Supporting Information

Surfactants and alcohols induced disaggregation of perylene probes and a novel sensing strategy for distinguishing the brand and authenticity of makeup remover

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Synthesis of the perylene probes

Probe 1 and Probe 3 were synthesized according to our previous work [S1-S2]. Probe 2 and Probe 4 were designed and synthesized according to the following route (Fig. S1, Supporting Information).

Synthesis of compound 1: Perylene-3,4,9,10-tetracarboxylic acid dianhydride (3 g, 7.6 mmol) was stirred in KOH solution (5%, 35 mL) for 4 h at 90 ℃. After cooling to room temperature, 12.5 mL H_3PO_4 (10%) was added and stirred for 1 h at 90 ℃. The precipitate formed was filtered, washed with water and dried in vacuum at 100 ℃.

Synthesis of compound 2: Compound 1 (1 g, 2.2 mmol), N,N-dimethylpropane-1,3-diamine (11 mmol), and water (50 mL) were stirred at 0-5 ℃ for 4 h. After stirring the mixture at 90 ℃ for 2 h, potassium carbonate (25%, 12.5 mL) was added and stirred for another 1 h at 90 ℃. The precipitate was collected by vacuum filtration and washed with potassium carbonate (2%). The precipitate was dissolved in KOH (3.5%, 100 mL), heated to 90 ℃, kept at this temperature for 5 min and filtered while hot. After acidification with hydrochloric acid (10%), the precipitate was collected by vacuum filtration and dried in vacuum at 100 ℃.

Synthesis of compound 3: Compound 2 (1.55 g, 3.25 mmol) was added to 3-methylpyridine (50 mL) with stirring under nitrogen. Copper powder (2.0 g, 31.5 mmol) was added and the mixture heated at 160 °C for 48 h under a nitrogen

atmosphere. The reaction mixture was cooled, poured into aqueous saturated ammonium chloride solution (50 mL). The mixture was extracted with chloroform for two times (100 mL). The combined organic fractions were washed with aqueous saturated ammonium chloride solution then water and subsequently dried (anhyd. Na_2SO_4). The solution was filtered and the solvent was evaporated giving an orange green solid, which was subjected to column chromatography (SiO_2/CH_2Cl_2). The product was collected as the first intense orange band. Evaporation of the solvent gave a red solid, which was dried in vacuum and used without further purification.

Synthesis of Probe 2: 1.0 g of the obtained compound 3 and 4.5 mL of methyl iodide were added to 150 mL of toluene, refluxed for 3 h under N_2 atmosphere. After the mixture was cooled to room temperature, the precipitate was filtered and washed with ether and dried under vacuum to give the final product (Probe 2). ^{1}H NMR (400 MHz, TFA) δ 8.50 (d, J = 44.5 Hz, 3H), 8.30 (d, J = 17.0 Hz, 3H), 7.76 (s, 2H), 7.46 (s, 2H), 4.34 (s, 2H), 3.49 (s, 2H), 3.02 (s, 9H), 2.30 (s, 2H).

Synthesis of compound 4: Compound 1 (1 g, 2.2 mmol), 3-amino-1-propanol (11 mmol) and water (50 mL) were stirred at 0-5 ℃ for 4 h. After stirring the mixture at 90 ℃ for 2 h, potassium carbonate (25%, 12.5 mL) was added and stirred for another 1 h at 90 ℃. The precipitate was collected by vacuum filtration and washed with potassium carbonate (2%). The precipitate was dissolved in KOH (3.5%, 100 mL), heated to 90 ℃, kept at this temperature for 5 min and filtered while hot. After

acidification with hydrochloric acid (10%), the precipitate was collected by vacuum filtration and dried in vacuum at 100 ℃.

Synthesis of Probe 4: Into a 50 ml Schlenk flask were charged aminocaproic acid (21 mmol), compound 4 (4.51 g, 10 mmol), and imidazole (28 g). The mixture was purged with argon for 15 minutes before being heated at 120 ℃ until the reaction mixture was completely soluble in water. Subsequently, the reaction mixture was cooled to 90 °C. Deionized water was then added under argon atmosphere. The dark red solution was filtered to remove the trace amount of unreacted compound 4. The solution was then acidified with 2 M HCl aqueous solution to a pH value of 3-4, the precipitate was collected by suction-filtration and thoroughly washed with deionized water until the filtrate was neutral; the red solid was collected and dried at 75 ℃ in vacuum oven until constant weight. ^{1}H NMR (500 MHz, TFA-d1) δ 8.27 (s, 8H), 7.07 (s, 1H), 4.18 (d, J = 59.7 Hz, 2H), 3.93 (s, 2H), 2.17 (s, 2H), 1.91 (d, J = 80.2 Hz, 2H), 1.48 (s, 6H), 1.22 (s, 2H).

