Electronic Supplementary Information (ESI)

Mussel-Inspired, Perfluorinated Polydopamine for Self-Cleaning Coating on Various Substrates

Daewha Hong,[a,‡] KiEun Bae,[a,‡] Seok-Pyo Hong,[a] Ji Hun Park,[a] Insung S. Choi[a,*]
and Woo Kyung Cho[b,*]

[a] Center for Cell-Encapsulation Research and Molecular-Level Interface Research Center,
Department of Chemistry, KAIST, Daejeon 305-701, Korea
[b] Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea

‡ These authors equally contributed to this work.

* To whom correspondence should be addressed
Email: ischoi@kaist.ac.kr or wkcho@cnu.ac.kr
Tel: +82-42-350-2840
Fax: +82-42-350-2810

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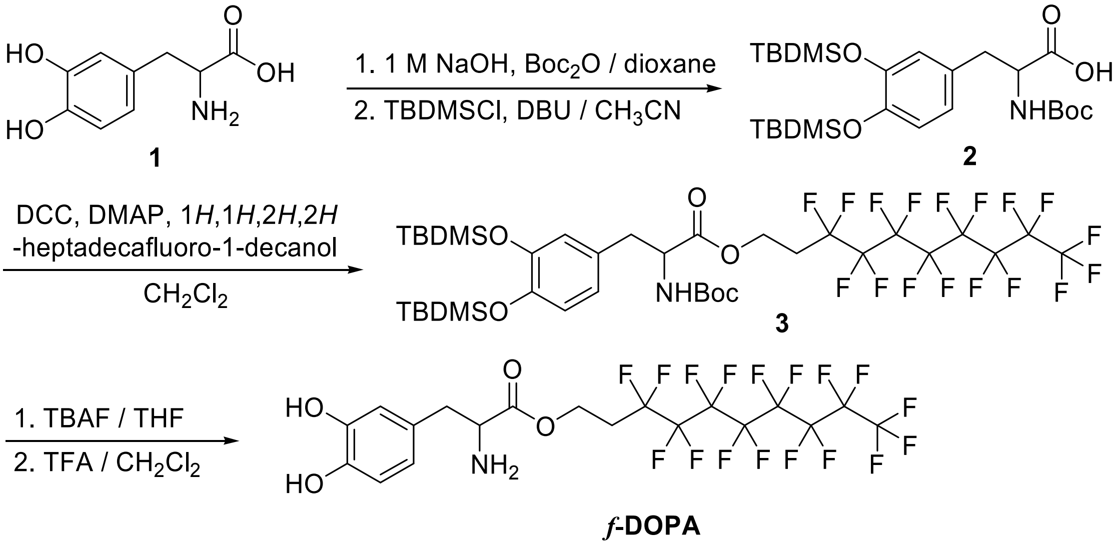
Experimental Section

