Electronic Supplementary Information

Sensitive discrimination of glycoproteins and cell differentiation with array sensing platform exploiting pyrene-derived amphiphile/surfactant assemblies

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Experimental section

Materials and reagents

Ovalbumin (Ob, A5503), conalbumin (Cona, C0880), immunoglobulin G (IgG, I4506), horseradish peroxidase (HRP, V900503), transferrin (Trf, T3309), glucose oxidase (Glu, G6125), hyaluronidase (Hya, H3506) and fibrinogen (Fib, F3879) are obtained from Sigma-Aldrich (St. Louis, USA). Normal and differentiated gastric cancer cells of GES-1, Mgc803, and AGS are obtained from BeiNa Culture Collection (Beijing, China). 1-Pyrenebutyric acid, N, N-Diisopropylethylamine (DIPEA), triethylamine (TEA), sodium dodecyl sulfate (SDS) and N-(2-hydroxyethyl) piperazine-N′-ethanesulfonic acid (HEPES) are purchased from Aladdin Reagent (Shanghai, China). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC❿HCl), HCl, sodium carbonate (Na_2CO_3), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), trifluoroacetic acid (TFA), glacial acetic acid (HAc), dichloromethane (CH_2Cl_2), methanol (MeOH), decyl trimethyl ammonium bromide (DTAB) and Triton X-100 (TX100) are obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 1-Hydroxybenzotriazole (HOBt) and N, N-Dimethylformamide (DMF) are purchased from J&K Scientific Ltd. (Beijing, China). Tert-Butyl (3-(2-(2-(3-aminopropoxy) ethoxy) ethoxy) propyl) carbamate (TBC) is obtained from Bide Pharmatech Ltd. (Shanghai, China). 18.2 MΩ Milli-Q water is applied throughout the whole experiment.

Characterization

Fluorescence spectra are measured by using an F-7000 spectrofluorometer

(Hitachi, Japan). Zeta potential and size distribution are obtained by a Zetasizer Nano S90 (Malvein, UK). Fluorescence intensities of phenylboronic acid-functionalized pyrene amphiphilie in three surfactants before/after the addition of glycoproteins are recorded on a Synergy H1 microplate reader (Biotek, USA). The ^{1}H and ^{13}C NMR spectra are acquired on a Bruker Avance 400 MHz NMR spectrometer (Bruker, Switzerland). The high resolution mass spectra are recorded on a 6540 UHD Accurate-Mass Q-TOF LC-MS system (Agilent Technologies, USA). Transmission electron microscopy (TEM) is obtained by a JEM 2100F transmission electron microscope (JEOL, Japan).

Discrimination of glycoproteins

Three sensing units are built based on the ensembles of three types of surfactant (DTAB, TX100, SDS) and phenylboronic acid-functionalized pyrene amphiphilie (**P2**). DTAB (4 mmol L^{-1}), TX100 (0.05 mmol L^{-1}) and SDS (0.5 mmol L^{-1}) are prepared in 10 mmol L^{-1} HEPES buffer solution (pH=7.4). 70 μL of stock solution of **P2** is added into 14 mL of each of the surfactant solution, followed by sonication for 30 min. 14 μL of glycoprotein is added into 1386 μL of above sensing units, and the mixture is processed with mildly shaking for 30 min at 37 ^{o}C. Subsequently, the fluorescence intensity at 377 nm/477 nm (λ_{ex}=340 nm) are recorded by a microplate reader. The raw data are processed by LDA for pattern recognition of eight glycoproteins.

Applications

Discrimination of glycoproteins in human urine

Healthy human morning urine is collected and centrifugation at 12000 rpm (14800 g) for 10 min to eliminate the insoluble impurity. The processes for glycoprotein discrimination in urine are consistent with that in HEPES buffer solution, except replacing HEPES buffer solution with 50-fold diluted urine.

Discrimination of normal and differentiated cells

GES-1 (normal gastric cells), Mgc803 (low differentiated gastric cancer cells), and AGS (high differentiated gastric cancer cells) are cultured in DMEM culture medium containing 10% fetal bovine serum and 1% antibiotics. The cells are washed with PBS buffer solution for three times and dispersed in 20 mM HEPES buffer solution (pH=7.4, 125 mM KCl, 0.5 mM $MgCl_2$, 0.5 mM $CaCl_2$, 20 mM NaCl, 5 mM glucose) for further using. 10000 cells are incubated with three sensing solutions of DTAB/**P2**, TX100/**P2**, and SDS/**P2** in 96-well plate with a final volume of 200 μL for 30 min at 37 ^{o}C. Each type of cell is repeated six times. The fluorescence intensity at 377 nm/477 nm (λ_{ex}=340 nm) are recorded as raw data, and then are subjected to LDA for realizing the different response patterns of array sensing platform to three cell lines.

Supporting figure

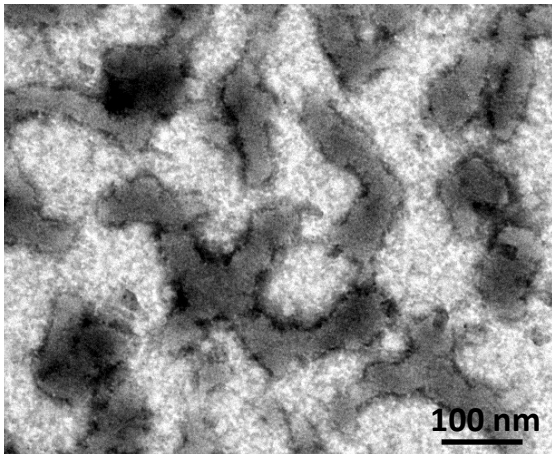


Fig. S1 TEM image of DTAB/**P2** in presence of 6.5 μM Trf.

