Electronic Supplementary Material (ESI) for Materials Horizons.

Amphibious Superamphiphilic Fabrics with Self-healing Underwater Superoleophilicity

Sida Fu†[a], Hua Zhou†[a], Hongxia Wang[a]*, Haitao Niu[a], Weidong Yang[b], Hao Shao[a], Tong Lin[a]*

a Institute for Frontier Materials, Deakin University, Geelong, VIC 3216, Australia.
b Future Manufacturing Flagship, CSIRO, Clayton South, VIC 3169, Australia.
†Authors who equally contribute to the paper.
Corresponding authors' emails: hong.wang@deakin.edu.au; tong.lin@deakin.edu.au

Electronic Supplementary Information

Experimental Section

Materials: Glycerol propoxylate triglycidyl ether (GPTE, molecular weight 434, epoxy value 0.69) was supplied by Alfa Chemistry and used as received. Octadecylamine (ODA), 1-methylimidazole, ethanol, acid yellow, oil red and oil blue were provided by Sigma-Aldrich. Commercial polyester fabric (plain weave, 168 g·m^{-2}, thickness ≈ 420 μm) was purchased from a local textile shop, and it was cleaned with acetone and distilled water prior to use.
Preparation of Coating Solution: 5 g GPTE and a drop of 1-methylimidazole were added to 50 ml ethanol and then stirred for 30 min. 1 g ODA was added to the as-prepared solution and stirred overnight. The slight turbid solution further stirred for 15 min at 50 °C. After that, a transparent solution was prepared for coating.

Coating treatment: Polyester fabric was immersed into the coating solution for 1 min, and dried at room temperature for 5 min and finally cured at 150 °C for 1 hour. After heating, the fabric was rinsed with ethanol, and then heated at 150 °C for 10 min。

Self-healing test: Two methods, UV-irradiation and air plasma treatment, were employed to deliberately damage the coating on the fabrics. For UV-irradiation, a UV lamp (Spectroline, model EPS-100/F, wavelength mainly at 254 nm, intensity 38 mW/cm^2) was used to irradiate the superamphiphilic fabric on one fabric side. For each UV-irradiation treatment, 10 hours of irradiation was employed, and the irradiated fabric was heated at 150 °C for 30 min. For air plasma treatment, the coated fabrics were subjected to a vacuum plasma treatment using a purpose made plasma machine consisting of a vacuum chamber, a radio-frequent plasma generator (T & C Power Conversion, Inc. AG0201HV), an electrode system, and a gas supplying system. For each plasma treatment, 5 min of plasma treatment under a power of 28 W was used, and plasma treated fabric was then heated at 150 °C for 30 min.

Characterizations: SEM images were taken using an SEM Supra 55VP operated at an acceleration voltage of 5.0 kV. The contact angle was measured using a Contact Angle Meter (KSV Model CAM 101) with liquid droplets about 5 μL in volume. All the CA values were the average of 6 measurements. The spreading time was measured using a Contact Angle Meter (interval time is 0.033 s) or a stopwatch. FTIR spectra were measured using a Burker Vetex 70 instrument in Attenuated Total Reflection mode. The spectra were obtained under 64 scans at 4 cm^{-1} resolution. The XPS spectra were recorded using a VG ESCALAB 220-iXL XPS spectrometer with a monochromated AL Kα source (1486.6 eV) using samples of ~3 mm^2 in size. The collected XPS results were analyzed by the CasaXPS software. 1H-NMR was performed on Bruker BioSpin Av400H NMR spectrometer using $CDCl_3$ as solvent. GPTE-ODA were dried under vacuum before NMR experiments. GPC was performed using tetrahydrofuran (THF) as the eluent. The GPC system was a Shimadzu modular system comprising an auto injector, two MIX C columns provided by Polymer Lab, and a differential refractive-index detector and a UV detector. The system was calibrated with narrow molecular weight distribution polystyrene standards with molecular weights of 200 to 106 g mol^{-1}. AFM was conducted with a Cypher AFM (Asylum Research) using the tapping model.

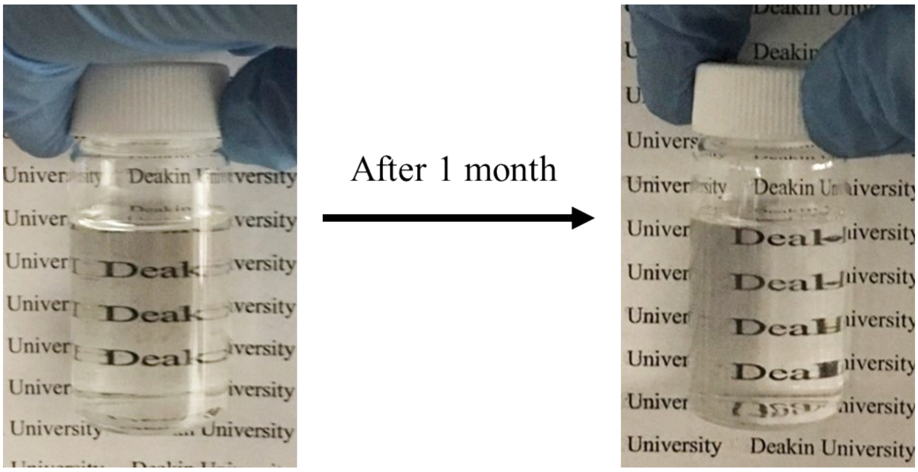

Fig. S1 Photos to show the coating solution before and after one-month storage at room temperature.