Materials. 3-(3,4-Dihydroxyphenyl)-L-alanine (L-DOPA, >98.0%, Tokyo Chemical Industry), 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol (>96.0%, Tokyo Chemical Industry), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU, 98%, Aldrich), di-*tert*-butyl dicarbonate (Boc_2O, ReagentPlus®, 99%, Aldrich), *tert*-butyldimethylsilyl chloride (TBDMSCl, reagent grade, 97%, Aldrich), tetrahydrofuran (THF, anhydrous, ≥99.9%, Sigma-Aldrich), tetrabutylammonium fluoride solution (TBAF, Aldrich), trifluoroacetic acid (TFA, ReagentPlus®, 99%, Sigma-Aldrich), dioxane (anhydrous, 99.8%, Sigma-Aldrich), acetonitrile (anhydrous, 99.8%, Sigma-Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, ≥98.0%, Tokyo Chemical Industry), 4-(dimethylamino)pyridine (DMAP, ≥99.0%, Fluka), sodium periodate ($NaIO_4$, 99%, Acros Organics), ammonium chloride (extra pure, Junsei Chemical), calcium hydride (reagent grade, 95%, Sigma-Aldrich), methanol (Absolute, Merck), ethyl acetate (95%, Samchun Chemicals), hexane (95%, Samchun Chemicals), magnesium sulfate ($MgSO_4$, anhydrous, 99.5%, Junsei Chemical), Sylgard 184 silicone elastomer kit (Dow Corning), microscope glass slides (76 mm × 26 mm, 1-mm thickness, Paul Marienfeld GmbH & Co. KG), zinc (Zn, foil, 0.25-mm thick, 99.9%, Sigma-Aldrich), vanadium (V, foil, 0.127-mm thick, 99.7% metals basis, Aldrich), polyethylene terephthalate (PET, Kumjeong), and polytetrafluoroethylene (PTFE, Daedok Science) were used as received. Gold and titanium dioxide (TiO_2) substrates were prepared by coating each component onto a silicon wafer with the thickness of 100 nm by using a thermal evaporator. Dichloromethane (J. T. Baker, HPLC grade) was distilled with calcium hydride before its use for the synthetic reactions. Deionized water from the Human Ultrapure System (Human Corp.) was used.



Synthesis of 1*H*,1*H*,2*H*,2*H*-Heptadecafluorodecyl 2-Amino-3-(3,4-dihydroxyphenyl)propanoate, *f*-DOPA. L-DOPA (**1**) (2.0 g, 10.0 mmol) was dissolved in dioxane (10.0 mL), and to the L-DOPA solution were added 1 M NaOH (11.0 mL, 11.0 mmol) and Boc_2O (2.4 g, 11.0 mmol) at 0 °C. The mixture solution was stirred for 6 h at room temperature. The solvent was evaporated, and the resultant was washed with 1 M HCl, water, and brine, and then dried over $MgSO_4$. The product was concentrated in vacuo to give 2.6 g (86.2%), and the obtained Boc-DOPA was used without further purification. ^1H NMR (300 MHz, $CDCl_3$): δ 6.61 (m, 3H), 5.15 (m, 1H), 4.48 (m, 1H), 2.92 (m, 2H), 1.38 (s, 9H).

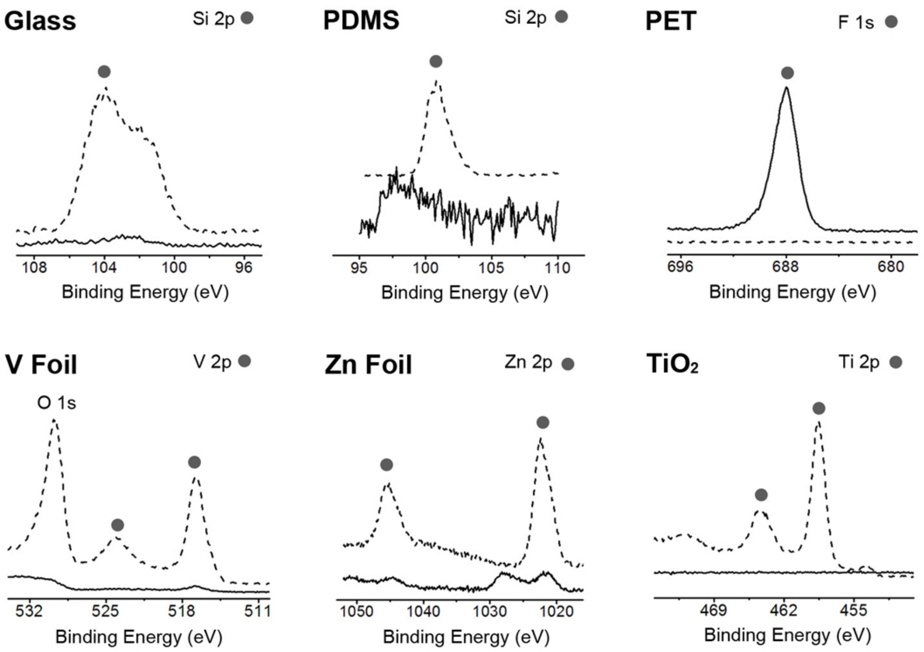
To the acetonitrile solution (30.0 mL) of Boc-DOPA (2.4 g, 8.1 mmol) was added TBDMSCl (3.0 g, 20.2 mmol). The mixture was cooled to 0 °C, and DBU (3.0 mL, 20.2 mmol) was added dropwise over 10 min. The resulting mixture was stirred at room temperature for 16 h and then evaporated. The crude product was purified by silica-gel column chromatography (2% methanol/dichloromethane) to give 2.6 g (61.3%) of (**2**) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.72 (d, J = 8.0 Hz, 1H), 6.60 (m, 2H), 4.88 (d, J = 8.0 Hz, 1H), 4.50 (m, 1H), 2.99 (m, 2H), 1.39 (s, 9H), 0.94 (s. 18H), 0.16 (s, 12H). EI-MS: *m/z* calcd for $C_{26}H_{47}NO_6Si_2$ 548.3 $[M+Na]^+$, found 548.3.