References:

[S1] J. Li, H. Zhou, Y. Zhang, S.A. Shahzad, M. Yang, Z. Hu, et al., Tuning of the perylene probe excimer emission with silver nanoparticles, Anal. Chim. Acta 1016 (2018) 40-48.

[S2] Y. Wang, J. Chen, Y. Chen, W. Li, C. Yu, Polymer-Induced Perylene Probe Excimer Formation and Selective Sensing of DNA Methyltransferase Activity through the Monomer–Excimer Transition, Anal. Chem. 86 (2014) 4371-4378.

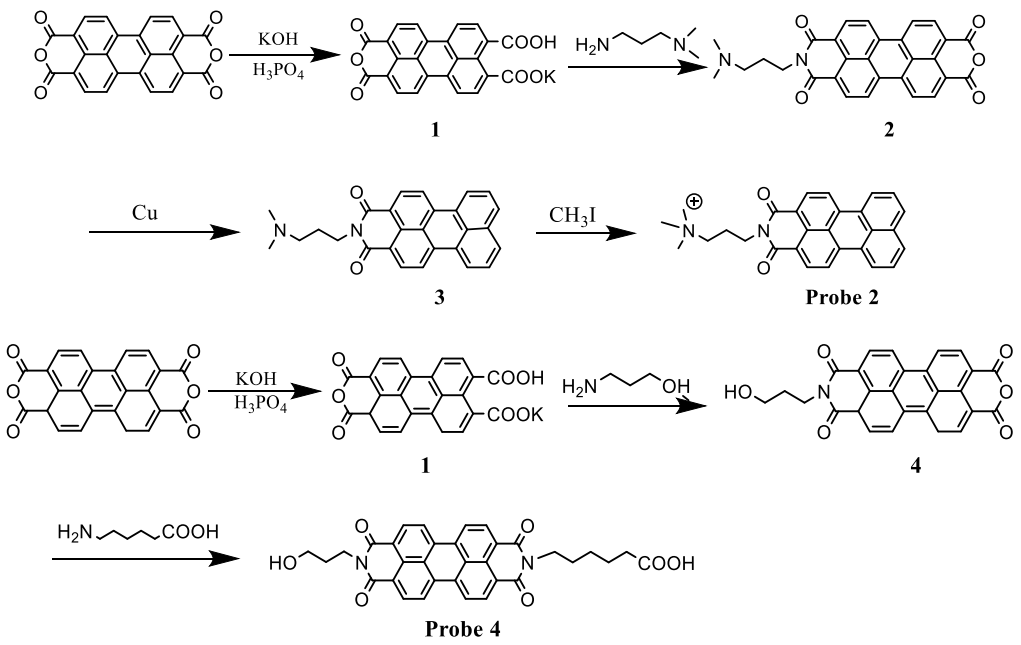

Fig. S1. The synthetic routes for Probe 2 and Probe 4.