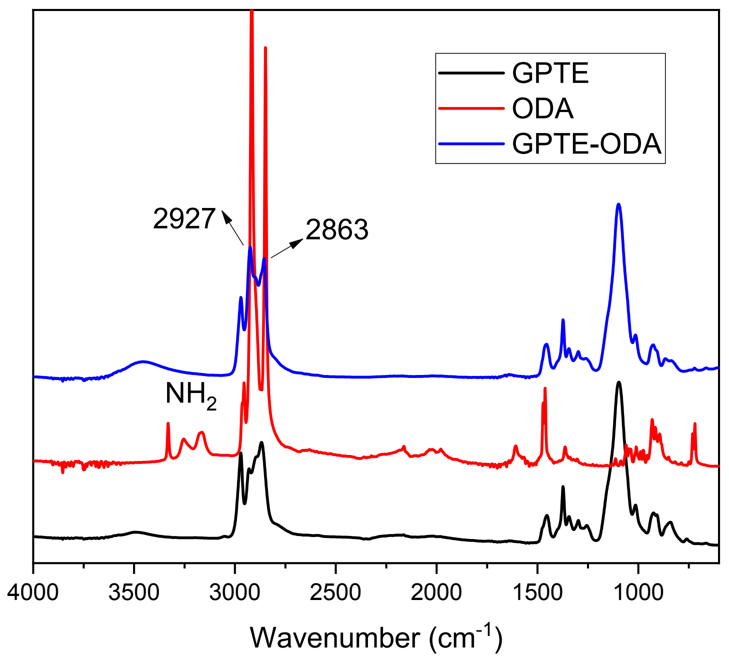

Fig. S2 FTIR spectra of GPTE, ODA, and GPTE-ODA.

After grafting with ODA, new peaks at 2927 cm^{-1} and 2863 cm^{-1} occurred, which were assigned to the C–H stretching vibrations of methylene in alkyl group. In addition, the peaks of amino disappeared, which confirmed that one amino group reacted with two epoxy groups to form tertiary amine.

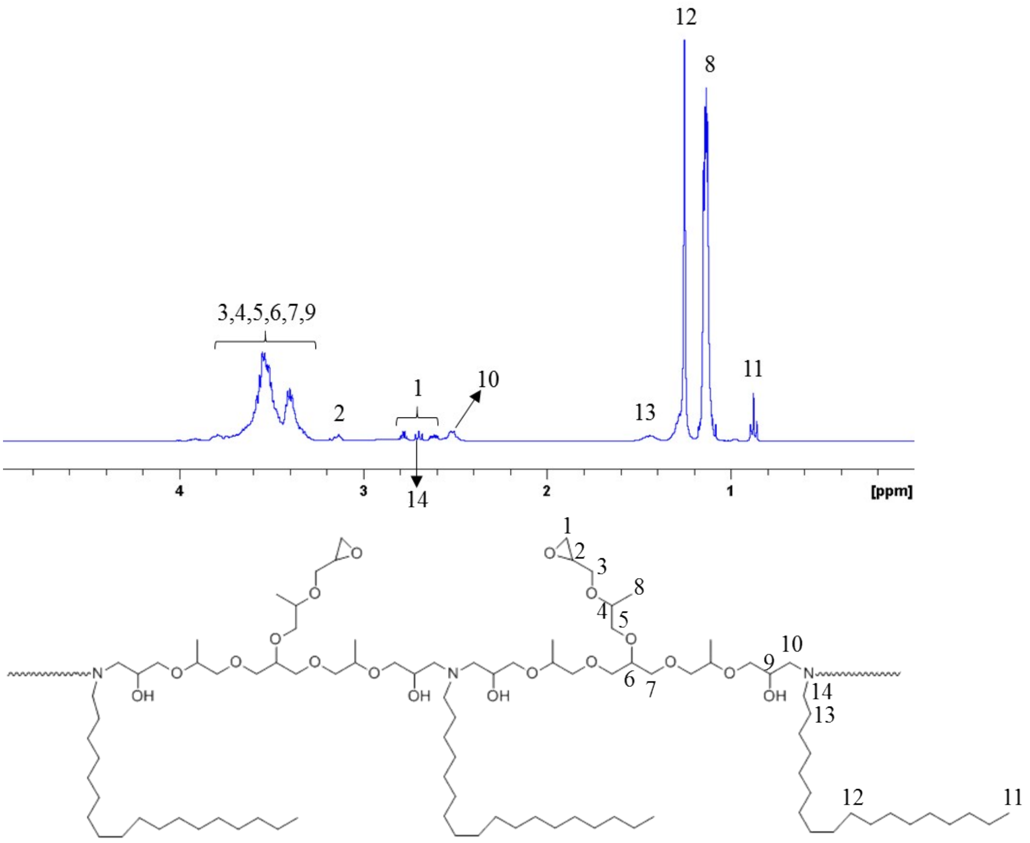

Fig. S3 ^{1}H NMR spectrum of GPTE-ODA compound.