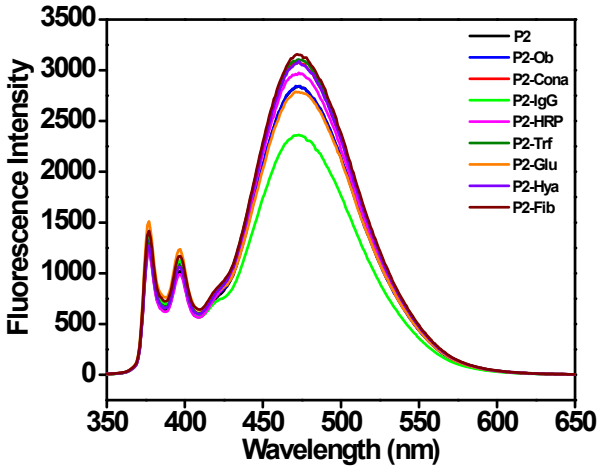


Fig. S2 Fluorescence response of pyrene-dervied amphiphilie (50 μM) to 1000 nM glycoproteins in HEPES buffer solution (pH=7.4).

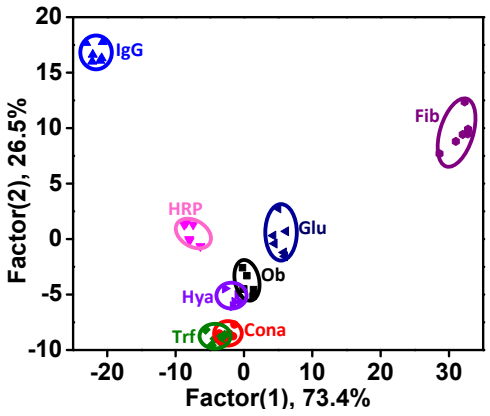


Fig. S3 LDA canonical score plots for the response of the pyrene-derived amphiphilie/surfactant assemblies to 8 kinds of glycoproteins at 30 nM.

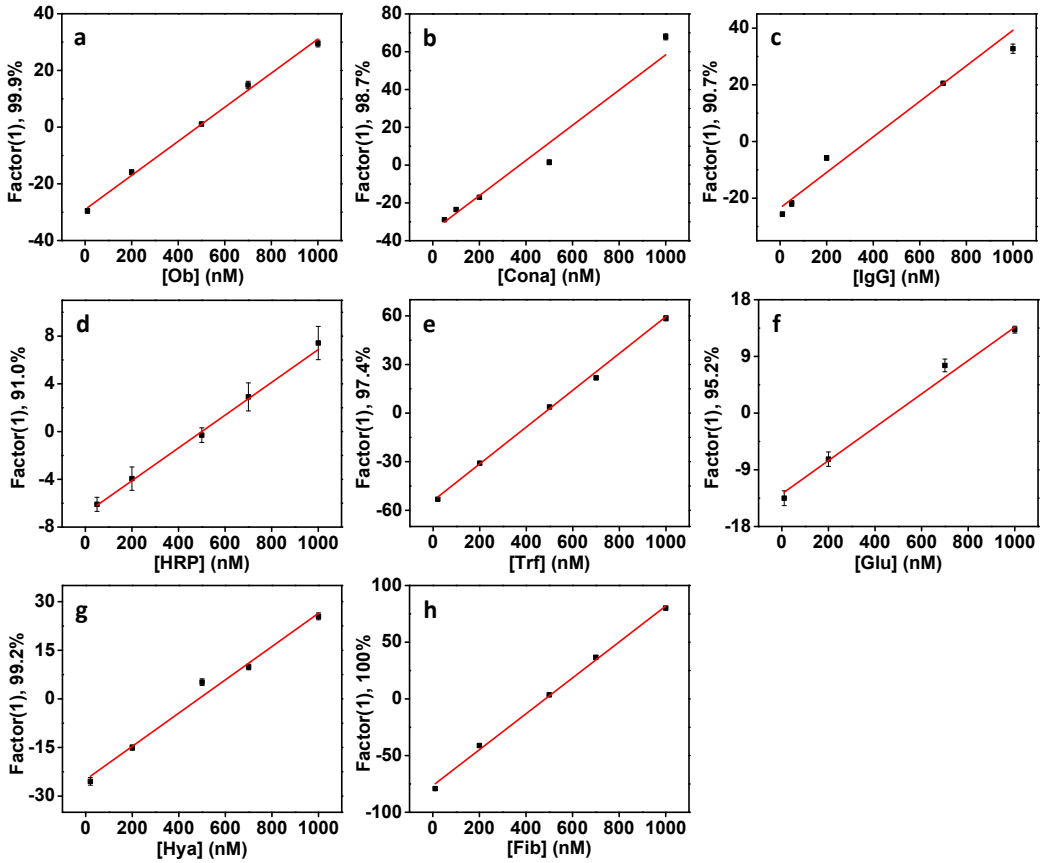


Fig. S4 Quantitative analysis of glycoproteins at various concentration levels by using the pyrene-derived amphiphilie/surfactant assembly system, linear response of factor (1) vs the concentrations of (a) Ob, (b) Cona, (c) IgG, (d) HRP, (e) Trf, (f) Glu, (g) Hya, (h) Fib.

Supporting table

Table S1 Basic properties of target glycoproteins.