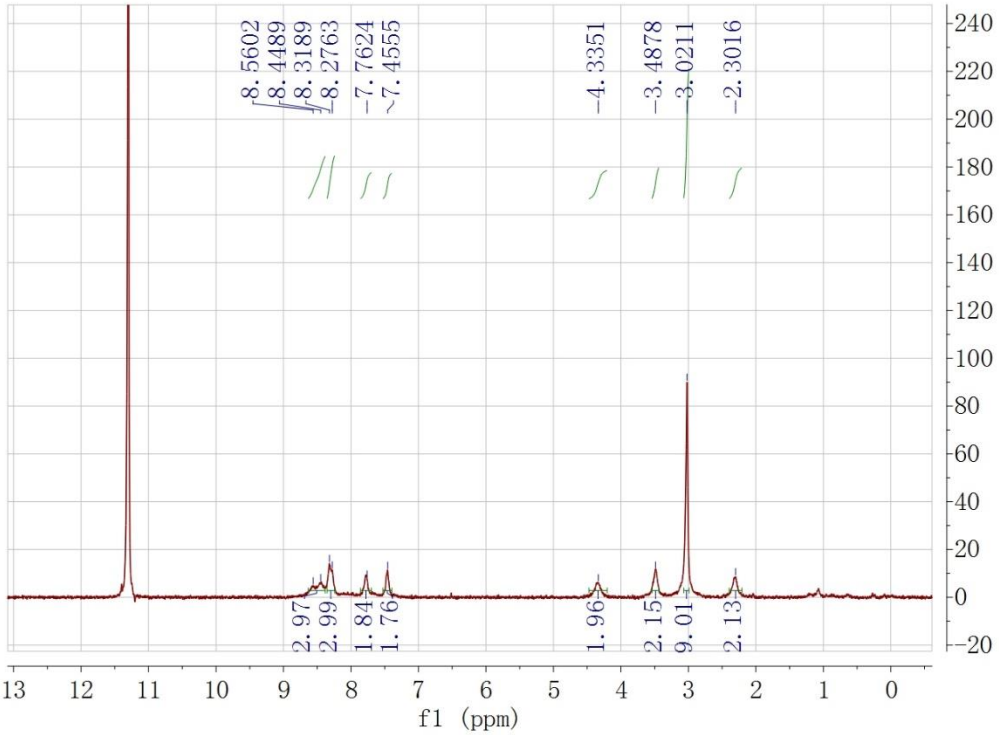

Fig. S2. ^{1}H NMR of Probe 2.

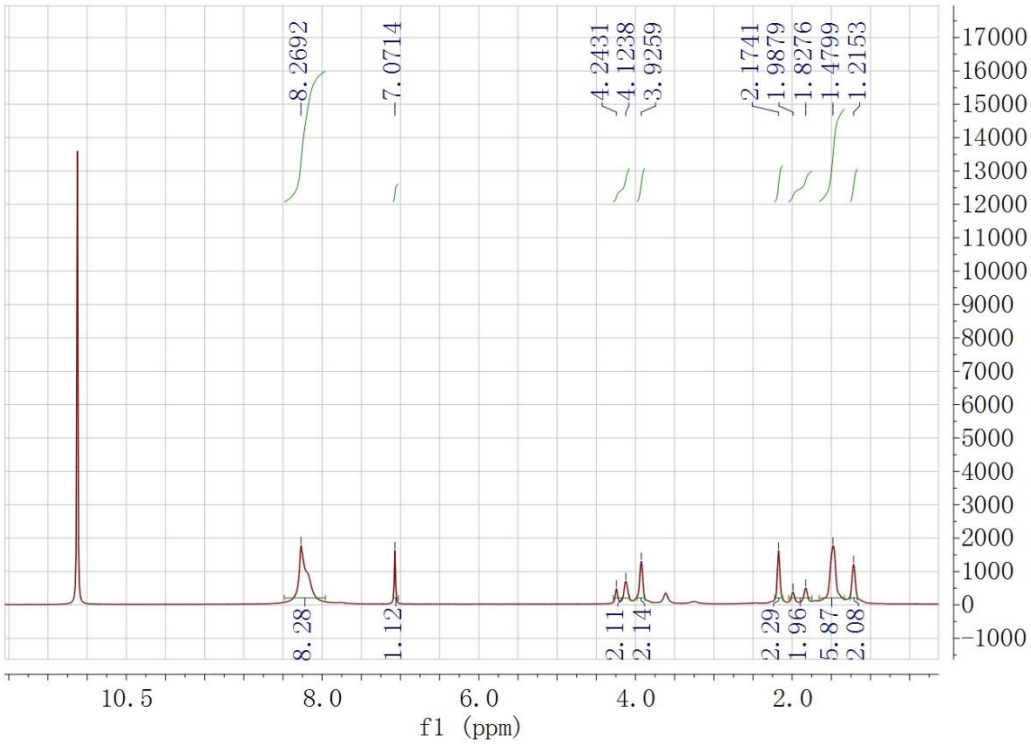

Fig. S3. ^{1}H NMR of Probe 4.

Table S1. LDA data for the discrimination of surfactants.

