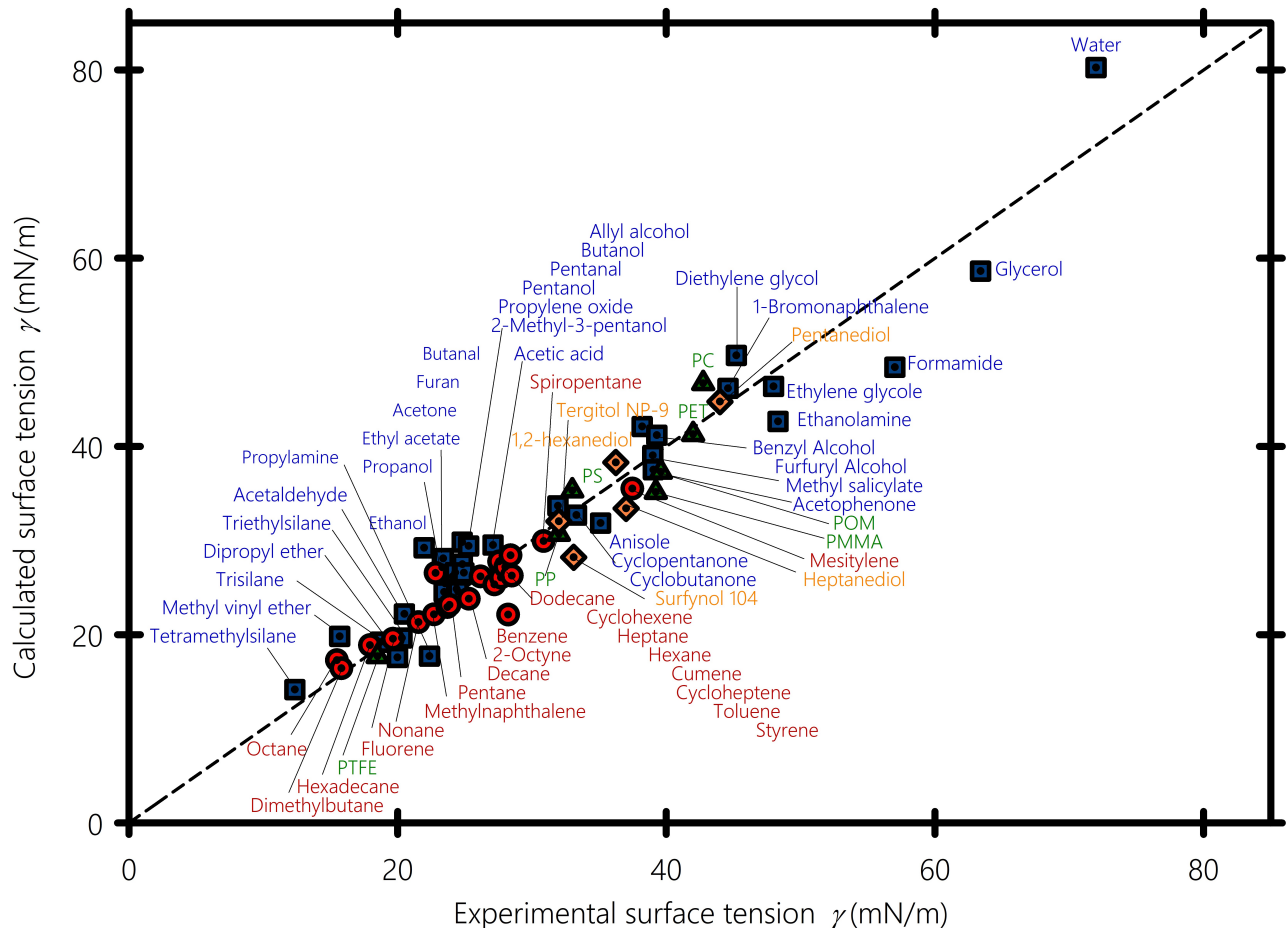

Fig. S5 Calculated versus experimental surface tensions obtained using our equation (7), where each liquid is labeled.
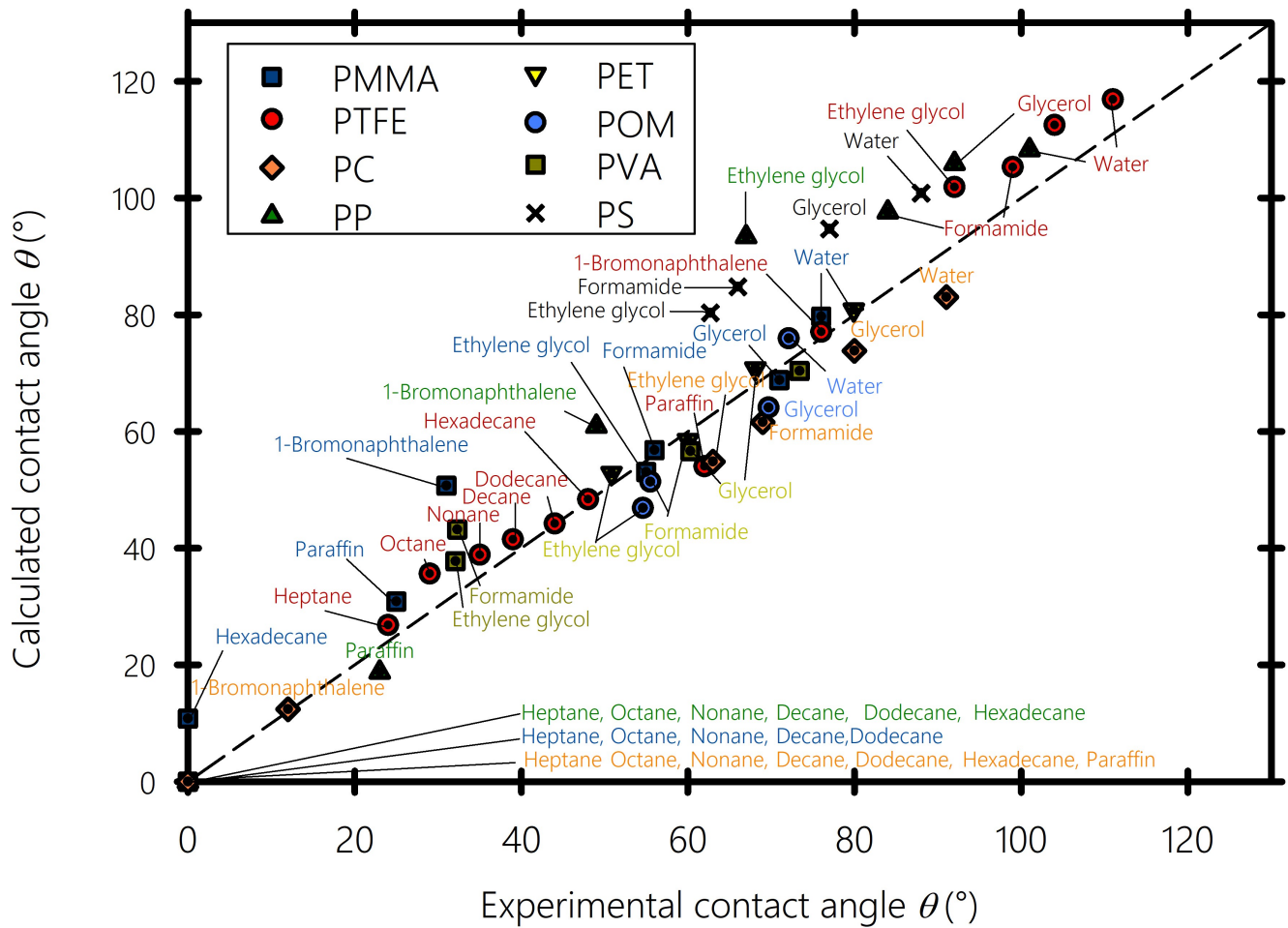
Fig. S6 Experimental versus calculated contact angles of liquids on different polymeric substrates. PMMA: polymethyl methacrylate, PTFE: polytetrafluoroethylene, PP: polypropylene, PC: polycarbonate, PET: polyethylene terephthalate, POM: polyoxymethylene, PS: polystyrene and PVA: polyvinyl alcohol.