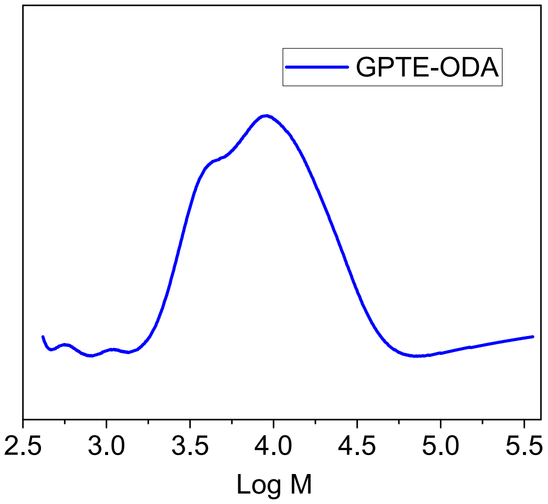

Fig. S4 Differential molecular weight distribution curve for GPTE-ODA.

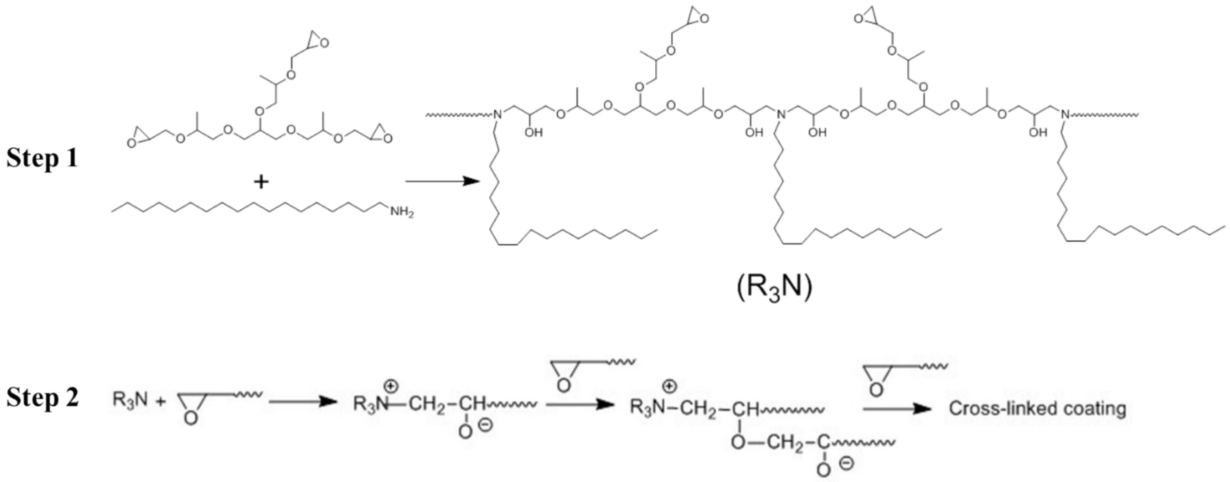

Fig. S5 The reaction mechanism of crosslinking reaction.

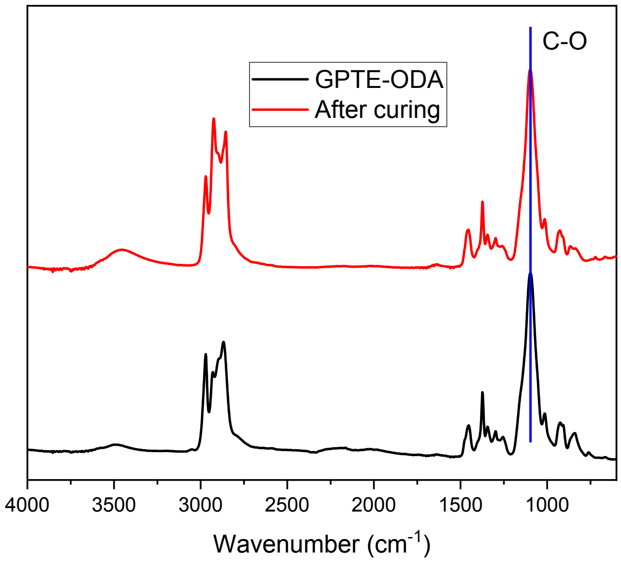

Fig. S6 FTIR spectra of GPTE-ODA before and after curing.