Glycoprotein	Carbohydrate content	pI
ovalbumin (Ob)	3.2%-5.0%	4.7
conalbumin (Cona)	2.2%	6.0
immuneglobulin G (IgG)	2.5%	8.0
horseradish peroxidase (HRP)	18%-22%	3.0~9.0
transferrin (Trf)	6%	9.6
glucose oxidase (Glu)	16%	4.2
hyaluronidase (Hya)	5%	5.0
fibrinogen (Fib)	3.5%	5.5

Table S2 Training matrix of pyrene-derived amphiphilie/surfactant assemblies against 8 glycoproteins (1000 nM)

sample	DTAB/**P2**	TX100/**P2**	SDS/**P2**	Identification	Verification
1	124.869	1.051	1.911	Ob	Ob
2	99.886	1.056	1.922	Ob	Ob
3	137.898	1.052	1.915	Ob	Ob
4	99.784	1.042	1.881	Ob	Ob
5	128.591	1.039	1.913	Ob	Ob
6	92.766	1.042	1.912	Ob	Ob
7	2.176	0.956	1.840	Cona	Cona
8	2.265	0.967	1.856	Cona	Cona
9	2.278	0.962	1.809	Cona	Cona
10	2.232	0.969	1.837	Cona	Cona
11	2.302	0.982	1.832	Cona	Cona
12	2.372	0.971	1.854	Cona	Cona
13	1.240	19.943	1.595	IgG	IgG
14	1.226	18.344	1.593	IgG	IgG
15	1.232	17.229	1.575	IgG	IgG
16	1.253	17.031	1.594	IgG	IgG
17	1.250	16.934	1.595	IgG	IgG
18	1.283	21.414	1.592	IgG	IgG
19	1.017	1.008	1.179	HRP	HRP
20	0.998	0.993	1.158	HRP	HRP
21	1.008	0.989	1.180	HRP	HRP
22	1.013	0.976	1.172	HRP	HRP
23	1.037	0.994	1.176	HRP	HRP
24	1.049	0.987	1.178	HRP	HRP
25	3.479	0.986	2.790	Trf	Trf
26	3.625	0.993	2.758	Trf	Trf
27	3.496	0.989	2.785	Trf	Trf

28	3.487	0.989	2.764	Trf	Trf
29	3.609	0.993	2.764	Trf	Trf
30	3.524	0.991	2.828	Trf	Trf
31	161.138	1.257	1.298	Glu	Glu
32	187.405	1.280	1.324	Glu	Glu
33	198.902	1.248	1.327	Glu	Glu
34	202.520	1.252	1.312	Glu	Glu
35	185.237	1.256	1.296	Glu	Glu
36	180.375	1.269	1.318	Glu	Glu
37	64.257	0.952	1.292	Hya	Hya
38	47.175	0.930	1.319	Hya	Hya
39	47.493	0.947	1.309	Hya	Hya
40	42.159	0.929	1.305	Hya	Hya
41	49.171	0.945	1.311	Hya	Hya
42	66.673	0.942	1.310	Hya	Hya
43	144.223	1.030	3.715	Fib	Fib
44	120.054	1.026	3.770	Fib	Fib
45	103.820	1.022	3.802	Fib	Fib
46	142.042	1.034	3.832	Fib	Fib
47	124.443	1.025	3.864	Fib	Fib
48	117.256	1.013	3.750	Fib	Fib

Table S3 Training matrix of pyrene-derived amphiphilie/surfactant assemblies against 8 glycoproteins (500 nM)

sample	DTAB/**P2**	TX100/**P2**	SDS/**P2**	Identification	Verification
1	7.259	0.999	1.592	Ob	Ob
2	7.206	0.993	1.611	Ob	Ob
3	7.331	0.993	1.600	Ob	Ob
4	7.042	1.001	1.646	Ob	Ob
5	6.988	1.013	1.637	Ob	Ob
6	6.869	1.011	1.624	Ob	Ob
7	1.089	0.933	1.460	Cona	Cona
8	1.117	0.920	1.488	Cona	Cona
9	1.123	0.919	1.506	Cona	Cona
10	1.145	0.941	1.478	Cona	Cona
11	1.136	0.924	1.514	Cona	Cona
12	1.144	0.949	1.500	Cona	Cona
13	0.985	5.290	1.257	IgG	IgG
14	0.996	5.185	1.281	IgG	IgG
15	0.985	5.194	1.285	IgG	IgG
16	0.984	5.358	1.275	IgG	IgG
17	0.974	5.309	1.293	IgG	IgG
18	0.984	5.449	1.307	IgG	IgG
19	1.033	0.990	1.103	HRP	HRP
20	1.035	1.004	1.112	HRP	HRP
21	1.034	0.995	1.109	HRP	HRP
22	1.043	1.010	1.125	HRP	HRP
23	1.060	0.999	1.126	HRP	HRP
24	1.052	1.026	1.110	HRP	HRP
25	3.811	0.951	2.158	Trf	Trf
26	4.059	0.936	2.152	Trf	Trf

27	3.936	0.933	2.164	Trf	Trf
28	4.063	0.947	2.150	Trf	Trf
29	4.067	0.923	2.147	Trf	Trf
30	4.045	0.946	2.157	Trf	Trf
31	12.269	1.089	1.151	Glu	Glu
32	14.222	1.107	1.176	Glu	Glu
33	13.837	1.097	1.156	Glu	Glu
34	12.966	1.100	1.166	Glu	Glu
35	13.720	1.117	1.177	Glu	Glu
36	13.623	1.111	1.169	Glu	Glu
37	5.205	0.931	1.208	Hya	Hya
38	5.077	0.922	1.244	Hya	Hya
39	5.108	0.942	1.212	Hya	Hya
40	5.203	0.949	1.212	Hya	Hya
41	5.315	0.952	1.241	Hya	Hya
42	5.278	0.959	1.219	Hya	Hya
43	22.964	0.966	2.518	Fib	Fib
44	25.054	0.964	2.510	Fib	Fib
45	24.778	0.972	2.523	Fib	Fib
46	28.255	0.951	2.540	Fib	Fib
47	27.611	0.956	2.523	Fib	Fib
48	27.447	0.987	2.510	Fib	Fib