S7   Contact angles and wetting graph of liquids on PS and PP

In Fig. S10, the experimental versus calculated contact angles of highly polar liquids on polystyrene and polypropylene are plotted. For these liquids on these two overwhelmingly dispersive polymers, and for these two only, we curiously find that using the total solubility parameter

$$\cos\theta = -1 + 2\sqrt{\frac{V_a^s S_a^f}{V_a^f S_a^s}}\,\frac{\delta^s}{\delta^f}, \tag{S1}$$

gives better results than using its components.
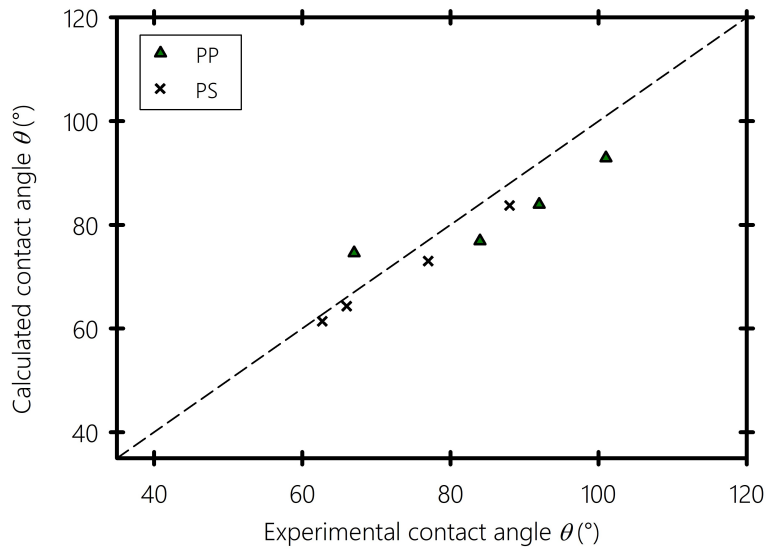
Fig. S7 Experimental versus calculated contact angles of highly polar liquids on polystyrene (PS) and polypropylene (PP).

When using equation (S1), one can use a 1D wettability graph rather than a 3D sphere to identify wetting and non wetting liquids. We show in Fig. S8 the 1D wettability graphs of PP and PS. Liquids positioned to the left of the blue line completely spread on the polymer, those between the red and the blue lines tend to partially spread, and liquids placed to the right of the red line dewet the substrate. Notice that for the case of PP, the only dewetting liquids (in black dots) are water and glycerol, and no liquid dewets PS, which corresponds to the experimental data.
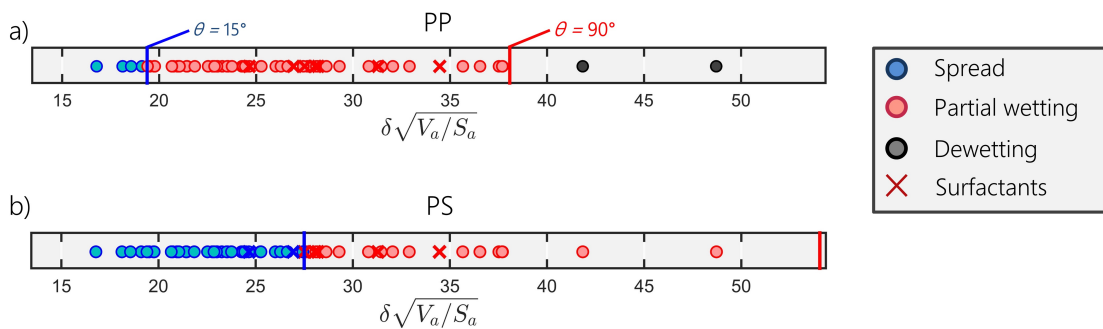

Fig. S8 1D wettability graph of a) polypropylene (PP) and b) polystyrene (PS). All data are in $(J/cm^2)^{1/2}$.