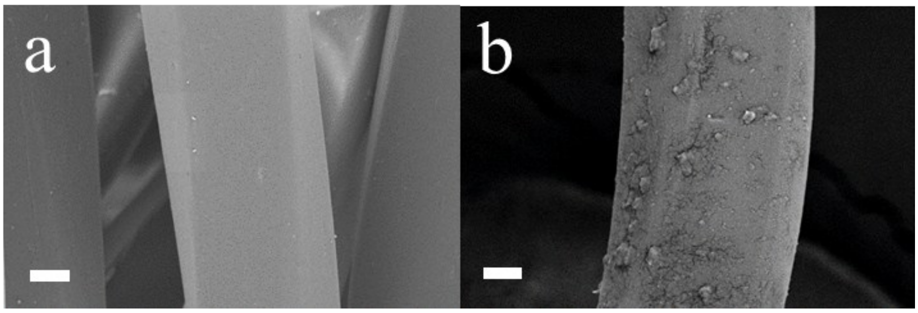

Fig. S7 SEM images of polyester fibers a) before and b) after coating treatment (scale bar 5 μm).

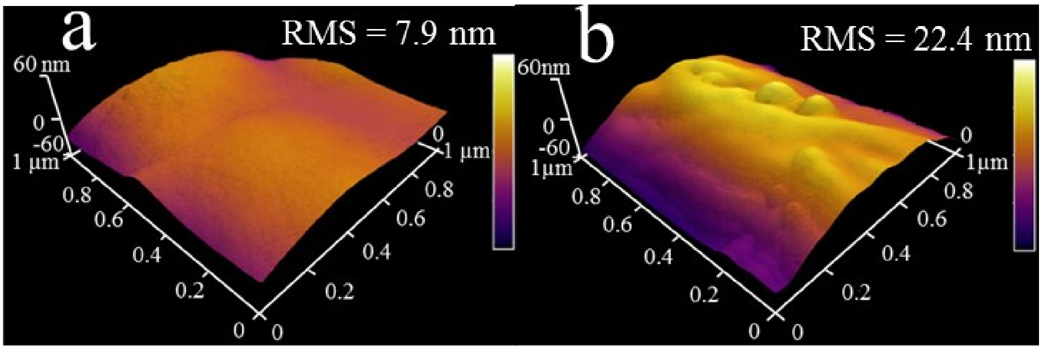

Fig. S8 AFM images of polyester fibers a) before and b) after coating.

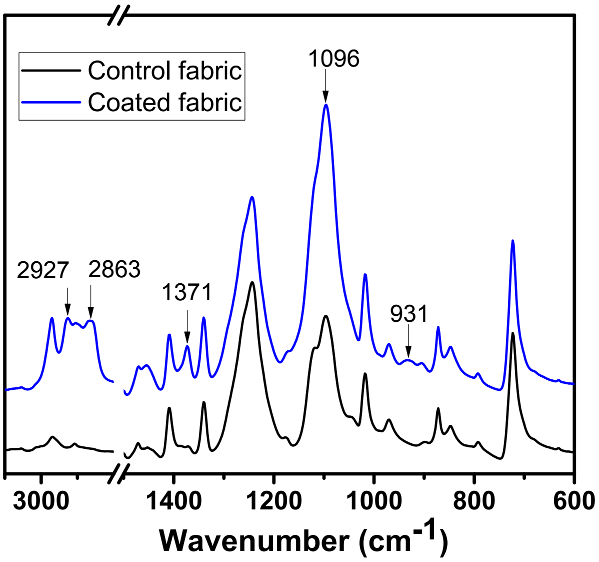

Fig. S9 FTIR spectra of polyester fabric before and after coating.

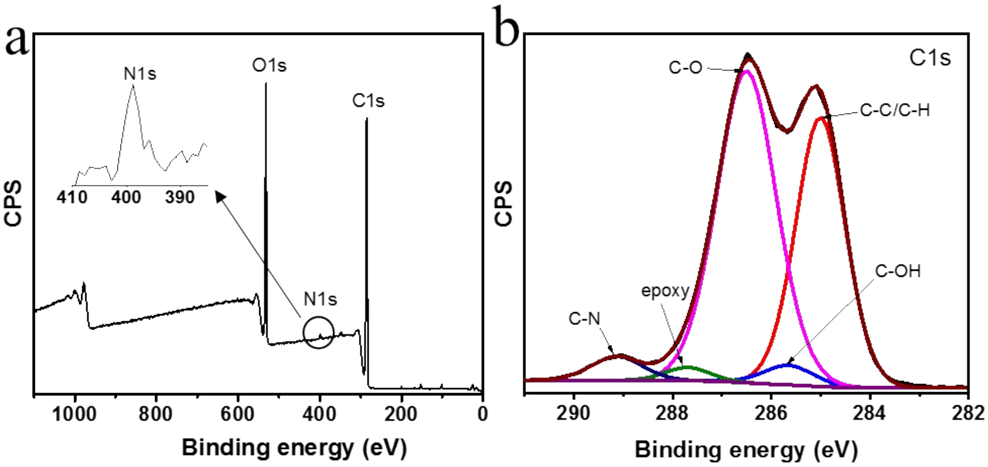

Fig. S10 XPS a) survey and b) high-resolution C1s spectra of the coated polyester fabric.