	20 mM		**10 mM**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**
CTAB	-31.48532	1.24763	-31.30503	10.55773
	-28.9016	3.45186	-31.57726	11.33069
	-32.18633	1.52518	-31.93007	7.50043
	-30.11394	3.43722	-31.96094	10.06688
	-30.12112	0.58024	-32.07319	7.5571
	-30.95573	4.99127	-31.87894	10.31291
SDS	111.74399	-3.30119	135.86123	-0.06282
	113.01914	-3.58808	133.85231	-1.1341
	110.42551	-1.06808	138.54591	-3.34429
	110.7114	-2.7588	132.77375	-2.78775
	114.74032	-1.65996	133.28009	-2.36906

	113.83278	-3.37952	136.17325	-3.1518
Triton X-100	-28.74102	-27.84534	-43.21983	-16.45541
	-28.58347	-27.95542	-43.22675	-16.51893
	-28.79174	-27.73725	-43.19626	-16.32766
	-28.89471	-27.82518	-43.20041	-16.51003
	-28.75465	-27.83527	-43.21547	-16.53051
	-29.05829	-27.55559	-43.22295	-16.59119
Tween-20	-18.48819	31.62202	-22.95483	15.52216
	-18.40302	32.40364	-22.67402	15.9257
	-18.73485	32.28094	-22.69277	15.80026
	-18.7664	34.53052	-23.44966	13.96437
	-17.45656	32.74928	-22.82508	15.01242
	-17.21743	32.27319	-22.74226	15.24299
Tween-80	-35.37282	-4.4865	-37.1454	-5.85015
	-34.69704	-4.49344	-36.9562	-5.74801
	-35.15572	-4.71789	-36.8852	-5.74929
	-34.72216	-5.28915	-37.4005	-6.62413
	-34.54389	-4.9063	-37.42914	-6.63925
	-34.32713	-4.69001	-37.32439	-6.39924

	1 mM		**0.5 mM**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**
CTAB	19.6495	0.96303	39.22931	-2.93253
	22.24078	1.42895	41.56526	-1.93078
	23.3498	1.25648	39.43084	-2.19926
	20.30619	0.2367	41.40187	-2.85156
	23.96941	0.53881	36.95558	-1.69622
	24.93029	1.25869	42.47401	-2.90497
SDS	-0.73476	-12.24197	-15.02223	-5.22659
	-1.8583	-12.07254	-16.10874	-5.76411
	-2.02223	-11.6807	-16.3955	-6.01103
	-2.33362	-11.49291	-16.63094	-6.67525
	-2.70709	-11.47444	-17.00978	-7.29708
	-2.85596	-11.72174	-17.23188	-7.57628
Triton X-100	-9.41936	-4.40925	-15.51192	-2.3512
	-9.21375	-5.65236	-15.34898	-2.08047
	-9.31227	-5.33401	-15.55566	-2.71361
	-9.09583	-6.20258	-15.53243	-2.13724

	-9.06636	-6.36012	-15.47769	-2.25243
	-9.25366	-5.20331	-15.49259	-2.11421
Tween-20	-2.22663	7.79379	0.66792	3.70456
	-1.98696	9.22954	0.68907	4.07803
	-2.05527	9.1148	0.30715	4.84659
	-1.90157	5.58302	0.25165	7.96707
	-2.25181	5.93911	0.28921	7.36748
	-2.36543	6.13374	0.22785	7.16241
Tween-80	-9.11776	9.71944	-8.90017	4.72965
	-8.81123	7.64008	-9.33753	4.5508
	-8.7849	7.41842	-9.06895	5.08055
	-9.00347	9.44059	-8.24822	6.14803
	-9.04184	9.86966	-8.21982	5.46406
	-9.02592	10.28104	-8.39665	5.6156

Table S2. LDA data for the discrimination of alcohols.

	40%		**20%**		**10%**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**	**Factor 1**	**Factor 2**
Glycerin	-41.932	-4.855	-28.12893	2.57458	-15.30084	-4.08551
	-42.072	-4.577	-27.99251	2.52225	-14.14666	-4.37926
	-42.164	-4.392	-27.44946	2.11053	-15.45775	-4.64506
	-42.048	-4.742	-27.35857	1.88532	-15.81786	-3.86923
	-41.785	-4.52	-28.2619	2.35371	-15.29815	-4.04676
	-42.224	-4.485	-27.77514	1.72896	-14.28234	-3.55918
Ethylene glycol	-31.78	0.999	-17.67421	-1.02504	-8.14719	-1.04566
	-32.614	2.021	-16.97568	-0.80234	-8.56904	-1.25377
	-33.056	2.408	-17.94975	-1.65704	-8.33587	0.06416
	-32.99	2.514	-16.35043	-1.88073	-9.85252	-0.07238
	-33.415	2.043	-17.50507	-1.31603	-8.91472	-1.35384
	-33.085	2.001	-17.43965	-1.86759	-9.38565	0.79765
Isopropanol	46.725	-5.935	23.29597	0.44624	7.01274	-4.38721