Table S4 Training matrix of pyrene- derived amphiphilie/surfactant assemblies against 8 glycoproteins (50 nM)

sample	DTAB/**P2**	TX100/**P2**	SDS/**P2**	Identification	Verification
1	1.203	1.034	1.085	Ob	Ob
2	1.261	1.039	1.044	Ob	Ob
3	1.256	1.044	1.066	Ob	Ob
4	1.256	1.039	1.043	Ob	Ob
5	1.264	1.068	1.061	Ob	Ob
6	1.228	1.062	1.075	Ob	Ob
7	0.917	1.015	1.060	Cona	Cona
8	0.926	1.018	1.042	Cona	Cona
9	0.947	1.026	1.056	Cona	Cona
10	0.933	1.031	1.015	Cona	Cona
11	0.971	1.019	1.032	Cona	Cona
12	0.973	1.030	1.012	Cona	Cona
13	1.041	1.486	1.041	IgG	IgG
14	1.015	1.469	1.024	IgG	IgG
15	1.046	1.456	1.043	IgG	IgG
16	1.024	1.473	1.045	IgG	IgG
17	0.993	1.491	1.027	IgG	IgG
18	1.020	1.456	1.046	IgG	IgG
19	0.986	1.068	1.057	HRP	HRP
20	0.997	1.076	1.068	HRP	HRP
21	1.006	1.070	1.044	HRP	HRP
22	0.998	1.068	1.085	HRP	HRP
23	1.002	1.070	1.046	HRP	HRP
24	1.001	1.059	1.023	HRP	HRP
25	1.394	1.043	1.072	Trf	Trf
26	1.421	1.021	1.073	Trf	Trf
27	1.431	1.031	1.096	Trf	Trf

28	1.444	1.024	1.079	Trf	Trf
29	1.454	1.032	1.113	Trf	Trf
30	1.453	1.021	1.079	Trf	Trf
31	1.088	1.033	1.032	Glu	Glu
32	1.103	1.040	1.040	Glu	Glu
33	1.089	1.063	1.038	Glu	Glu
34	1.098	1.045	1.049	Glu	Glu
35	1.136	1.026	1.029	Glu	Glu
36	1.125	1.015	1.030	Glu	Glu
37	1.018	0.991	1.033	Hya	Hya
38	1.026	1.021	1.041	Hya	Hya
39	1.026	1.039	1.015	Hya	Hya
40	1.022	1.027	1.029	Hya	Hya
41	1.049	1.014	1.042	Hya	Hya
42	1.000	0.985	1.035	Hya	Hya
43	1.473	0.954	1.112	Fib	Fib
44	1.482	0.961	1.106	Fib	Fib
45	1.495	0.977	1.110	Fib	Fib
46	1.549	0.977	1.138	Fib	Fib
47	1.569	0.966	1.127	Fib	Fib
48	1.516	0.981	1.109	Fib	Fib

Table S5 Training matrix of pyrene-derived amphiphilie/surfactant assemblies against 28 unknown glycoproteins at 1000 nM

sample	DTAB/**P2**	TX100/**P2**	SDS/**P2**	Identification	Verification
1	17.154	1.061	1.518	Ob	Ob
2	17.030	1.069	1.527	Ob	Ob
3	17.256	1.075	1.541	Ob	Ob
4	14.542	1.079	1.534	Ob	Ob
5	7.624	1.010	1.536	Cona	Cona
6	7.282	1.016	1.524	Cona	Cona
7	8.012	1.032	1.496	Cona	Cona
8	1.454	40.812	1.323	IgG	IgG
9	1.498	37.011	1.333	IgG	IgG
10	1.470	37.012	1.340	IgG	IgG
11	1.486	36.226	1.340	IgG	IgG
12	1.082	1.021	1.112	HRP	HRP
13	1.075	1.014	1.134	HRP	HRP
14	1.050	1.027	1.104	HRP	HRP
15	1.078	1.028	1.108	HRP	HRP
16	5.918	1.047	1.885	Trf	Trf
17	6.501	1.046	1.929	Trf	Trf
18	6.306	1.027	1.877	Trf	Trf
19	11.971	1.260	1.255	Glu	Glu
20	13.378	1.259	1.205	Glu	Glu
21	11.966	1.267	1.277	Glu	Glu
22	11.075	0.959	1.301	Hya	Hya
23	10.292	0.969	1.308	Hya	Hya
24	10.997	0.971	1.282	Hya	Hya
25	11.064	0.957	1.314	Hya	Hya
26	14.430	1.047	2.730	Fib	Fib
27	16.602	1.077	2.732	Fib	Fib
28	17.770	1.047	2.725	Fib	Fib

Table S6 Training matrix of pyrene-derived amphiphilie/surfactant assemblies against 28 unknown glycoproteins at 500 nM

sample	DTAB/**P2**	TX100/**P2**	SDS/**P2**	Identification	Verification
1	63.736	1.023	1.369	Ob	Ob
2	61.763	1.043	1.384	Ob	Ob
3	65.329	1.006	1.440	Ob	Ob
4	63.279	1.028	1.390	Ob	Ob
5	1.388	0.973	1.411	Cona	Cona
6	1.316	0.990	1.422	Cona	Cona
7	1.426	1.003	1.377	Cona	Cona
8	1.366	15.256	1.296	IgG	IgG
9	1.438	16.422	1.295	IgG	IgG
10	1.560	20.809	1.285	IgG	IgG
11	1.376	26.660	1.246	IgG	IgG
12	0.931	1.088	1.138	HRP	HRP
13	0.912	1.073	1.066	HRP	HRP
14	0.950	1.079	1.100	HRP	HRP
15	0.893	1.051	1.140	HRP	HRP
16	2.582	1.000	1.545	Trf	Trf
17	3.018	1.076	1.650	Trf	Trf
18	2.391	1.076	1.660	Trf	Trf
19	61.303	1.159	1.192	Glu	Glu
20	55.971	1.102	1.217	Glu	Glu
21	62.875	1.178	1.198	Glu	Glu
22	34.490	1.020	1.168	Hya	Hya
23	36.885	1.006	1.112	Hya	Hya
24	37.935	1.007	1.125	Hya	Hya
25	32.475	1.005	1.135	Hya	Hya
26	61.651	1.066	2.099	Fib	Fib
27	68.705	1.035	2.206	Fib	Fib
28	60.385	1.091	2.269	Fib	Fib