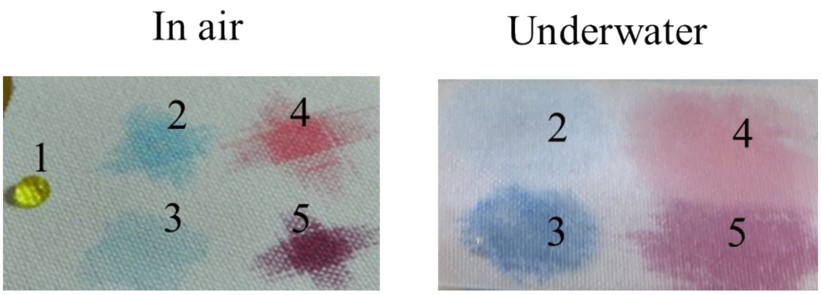

Fig. S11 Photos of water (1), gasoline (2), dichloromethane (3), diesel (4), and diiodomethane (5) droplets (10 μL each) on the uncoated polyester fabrics.

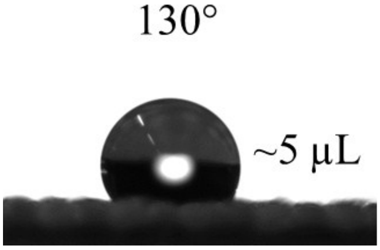

Fig. S12 Water CA of uncoated polyester fabric.

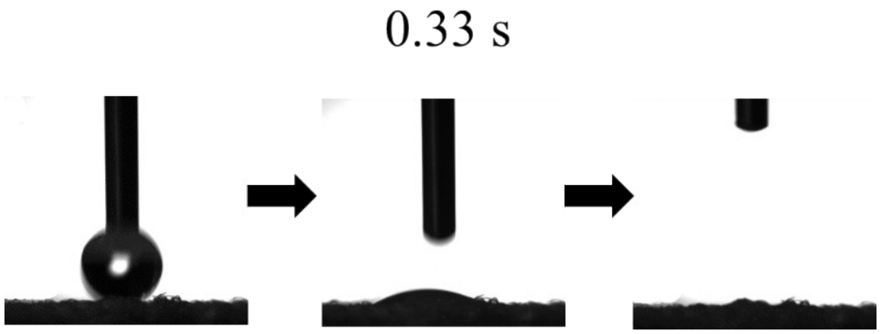

Fig. S13 A water droplet (~5 μL) spread on the coated polyester fabric.

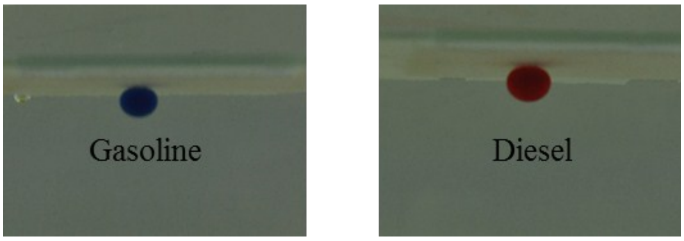

Fig. S14 After vacuuming to remove the plastron layer, the uncoated polyester fabric showed a superoleophobic surface.

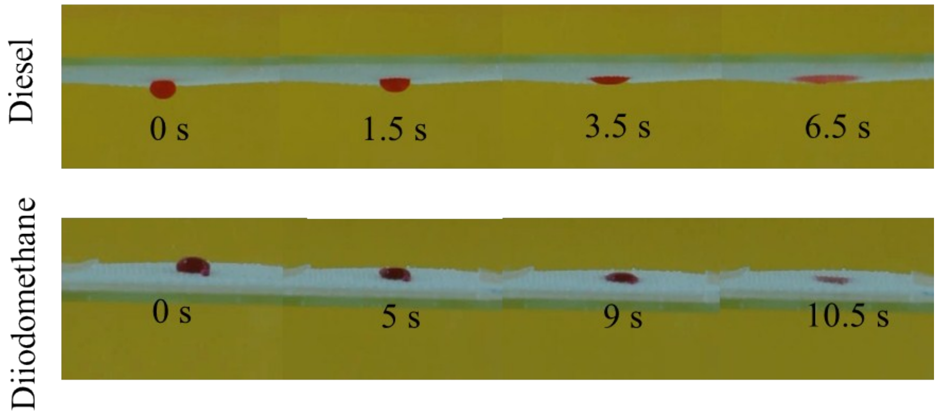

Fig. S15 Still frames taken from videos to show the wetting of oil droplets (~10 μL) on the coated polyester fabric underwater

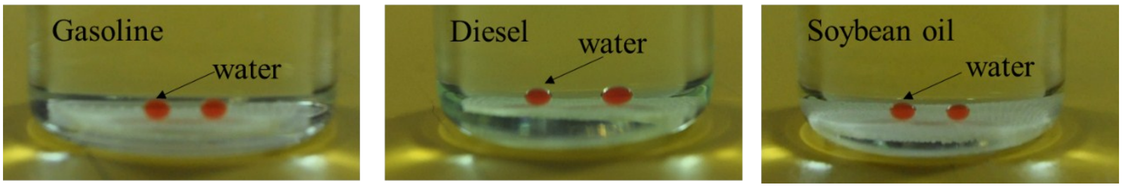

Fig. S16 Dropping water on the coated polyester under gasoline, diesel and soybean oil.