	45.793	-6.684	26.00403	-0.11515	10.4157	-4.92636
	43.799	-9.304	25.03517	-4.13102	6.82086	-5.04171
	45.121	-8.763	24.57012	-1.48885	9.41816	-4.71467
	45.055	-6.349	24.47795	-2.07805	5.31838	-3.18409
	44.719	-7.705	23.06997	1.2205	10.13718	-1.52373
Methanol	-22.653	3.179	-22.97898	6.17584	-15.99899	5.29776
	-24.91	4.228	-21.26181	6.65625	-15.08253	7.11728
	-26.73	3.353	-22.84753	5.63583	-16.7751	5.31758
	-23.775	1.888	-22.84181	7.03489	-16.07394	6.06813
	-23.877	1.681	-22.85078	4.92817	-16.5055	4.11414
	-24.042	1.046	-22.85346	6.41724	-15.13219	5.10182
Ethanol	8.287	7.025	-0.49977	-4.30826	4.24166	-1.07993
	6.566	6.811	-1.46003	-6.08594	3.28004	0.21642
	5.168	4.224	-0.59616	-4.97586	4.17508	-1.54376
	8.023	4.97	-3.25808	-5.28597	3.31569	-1.04035
	7.959	4.49	-0.03754	-5.70242	3.81457	-2.69275
	8.765	4.733	-2.55862	-6.37019	3.13143	-1.23867
Propylene glycol	-9.667	-3.047	2.19617	-4.73299	14.26201	0.34942
	-12.479	-1.03	3.66223	-4.87255	13.68229	0.01993
	-13.198	-1.714	3.70081	-5.78908	14.41821	-0.06467
	-12.788	-1.588	4.73234	-5.93772	13.28279	1.01609
	-12.484	-0.689	3.91293	-6.1324	14.691	-0.72153
	-11.761	-1.077	4.88008	-6.60151	15.18296	0.20845
Tert-butanol	59.007	3.859	40.33157	5.66437	14.70763	2.84792
	59.189	5.199	43.33217	5.81353	14.43891	6.36069
	58.577	1.874	42.072	6.26588	12.86584	3.43049
	59.01	3.955	39.73619	4.60525	13.85892	3.54099
	58.137	3.664	39.24362	3.32002	13.68336	3.18325
	57.629	3.292	40.65254	5.79736	12.92145	5.41792

Table S3. LDA data for the discrimination of nine brands of commercial makeup removers (1-9) and common liquid goods (10-21).

	Factor 1	Factor 2		Factor 1	Factor 2
1	-14.30902	42.39193	**12**	-8.17729	-8.70368
	-14.9273	40.90953		-7.96452	-8.9346
	-14.31264	41.32041		-7.69833	-8.25683
	-14.66724	40.72283		-8.1499	-8.98039
	-14.16157	40.53745		-8.27082	-8.48684
	-15.2074	39.71205		-8.17367	-9.17418
2	5.38446	18.5846	**13**	-19.0293	-18.38052
	5.98473	18.44377		-19.41856	-18.32668
	4.31702	16.39685		-19.16997	-18.39529
	4.60351	18.411		-19.09423	-18.34069
	4.30968	16.8516		-19.18216	-18.40341
	4.33243	17.56129		-19.37718	-18.27613
3	136.79879	-35.16523	**14**	-11.44367	-10.40085
	136.00099	-35.10596		-12.03548	-11.38446
	130.51837	-34.22401		-11.56125	-10.2336
	133.02318	-32.3344		-11.94944	-11.694
	129.4244	-33.50917		-11.59907	-10.39638
	129.29262	-32.38505		-12.17743	-12.41465
4	0.22913	27.52343	**15**	-19.32127	-15.97274
	-0.42856	25.19206		-20.24242	-15.87092
	-0.96846	26.15559		-20.28796	-16.04119
	-0.41229	27.98859		-19.52587	-15.89483
	-1.69618	23.82801		-21.0053	-15.94204
	-0.93797	26.66636		-20.66699	-15.6862
5	-21.98823	11.40702	**16**	-21.00586	-17.00342
	-21.4989	11.24325		-20.86043	-16.90046
	-21.60231	12.21848		-21.35004	-16.90373
	-21.66981	11.1724		-20.79829	-16.92873
	-21.72077	12.05589		-21.06381	-16.94315
	-21.83324	10.76439		-20.80707	-16.90496
6	29.30031	66.96019	**17**	-20.34277	-15.96632
	27.31523	59.79203		-19.72317	-16.44333
	29.2044	67.36547		-20.11816	-15.89461
	28.03668	63.19335		-20.09855	-16.4368