S8 Wetting spheres of the remaining polymers

Figures S9, S10 and S11 shows the wetting sphere of the polymers. In contrast to PTFE shown in Fig. 9 of the paper, most liquids tend to spread on PMMA as shown in Fig. S9. There is no red sphere in this case since all liquids have a contact angle below $90°$ (i.e., there is no dewetting). All alkanes are inside the blue sphere and tend to spread, and only highly polar liquids partially wet PMMA. Equation S2 is the spherical Pythagorean form of equation (10), from which the radius and center of the wettability sphere are readily extracted:

$$\left(x_d^l - \frac{x_d^s}{a}\right)^2 + \sqrt{b}\left(x_p^l - \frac{x_p^s}{a}\right)^2 + \sqrt{b}\left(x_h^l - \frac{x_h^s}{a}\right)^2 = \frac{V_a^s}{S_a^s}\left(\frac{\delta^s}{a}\right)^2, \tag{S2}$$

with

$$x_k = \delta_k\sqrt{\frac{V_a}{S_a}}, \quad \text{and} \quad a = \cos\theta + 1, \tag{S3}$$

where k runs over the dispersive, Coulombic and hydrogen-bonding energies.
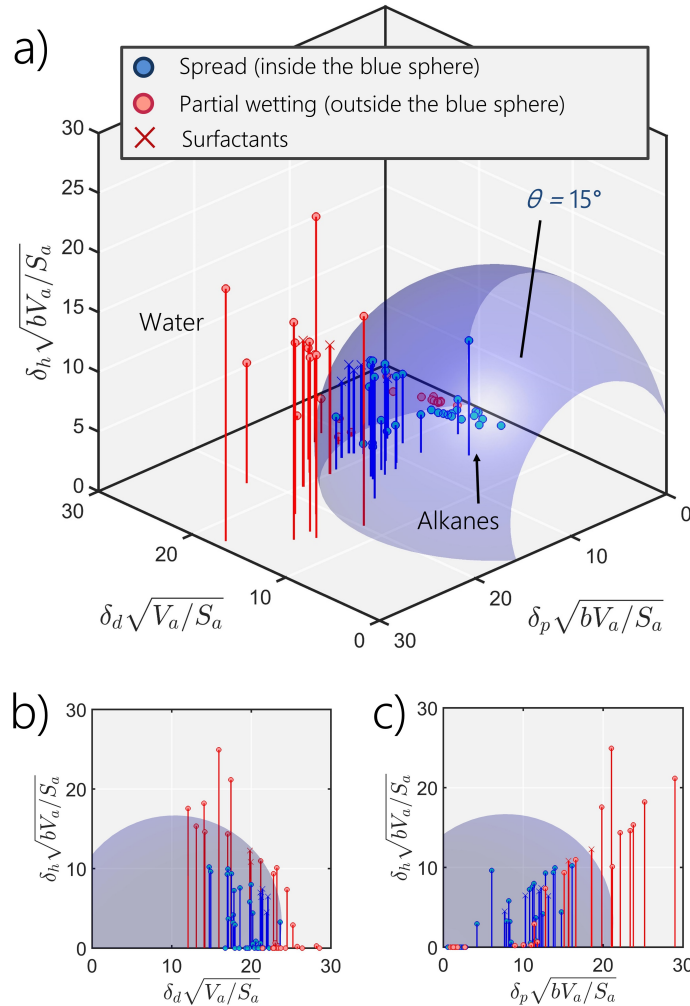