DCC (0.6 g, 3.2 mmol) and DMAP (0.3 g, 3.2 mmol) were added to the solution of (**2**) (1.5 g, 2.9 mmol) and 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol (1.5 g, 3.2 mmol) in dichloromethane (20 mL). The reaction mixture was stirred at room temperature for 16 h, and the resulting suspension was filtered off. After washing, the residue was purified by silica-gel column chromatography (ethyl acetate/hexane, 1/5) to give 2.2 g (79.3%) of (**3**) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.71 (d, J = 8.1 Hz, 1H), 6.59 (d, J = 2.1 Hz, 1H), 6.53 (dd, J = 2.1, 8.1 Hz, 1H), 4.88 (d, J = 8.1 Hz, 1H), 4.48 (m, 1H), 4.35 (t, J = 6.6 Hz, 2H), 2.92 (d, J = 5.3 Hz, 2H), 2.39 (m, 2H), 1.39 (s, 9H), 0.95 (s, 18H), 0.16 (s, 12H). EI-MS: *m/z* calcd for $C_{36}H_{50}F_{17}NO_6Si_2$ 994.3 $[M+Na]^+$, found 994.3.

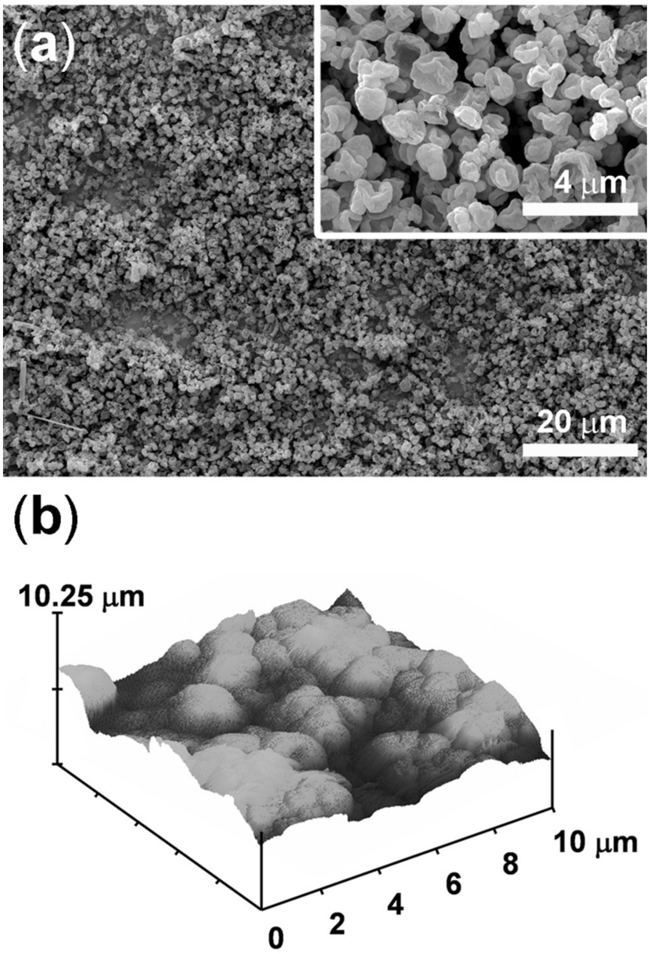
TBAF (4.6 mL, 4.6 mmol) was added to the solution of (**3**) (2.0 g, 2.1 mmol) in THF (20 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 30 min and then quenched with saturated ammonium chloride solution (40 mL). The resulting solution was concentrated in vacuo to give 1.8 g of a yellow oil (Boc-*f*-DOPA). The solution of Boc-*f*-DOPA (1.8 g, 2.4 mmol) in dichloromethane (30 mL) was added to TFA (10 mL) at 0 °C. The mixture was stirred at room temperature for 16 h. The crude product was purified by silica-gel column chromatography (2% methanol/dichloromethane) to give 1.0 g (75.5%) of *f*-DOPA·TFA as a yellow solid. ^{1}H NMR (300 MHz, DMSO-*d*): δ 6.65 (d, J = 7.9 Hz, 1H), 6.58 (d, J = 2.1 Hz, 1H), 6.42 (dd, J = 2.1, 7.9 Hz, 1H), 4.31 (m, 2H), 4.15 (t, J = 6.5 Hz, 1H), 3.67 (br, 2H), 2.91 (m, 2H), 2.60 (m, 2H). EI-MS: *m/z* calcd for $C_{21}H_{15}F_{20}NO_6$ 758.1 $[M+H]^+$, found 758.1.

Preparation of Self-Cleaning, Superhydrophobic Surfaces. The acetonitrile solution of *f*-DOPA (4 mg/mL) was used for superhydrophobic coating. The *f*-DOPA solution was carefully poured over a substrate, and then the aqueous solution of $NaIO_4$ (100 mM) as an oxidizing reagent was added to the sample solution. The final volumetric ratio of the *f*-DOPA solution and the $NaIO_4$ solution was 15:2. After 12 h, the substrate was washed with acetonitrile and dried under a stream of argon gas. The substrate was coated again with the freshly prepared solution of *f*-DOPA by following the same steps as described above.