	27.25821	65.06487		-20.10927	-15.84148
	28.77945	62.84179		-20.36973	-16.50923
7	59.24193	1.44869	**18**	-22.2323	-17.36188
	57.95345	3.9291		-20.83171	-17.85766
	60.52383	1.31988		-21.86509	-17.4847
	54.4684	2.92047		-21.08036	-17.85086
	60.37225	0.83121		-21.80642	-17.6272
	59.39569	2.03685		-21.41552	-17.72298
8	9.58461	47.01372	**19**	-21.43016	-14.56685
	9.2666	47.04732		-21.30144	-14.55239
	9.56883	46.79314		-21.40184	-14.68365
	7.49168	42.74172		-21.35438	-14.25368
	8.55597	45.23342		-21.33524	-14.23696
	8.28298	43.43859		-21.43468	-14.61794
9	-2.28591	-4.53816	**20**	-12.14648	-8.71407
	-2.89204	-3.48177		-12.17995	-8.37553
	-2.99507	-4.37595		-12.18701	-9.08584
	-4.13672	-3.45031		-11.89329	-8.45306
	-1.66947	-4.62642		-12.09081	-7.47025
	-3.57274	-3.87243		-12.47582	-8.37634
10	-10.87742	-13.6552	**21**	-15.90399	-18.42469
	-12.01716	-14.79519		-15.79786	-18.24951
	-11.14561	-14.24223		-16.06023	-18.31443
	-11.92433	-14.84376		-16.21588	-17.94584
	-11.11541	-14.55104		-16.24605	-18.22226
	-11.67412	-14.87524		-16.93417	-17.75877
11	-9.74441	-9.67023			
	-10.00783	-10.08103			
	-10.49521	-9.51835			
	-9.51775	-9.71651			
	-10.66129	-9.73772			
	-9.9555	-9.8006			

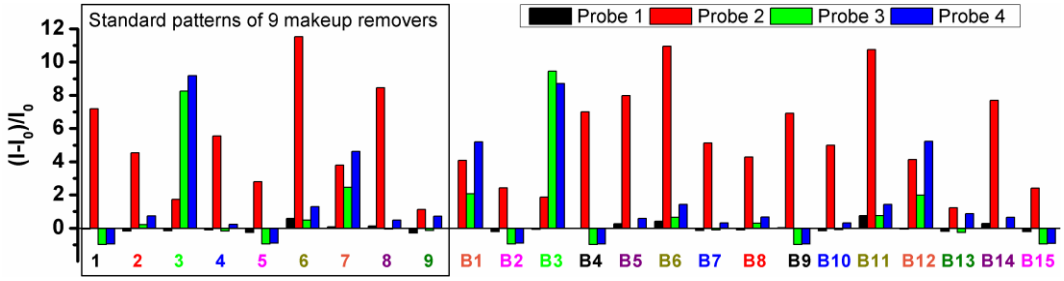

Fig. S4. Response of the four-channel sensor array against the 9 known makeup removers (1-9) and the 15 blind makeup remover samples (B1-B15). Same color represents the same brand of makeup remover.

Table S4. Identification of the 15 blind makeup remover samples.

Sample	Identification	Verification	Y/N
B1	#7	#7	Y
B2	#5	#5	Y
B3	#3	#3	Y
B4	#1	#1	Y
B5	#8	#8	Y
B6	#6	#6	Y
B7	#4	#4	Y
B8	#2	#2	Y
B9	#1	#1	Y
B10	#4	#4	Y
B11	#6	#6	Y
B12	#7	#7	Y
B13	#9	#9	Y
B14	#8	#8	Y
B15	#5	#5	Y
100% identified, 0% error rate			