Fig. S9 Wettability sphere for PMMA, a) 3D view of the sphere, b) projection on the hydrogen-bonding-dispersive plan, and c) projection on the-hydrogen-bonding-polar plan. All data are in $(\text{J/cm}^2)^{1/2}$. Liquids whose coordinates are inside the blue sphere spread on PMMA, while those outside it partially spread on PMMA.
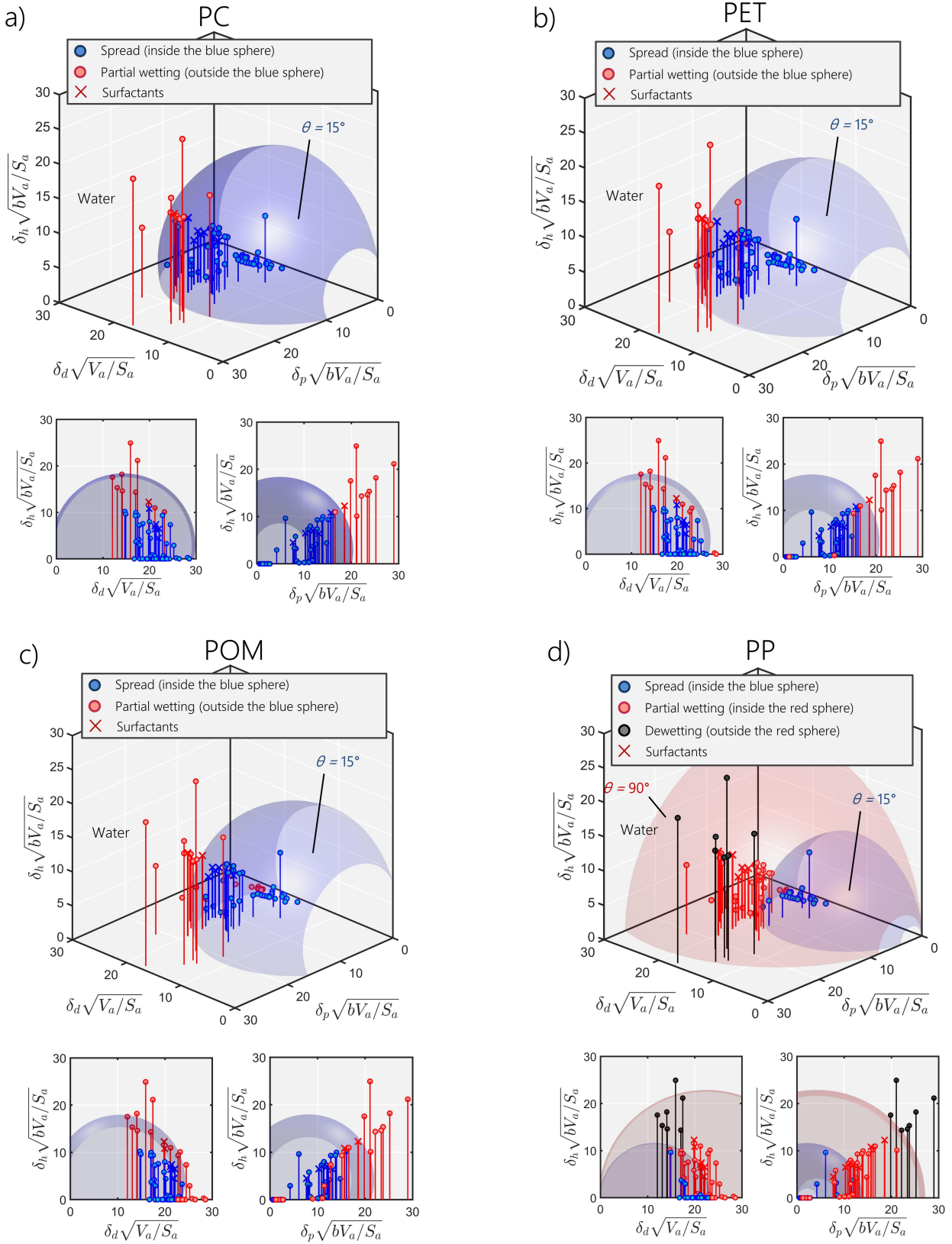
Fig. S10 Wettability spheres of, a) PC: polycarbonate, b) PET: polyethylene terephthalate, c) POM: polyoxymethylene, and d) PP: polypropylene. All data are in $(J/cm^2)^{1/2}$.