Table S7 Training matrix of pyrene-derived amphiphilie/surfactant assemblies against 28 unknown glycoproteins at 50 nM

sample	DTAB/**P2**	TX100/**P2**	SDS/**P2**	Identification	Verification
1	5.770	0.981	1.045	Ob	Ob
2	5.573	0.970	1.028	Ob	Ob
3	5.964	0.991	1.036	Ob	Ob
4	5.961	0.974	1.050	Ob	Ob
5	1.118	0.988	1.008	Cona	Cona
6	1.126	0.987	1.017	Cona	Cona
7	1.124	0.987	1.029	Cona	Cona
8	1.141	1.197	0.998	IgG	IgG
9	1.112	1.216	0.995	IgG	IgG
10	1.160	1.224	0.985	IgG	IgG
11	1.120	1.251	1.000	IgG	IgG
12	1.024	1.051	1.023	HRP	HRP
13	1.042	1.052	1.017	HRP	HRP
14	1.037	1.043	1.019	HRP	HRP
15	1.069	1.043	1.044	HRP	HRP
16	1.880	0.994	1.123	Trf	Trf
17	1.882	1.045	1.106	Trf	Trf
18	1.973	0.994	1.095	Trf	Trf
19	1.169	1.024	1.015	Glu	Glu
20	1.156	1.003	1.051	Glu	Glu
21	1.148	1.025	1.060	Glu	Glu
22	4.048	1.023	1.011	Hya	Hya
23	3.995	1.007	1.024	Hya	Hya
24	4.117	1.011	1.056	Hya	Hya
25	4.183	0.980	1.063	Hya	Hya
26	5.062	1.039	1.134	Fib	Fib
27	5.276	1.065	1.145	Fib	Fib
28	5.400	1.023	1.133	Fib	Fib

Table S8 Training matrix of pyrene- derived amphiphilie/surfactant assemblies against 8 glycoproteins at 500 nM in human urine

sample	DTAB/**P2**	TX100/**P2**	SDS/**P2**	Identification	Verification
1	1.236	0.969	1.837	Ob	Ob
2	1.812	0.979	1.835	Ob	Ob
3	2.243	0.976	1.854	Ob	Ob
4	2.135	0.989	1.818	Ob	Ob
5	2.068	0.982	1.839	Ob	Ob
6	1.262	1.008	1.855	Ob	Ob
7	0.958	0.874	1.600	Cona	Cona
8	0.769	0.889	1.663	Cona	Cona
9	0.990	0.901	1.615	Cona	Cona
10	1.019	0.878	1.631	Cona	Cona
11	1.054	0.895	1.657	Cona	Cona
12	1.082	0.918	1.638	Cona	Cona
13	0.906	1.322	1.364	IgG	IgG
14	0.902	1.279	1.397	IgG	IgG
15	0.929	1.292	1.380	IgG	IgG
16	0.852	1.313	1.384	IgG	IgG
17	0.827	1.321	1.416	IgG	IgG
18	0.840	1.334	1.421	IgG	IgG
19	0.856	0.905	1.076	HRP	HRP
20	0.883	0.873	1.079	HRP	HRP
21	0.929	0.903	1.066	HRP	HRP
22	0.900	0.901	1.090	HRP	HRP
23	0.911	0.907	1.083	HRP	HRP
24	0.898	0.908	1.097	HRP	HRP
25	0.863	0.922	2.157	Trf	Trf
26	0.863	0.933	2.214	Trf	Trf
27	0.893	0.926	2.188	Trf	Trf

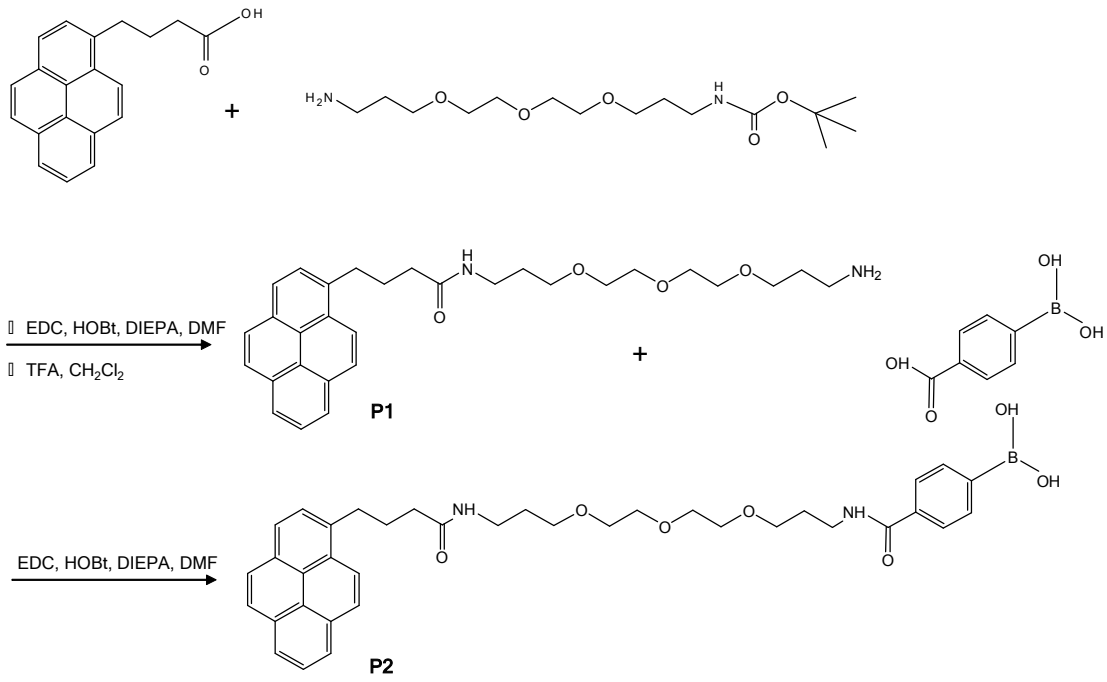
28	0.921	0.946	2.172	Trf	Trf
29	0.907	0.938	2.206	Trf	Trf
30	0.878	0.976	2.175	Trf	Trf
31	1.044	1.103	1.255	Glu	Glu
32	1.091	1.095	1.244	Glu	Glu
33	1.135	1.090	1.245	Glu	Glu
34	1.115	1.097	1.221	Glu	Glu
35	1.133	1.088	1.257	Glu	Glu
36	1.075	1.131	1.269	Glu	Glu
37	0.942	0.916	1.361	Hya	Hya
38	1.003	0.896	1.353	Hya	Hya
39	0.977	0.911	1.388	Hya	Hya
40	1.007	0.922	1.348	Hya	Hya
41	1.008	0.939	1.349	Hya	Hya
42	1.016	0.943	1.349	Hya	Hya
43	3.480	0.969	2.699	Fib	Fib
44	3.394	0.941	2.718	Fib	Fib
45	3.500	0.956	2.748	Fib	Fib
46	3.234	0.953	2.736	Fib	Fib
47	3.130	0.967	2.726	Fib	Fib
48	2.968	0.972	2.718	Fib	Fib