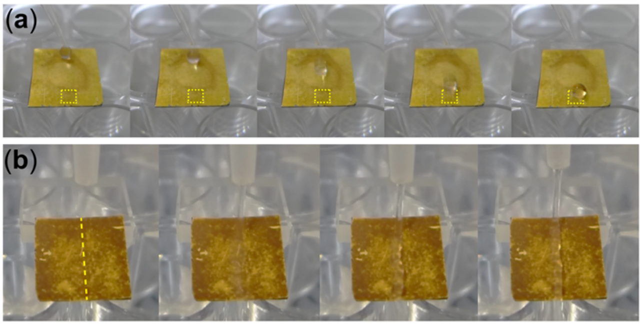
Characterizations. All synthesized compounds were characterized by nuclear magnetic resonance spectroscopy (NMR, Bruker) operated at the ultrashield of 300 MHz and high-resolution mass spectrometry (HR-MS, Bruker Daltonics). The X-ray photoelectron spectroscopy (XPS) study was performed with a VG-Scientific spectrometer (model: Sigma Prove) with a monochromatized Al Kα X-ray source (1486.6 eV). Emitted photoelectrons were detected by a multi-channel detector at a take-off angle of 40° relative to the surface. During the measurements, the base pressure was 8.0×10^{-8} Torr. Survey spectra were obtained at a resolution of 1 eV from 2 scans and high-resolution spectra were acquired at a resolution of 0.1 eV from 15 scans. Contact angle measurements were performed using Phoenix 300 apparatus (Surface Electro Optics Co.) equipped with a video camera. The static contact angles of 5-μL water droplets were measured at more than five different locations on each sample, and the average values were reported in this paper. Dynamic water contact angles were measured by Phoenix 300 touch (Surface Electro Optics Co.). A 5-μL water droplet was placed onto each sample, and the substrate was gradually tilted at a rate of 2°/sec. Three different samples were analyzed and the averaged values were reported in this paper. Field-emission scanning electron microscopy (FE-SEM) micrographs were acquired by INSPECT F50 FEI XL FEG/SFEG microscope (FEI Co.) with an accelerating voltage of 30 keV. Before FE-SEM imaging, the samples were coated with the mixture of platinum (Pt) and palladium (Pd) (the mixing ratio of Pt and Pd was 9:1) by using a sputter (Cressington Scientific, 108 Auto Sputter Coater). The atomic force microscopy (AFM) image was obtained by a Nanoscope IIIa multimode scanning probe microscope (Vecco) in tapping mode.