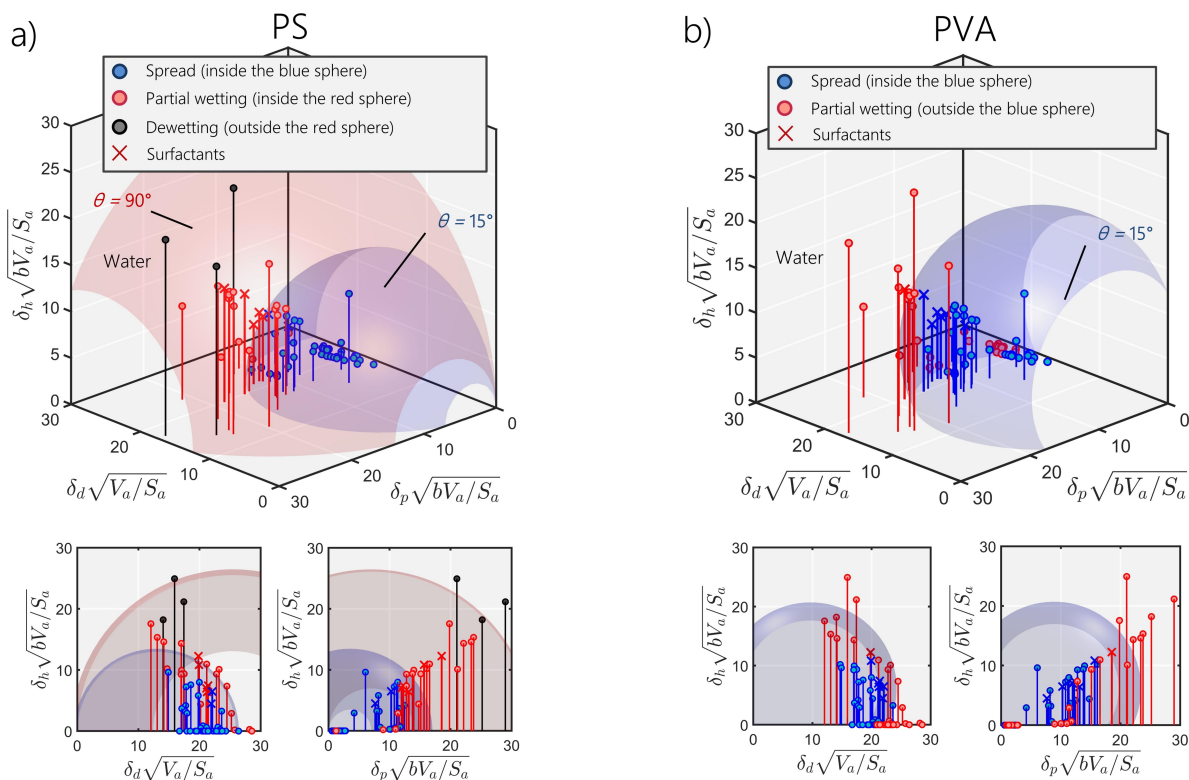**Fig. S11** Wettability sphere of, a) PS: polystyrene and b) PVA: polyvinyl alcohol. All data are in $(J/cm^2)^{1/2}$.

References

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