Table S9 Training matrix of pyrene-derived amphiphilie/surfactant assemblies against different differentiation degrees of cells (50000 cells/mL)

sample	DTAB/**P2**	TX100/**P2**	SDS/**P2**	Identification	Verification
1	7.259	0.999	1.592	Ob	Ob
2	7.206	0.993	1.611	Ob	Ob
3	7.331	0.993	1.600	Ob	Ob
4	7.042	1.001	1.646	Ob	Ob
5	6.988	1.013	1.637	Ob	Ob
6	6.869	1.011	1.624	Ob	Ob
7	1.089	0.933	1.460	Cona	Cona
8	1.117	0.920	1.488	Cona	Cona
9	1.123	0.919	1.506	Cona	Cona
10	1.145	0.941	1.478	Cona	Cona
11	1.136	0.924	1.514	Cona	Cona
12	1.144	0.949	1.500	Cona	Cona
13	0.985	5.290	1.257	IgG	IgG
14	0.996	5.185	1.281	IgG	IgG
15	0.985	5.194	1.285	IgG	IgG
16	0.984	5.358	1.275	IgG	IgG
17	0.974	5.309	1.293	IgG	IgG
18	0.984	5.449	1.307	IgG	IgG
19	1.033	0.990	1.103	HRP	HRP
20	1.035	1.004	1.112	HRP	HRP
21	1.034	0.995	1.109	HRP	HRP
22	1.043	1.010	1.125	HRP	HRP
23	1.060	0.999	1.126	HRP	HRP
24	1.052	1.026	1.110	HRP	HRP
25	3.811	0.951	2.158	Trf	Trf
26	4.059	0.936	2.152	Trf	Trf
27	3.936	0.933	2.164	Trf	Trf

28	4.063	0.947	2.150	Trf	Trf
29	4.067	0.923	2.147	Trf	Trf
30	4.045	0.946	2.157	Trf	Trf
31	12.269	1.089	1.151	Glu	Glu
32	14.222	1.107	1.176	Glu	Glu
33	13.837	1.097	1.156	Glu	Glu
34	12.966	1.100	1.166	Glu	Glu
35	13.720	1.117	1.177	Glu	Glu
36	13.623	1.111	1.169	Glu	Glu
37	5.205	0.931	1.208	Hya	Hya
38	5.077	0.922	1.244	Hya	Hya
39	5.108	0.942	1.212	Hya	Hya
40	5.203	0.949	1.212	Hya	Hya
41	5.315	0.952	1.241	Hya	Hya
42	5.278	0.959	1.219	Hya	Hya
43	22.964	0.966	2.518	Fib	Fib
44	25.054	0.964	2.510	Fib	Fib
45	24.778	0.972	2.523	Fib	Fib
46	28.255	0.951	2.540	Fib	Fib
47	27.611	0.956	2.523	Fib	Fib
48	27.447	0.987	2.510	Fib	Fib

Synthesis of pyrene-derived amphiphilie (P2)



Scheme S1 The route for the synthesis of pyrene-derived amphiphilie (**P2**).

Synthesis of product 1 (P1)

1-Pyrenebutyric acid (0.8650 g, 3 mmol), EDC·HCl (0.6901 g, 3.6 mmol) and HOBt (0.4865 g, 3.6 mmol) was dissolved in 25mL dry DMF at ice-bath. DIEPA (1.572 mL, 9 mmol) was dropwise added into above solution, followed by stirred for 1h at 25 ^{o}C. To this solution, TBC (1.0574 g, 3.3 mmol) in 5 mL dry DMF was slowly added and stirred at 0 ^{o}C for another 1 h and at room temperature overnight. 150 mL dry CH_2Cl_2 was added to the reaction system and washed successively by HCl (0.5 mol L^{-1}, 60 mL), Na_2CO_3 (5%, 60 mL) and brine (2 × 60 mL). The organic phase was collected and dried over Na_2SO_4 and the volatiles was evaporated under vacuum. The yellowish product was dissolved in 6 mL dry CH_2Cl_2 followed by the addition of 3 mL TFA and stirred at room temperature for 3h for removing of the Boc protective

group. After the addition of another 40 mL CH_2Cl_2, the solution was treated with saturated Na_2CO_3 solution to adjust the pH to 8-9 and washed with saturated brine (2 × 20 mL). The organic phase are collected and dried with anhydrous Na_2SO_4. After evaporated in vacuo, the crude product was chromatographed on 200-300 mesh silica gel with MeOH/CH_2Cl_2/TEA (1:10:0.5, v/v/v) to afford 0.7697 g (52%) of product 1 (**P1**). ^{1}H NMR (MeOD), δ (ppm) 8.27 (d, 1H), 8.12 (m, 2H), 8.07 (m, 2H), 7.98 (m, 4H), 7.83 (d, 1H), 3.48 (m, 8H), 3.33 (t, 4H), 3.23 (t, 2H), 2.91 (t, 2H), 2.66 (t, 2H), 2.31 (t, 2H), 2.24 (t, 2H), 2.12 (m, 2H), 1.76 (m, 2H), 1.71 (m, 2H) (Fig. S5a). ^{13}C NMR (MeOD), δ(ppm) 174.39, 135.91, 131.40, 130.88, 129.96,129.52, 127.12, 127.07, 126.95, 126.30, 125.60, 124.82, 124.70, 124.57, 124.53, 124.41, 122.99, 69.91, 69.64, 69.62, 69.51, 69.99, 69.38, 39.71, 36.39, 35.42, 32.36, 29.08, 27.69, 27.63 (Fig. S5b). LS-MS (m/z): $[M+H]^+$ calculated for $C_{30}H_{38}N_2O_4$, 491.63; found, 491.37 (Fig. S7a).