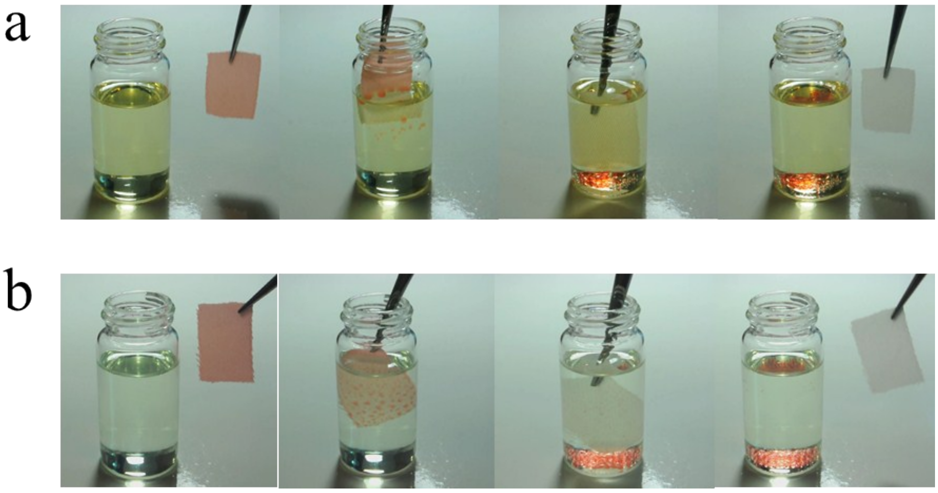

Fig. S17 Immersing a piece of water pre-wetted polyester fabric (GPTE-ODA coated) in a) gasoline, b) diesel.

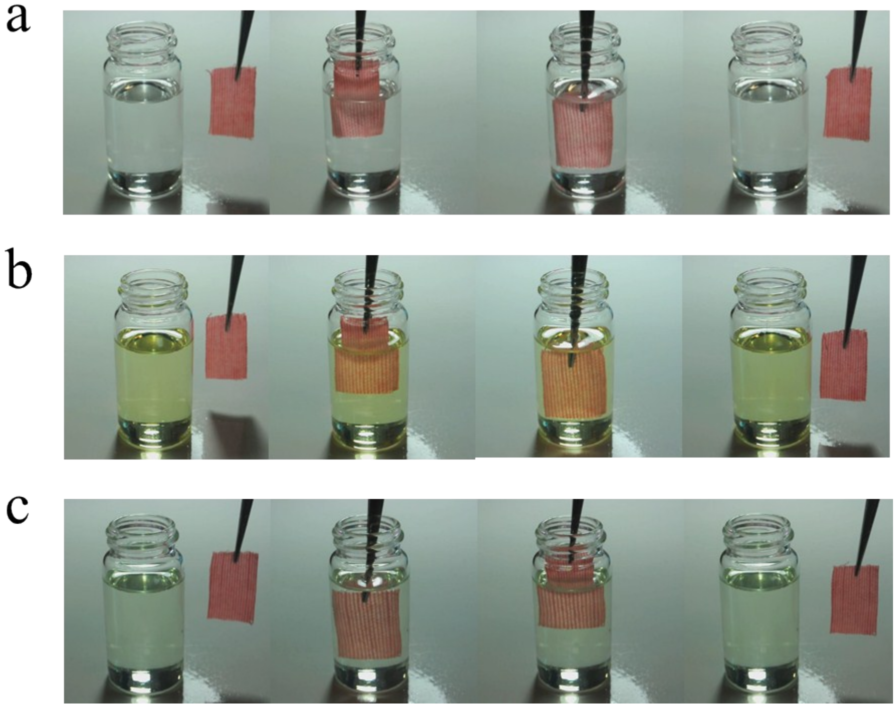

Fig. S18 Immersing a piece of water soaked cotton fabric (uncoated) in a) dichloromethane, b) gasoline, c) diesel.