Supporting Figure 1. XPS spectra of each substrate before and after *f*-DOPA coating. The dotted and solid lines present the spectra of the bare and *f*-DOPA-coated substrates, respectively. The intensity of the characteristic XPS peak(s) for glass, polydimethylsiloxane (PDMS), V foil, Zn foil or TiO_2 decreased after coating: 103.8 eV (Si 2p) for glass; 100.8 eV (Si 2p) for PDMS; 516.7 (V $2p_{3/2}$), 524.2 (V $2p_{1/2}$), and 529.7 eV (O 1s from vanadium oxide) for a V foil; 1022.3 (Zn $2p_{3/2}$) and 1045.3 eV (Zn $2p_{1/2}$) for a Zn foil; 458.6 (Ti $2p_{3/2}$) and 464.3 eV (Ti $2p_{1/2}$) for TiO_2. For PET, the peak from F 1s was used to confirm the coating formation. The XPS spectrum for bare PET did not show the F 1s peak (687.9 eV), which was observed after coating.



Supporting Figure 2. Surface topography of the *f*-DOPA-coated gold substrate: (a) FE-SEM and (b) AFM micrographs.



Supporting Figure 3. Photographs for the manipulation of water droplets and flow on the slightly tilted *f*-DOPA-coated gold substrate: (a) the capture of a sliding water droplet at the relatively hydrophilic area (dotted square) and (b) the control of water flow. The dotted line is the relatively hydrophilic area surrounded by superhydrophobic areas.

Supporting Table 1. Analytical data from dynamic water contact angle measurements.

Substrate	Advancing contact angle	Receding contact angle	Contact angle hyestresis (*H*)[a]	Water sliding angle[b]
Gold	155.5 ± 2.1^o	145.6 ± 3.2^o	9.9 ± 2.3^o	5.3 ± 2.3^o
Glass	159.6 ± 1.2^o	151.8 ± 1.8^o	7.8 ± 1.0^o	3.5 ± 2.1^o
PDMS	157.5 ± 5.6^o	149.3 ± 5.8^o	8.2 ± 2.0^o	4.4 ± 1.3^o
PET	156.9 ± 3.5^o	151.5 ± 0.5^o	5.4 ± 4.0^o	3.4 ± 1.8^o
V foil	156.2 ± 1.3^o	151.8 ± 1.6^o	4.4 ± 0.3^o	3.9 ± 2.5^o
Zn foil	160.4 ± 1.4^o	152.8 ± 1.3^o	7.6 ± 2.6^o	2.5 ± 0.8^o
TiO_2	159.7 ± 2.8^o	147.7 ± 1.4^o	12.0 ± 2.3^o	6.7 ± 0.6^o

[a] The contact angle hysteresis (*H*) was calculated as $H = (\theta_{adv} - \theta_{rec})$.

[b] Water sliding angle is defined as the tilt angle, where a water droplet starts to roll down the substrate when the substrate is tilted gradually.