Synthesis of product 2 (P2)

4-Carboxyphenylboronic acid (0.1659 g, 1.0 mmol), EDC·HCl (0.2300 g, 1.2 mmol) and HOBt (0.1622 g, 1.2 mmol) were dissolved in 8 mL dry DMF at 0 ^{o}C. DIEPA (0.524 mL, 3.0 mmol) was dropwise added into above solution, followed by stirred for 1h. To this solution, **P1** (0.5404 g, 1.1 mmol) in 2 mL dry DMF was slowly added and stirred at 0 ^{o}C for another 1 h and at room temperature overnight. 50 mL dry CH_2Cl_2 was added to the reaction solution and washed successively by HCl (0.5 mol L^{-1}, 60 mL), Na_2CO_3 (5%, 60 mL), and brine (2 × 60 mL). The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude product was chromatographed

on 200-300 mesh silica gel with MeOH/CH_2Cl_2/HAc (1:10:0.2 v/v/v) to afford 0.3916 g (61%) of product 2 (**P2**). ^{1}H NMR (MeOD), δ (ppm) 8.15 (d, 1H), 8.02 (t, 2H), 7.95 (d, 2H), 7.87 (m, 3H), 7.67 (m, 5H), 7.31 (d, 2H), 3.34 (m, 14H), 3.20 (t, 2H), 3.15 (t, 2H), 2.20 (t, 2H), 2.02 (m, 2H), 1.92 (s, 2H), 1.70 (m, 2H), 1.61 (m, 2H) (Fig. S6a). ^{13}C NMR (MeOD), δ (ppm) 174.25, 168.66, 135.95, 131.36, 130.95,130.00, 127.10, 127.03, 126.94, 126.26, 125.91, 125.55, 124.51, 124.40, 122.97, 69.97, 69.96, 69.71, 69.69, 69.82, 69.58, 37.34, 36.56, 36.43, 32.34, 29.94, 27.65 (Fig. S6b). LS-MS (m/z): $[M+H]^+$ calculated for $C_{37}H_{43}BN_2O_7$, 639.56; found, 639.33 (Fig. S7b). **P2** was dissolved with MeOH to 10 mmol L^{-1} as a stock solution.