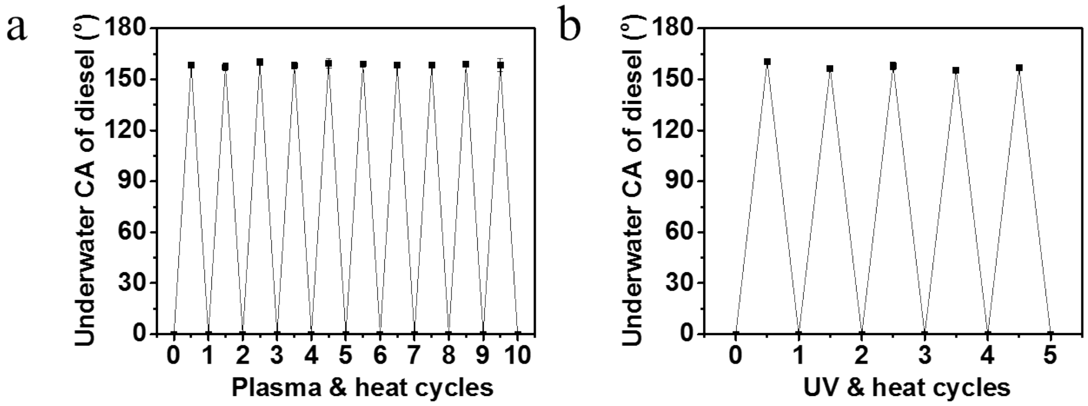

Fig. S19 Underwater CA of diesel changes with a) plasma-and-heat treatment cycles, and b) UV-and-heat treatment cycles.

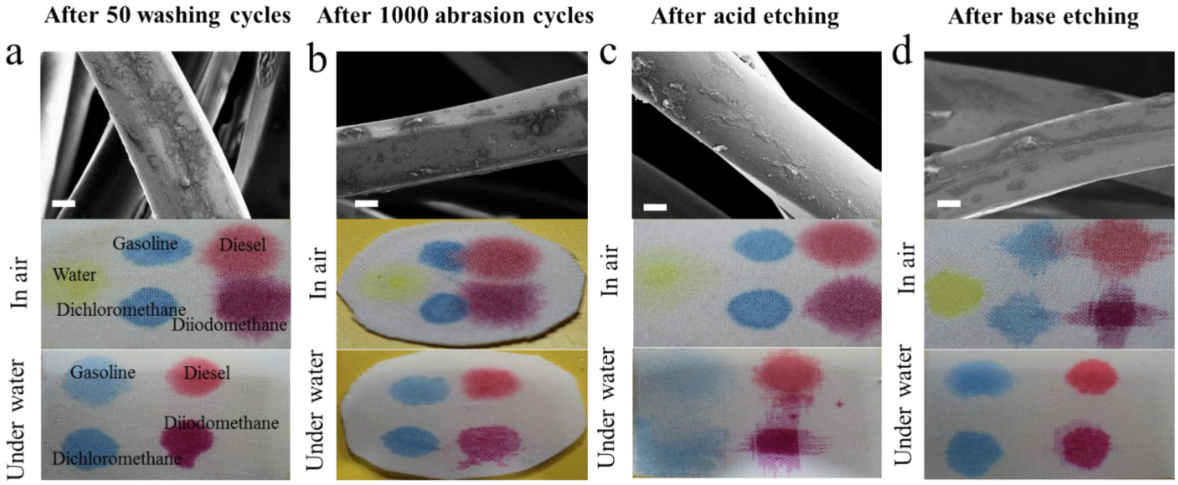

Fig. S20 SEM (scale bar 5 μm) and photos of coated polyester fabric after harsh damages, a) after 50 cycles of washing, b) after 1000 cycles of abrasion test, and after immersing in c) HCl solution (pH=1) and d) NaOH solution (pH=14) for 24 hours followed by rinsing with water and drying at 80 °C for 30 min.

Washing and abrasion durability of the coated fabrics were evaluated according to AATCC 61-2006 and ASTM D4966 standards. Acid and base stability were examined by immersing the coated fabric in hydrochloric acid (pH = 1) or sodium hydroxide solution (pH = 14) at room temperature for 24 hours. After these harsh damages, SEM images showed that slight coating was removed from the surface after harsh damages. The coated polyester fabric still showed superamphiphilic property both in air and underwater states. Water was still able to spread on the fabric completely. The underwater spreading times of gasoline, dichloromethane, diesel, and diiodomethane were almost unchanged or slightly increased (Table S4).

Durability test: Washing durability of the coated fabrics was tested by reference of the washing procedure specified in the AATCC (American Association of Textile Chemists and Colorists) Test Method 61-2006 test No. 2A. The sample (5 cm * 15 cm) and 50 steel balls were added to the washing solution. The test was performed using a standard laundering machine (MODEL H-240, NO. 4361, RAPID LABORTEX CO., LTD.). After running at 40 ± 2 rpm for 45 min at 49 °C, the sample was rinsed three times with distilled water and dried at room temperature. This standard washing procedure was equivalent to five cycles of home laundry washing. For convenience, we used equivalent number of home laundering in this paper. Abrasion resistance test was evaluated using the Martindale method according to American Society for Testing and Materials (ASTM) D4966 test method, which was often used to evaluate the coated fabrics for heavy duty. The process was performed under a commercial Martindale abrasion tester (I.D.M Instrument Design & Maintenance). The test procedure should be in the standard atmosphere, which was 21 ± 1^{o}C and 65 ± 2 %, and the load on the fabrics was 9 kPa. Acid/base etching stability was examined by immersing the coated fabric in hydrochloric acid (pH = 1) or sodium hydroxide solution (pH = 14) at room temperature for 24 hours. The immersed fabric was rinsed with water and then dried at 80°C for 30 min.