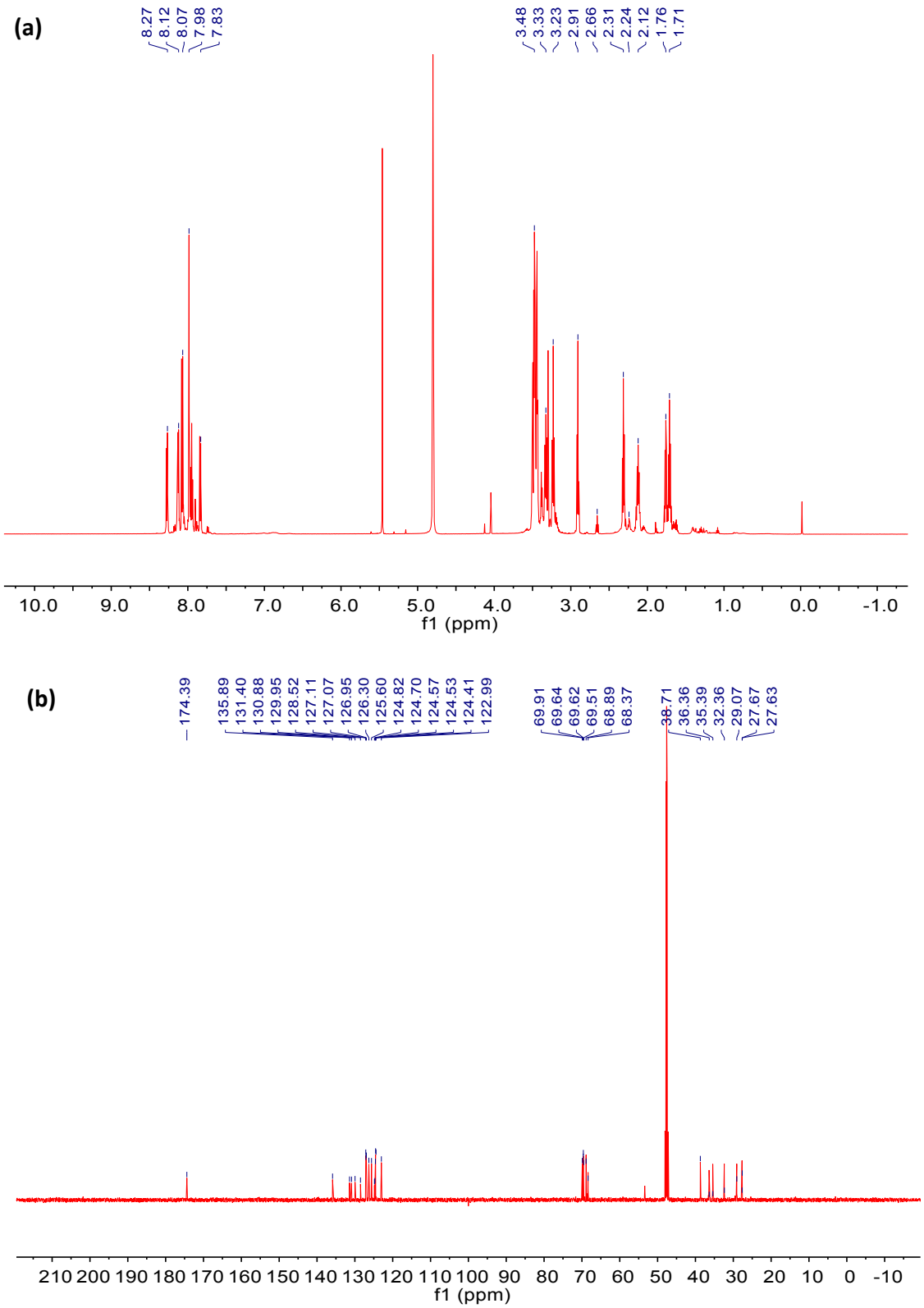


Fig. S5 ^{1}H NMR spectra (a) and ^{13}C NMR spectra (b) of **P1**.

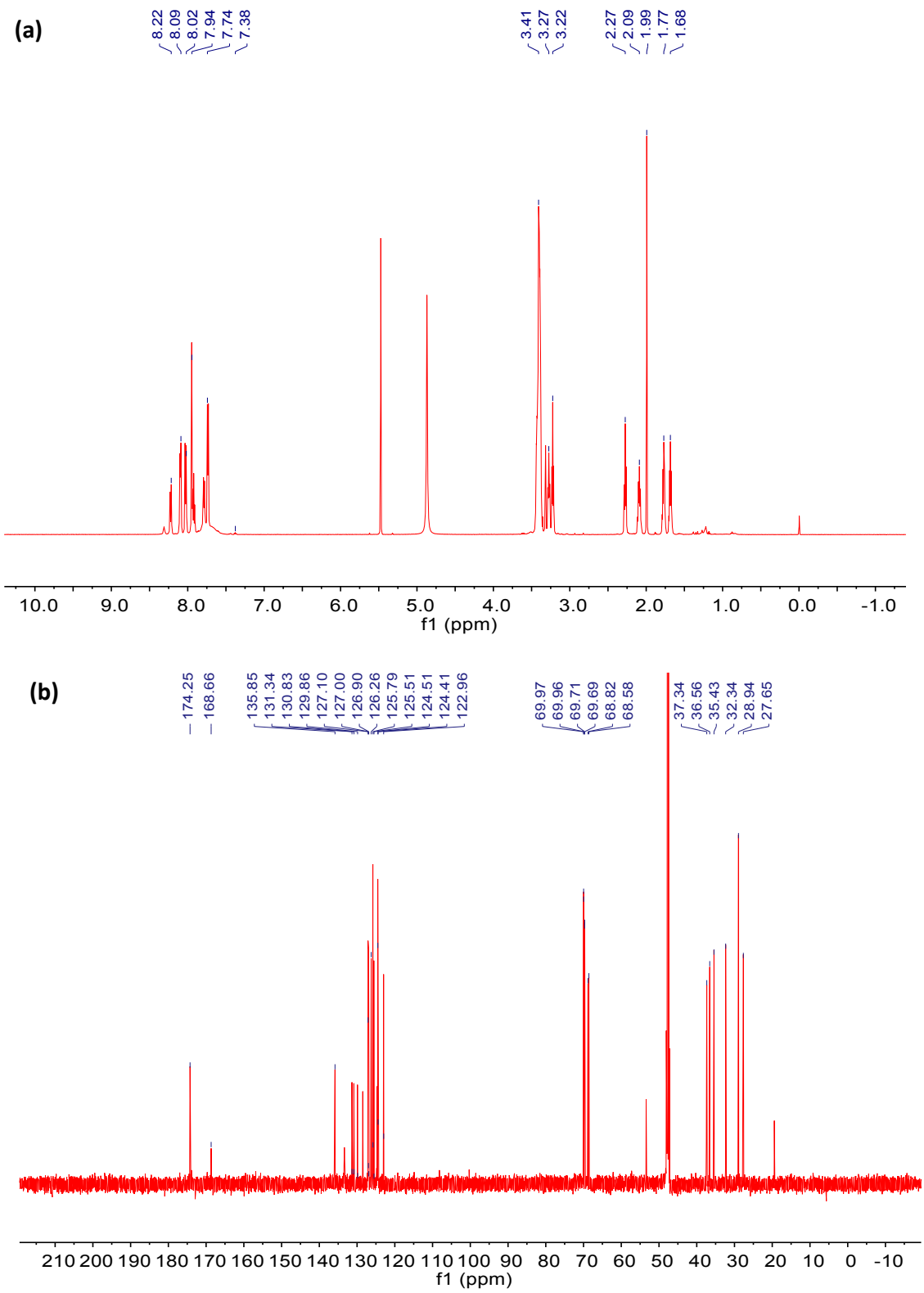


Fig. S6 ^{1}H NMR spectra (a) and ^{13}C NMR spectra (b) of **P2**.

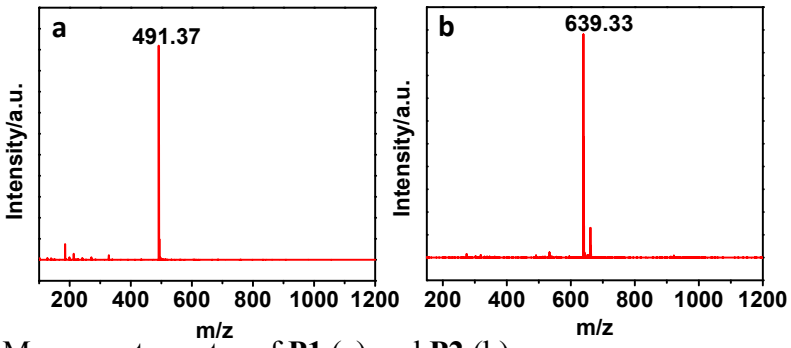


Fig. S7 Mass spectrometry of **P1** (a) and **P2** (b).