Table S1 Element contents on the coated polyester surface

Element	Element contents (Atomic %)
C1s	76.59
O1s	22.75
N1s	0.66

Table S2 Spreading time of coated polyester fabric for various liquids (~ 10 μL each drop)

Fluids	Surface tension (mN/m, 20 ^{o}C)	Viscosity (mPa·s, 20^{o}C)	Spreading time in air (s)	Spreading time under water (s)
Hexane	18.43	0.33	0.11 ± 0.02	1.10 ± 0.21
Heptane	20.14	0.42	0.08 ± 0.02	1.65 ± 0.17
Gasoline	21.56	0.55	0.11 ± 0.02	2.18 ± 0.50
Cyclohexane	24.95	0.98	0.18 ± 0.02	0.43 ± 0.09
Dodecane	25.35	1.34	0.11 ± 0.02	6.68 ± 1.85
Dichloromethane	26.50	0.43	0.09 ± 0.02	0.47 ± 0.07
Tetradecane	26.56	2.81	0.23 ± 0.06	8.94 ± 4.12
Pentadecane	26.90	3.73	0.28 ± 0.02	8.61 ± 2.56
Hexadecane	27.47	3.04	0.25 ± 0.02	12.04 ± 3.64
Chloroform	27.50	0.56	0.07 ± 0 .00	0.48 ± 0.05
Diesel	28.30	3.16	0.23 ± 0.03	5.90 ± 0.71
Soybean oil	31.50	80.00	5.27 ± 0.70	47.54 ± 6.80
Olive oil	32.00	81.00	5.40 ± 1.41	36.02 ± 4.65
1,2-Dichloroethane	32.20	0.84	0.08 ± 0.02	0.50 ± 0.09
Terpineol	33.20	40.00	5.23 ± 0.24	4.81 ± 0.21
Diiodomethane	50.80	2.76	0.12 ± 0.02	12.84 ± 5.03
Water	72.80	1.00	0.45 ± 0.13	/

Table S3 Effect of coating formula on wettability

	Fluids	Wettable (Yes or No)					
GPTE:ODA*		1:1	3:1	5:1	15:1	20:1	Only GPTE
Dry state in air	Water	NO (CA140°)	YES	YES	YES	YES	YES
Under water	Hexane	/	YES	YES	NO	NO	NO
	Heptane	/	YES	YES	NO	NO	NO
	Gasoline	/	YES	YES	YES	YES	NO
	Cyclohexane	/	YES	YES	YES	YES	YES
	Dodecane	/	YES	YES	NO	NO	NO
	Dichloromethane	/	YES	YES	YES	YES	YES
	Tetradecane	/	YES	YES	NO	NO	NO
	Pentadecane	/	YES	YES	NO	NO	NO
	Hexadecane	/	YES	YES	NO	NO	NO
	Chloroform	/	YES	YES	YES	YES	YES
	Diesel	/	YES	YES	YES	YES	NO
	Soybean oil	/	YES	YES	NO	NO	NO
	Olive oil	/	YES	YES	NO	NO	NO
	1,2-Dichloroethane	/	YES	YES	YES	YES	YES
	Terpineol	/	YES	YES	YES	YES	YES
	Diiodomethane	/	YES	YES	YES	YES	NO

Fluids		Spreading time (s)	
GPTE:ODA*		3:1	5:1
Dry state in air	Water	1.01	0.45
Under water	Gasoline	3.01	2.18
	Dichloromethane	0.50	0.47
	Diesel	6.89	6.21
	Diiodomethane	16.68	12.84

* GPTE in coating solution 10 wt%

Table S4 Wettability of coated polyester fabric after harsh damages

Fluids (~ 10 μL)	Spreading time (s)			
	After washing (50 cycles)	After abrasion (1000 cycles)	After acid etching (24 hours)	After base etching (24 hours)
Water (in air)	5.62 ± 0.38	1.42 ± 0.14	0.42 ± 0.10	0.52 ± 0.07
Gasoline (under water)	2.26 ± 0.34	2.13 ± 1.08	2.38 ± 1.04	2.15 ± 0.67
Dichloromethane (under water)	0.63 ± 0.03	0.47 ± 0.02	0.53 ± 0.09	0.51 ± 0.12
Diesel (under water)	9.53 ± 1.86	6.85 ± 2.19	5.74 ± 1.54	5.26 ± 1.95
Diiodomethane (under water)	30.96 ± 5.54	29.61 ± 3.35	15.15 ± 2.82	16.47 ± 4.01

Video S1: Dropping a water droplet (~5 μL) on the coated fabric.
Video S2: Oil droplets on the coated fabric in water.
Video S3: Dichloromethane droplet spreading on a water pre-wetted PET film (GPTE-ODA coated).
Video S4: Immersing water pre-wetted polyester fabric (GPTE-ODA coated) into dichloromethane.
Video S5: Immersing water pre-wetted polyester fabric (GPTE-ODA coated) into gasoline.