Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Sensing of Perfluorinated Compounds Using Functionalized Tricolor Upconversion Nanoparticles based Fluorescent Sensor Array

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Synthesis of Multicolour UCNPs

Multicolour $NaYF_4$ upconversion nanoparticles with different dopants (including $NaYF_4$:Yb/Er (20/2 mol%), $NaYF_4$:Er/Tm (10/2 mol%) and $NaYF_4$:Yb/Tm (20/1 mol%)) were synthesized by the typical thermal coprecipitation method. Herein, the synthesis of $NaYF_4$:Yb/Er (20/2 mol%) was taken as an example. In a typical experiment, RE $(CH_3COO)_3$ (1.0 mM, Y:Yb:Er 78:20:2) was dissolved in a three-necked flask containing OA (6.0 mL) and ODE (17.0 mL), and the system was kept at 160 °C for 30 min to form a transparent solution under vigorous stirring at argon atmosphere. Next, the system was kept at room temperature for 1h, and 10.0 mL methanol containing NaOH (2.5 mM) and NH_4F (4.0 mM) was dropwise added to keep for another 30 min. Then methanol was removed by rotary evaporation at 70 °C. Subsequently, the system was kept at 300 °C for 1 h under vigorous stirring at argon atmosphere, and then cooled down to room temperature. The UCNPs were collected via centrifugation (12186 × g, 10 min). The obtained materials were washed with ethanol and then dried in air.

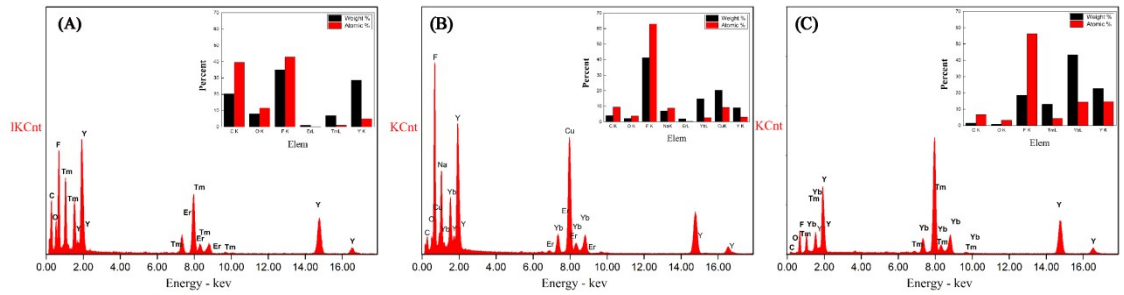


Figure S1 EDS of R-UCNPs (A), G-UCNPs (B), and L-UCNPs (C).

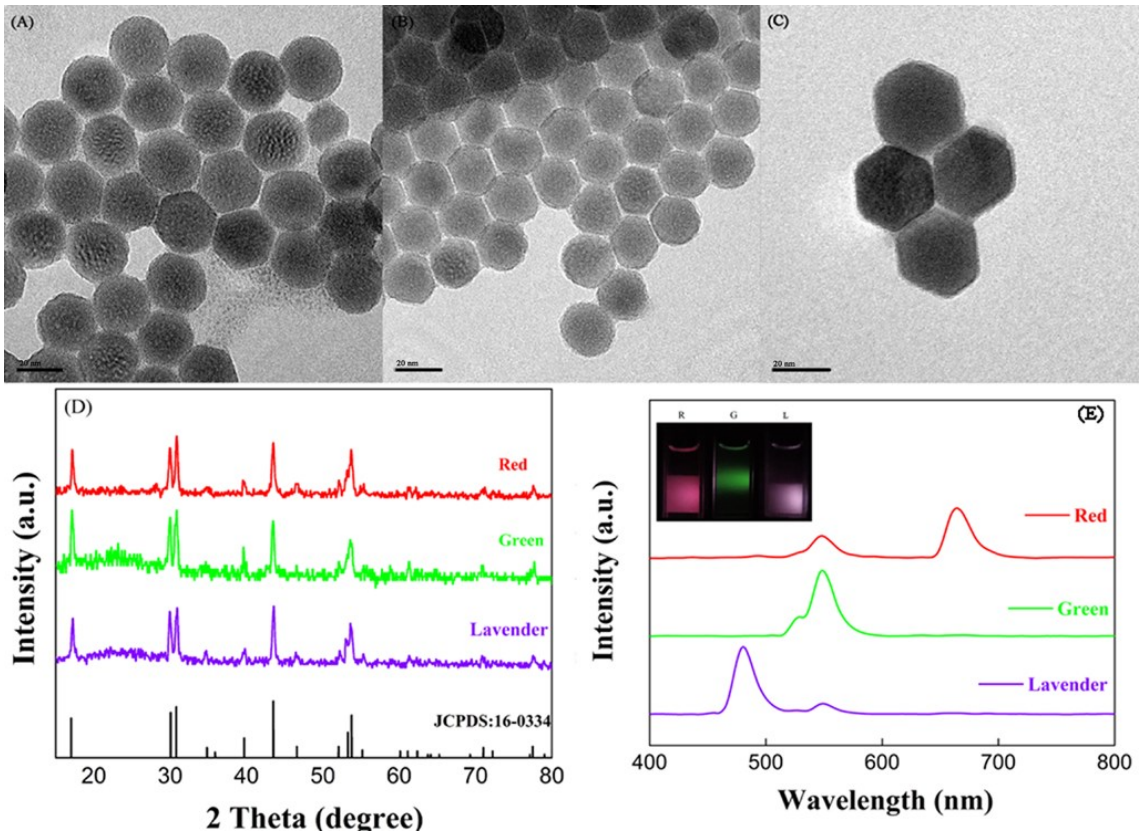


Figure S2 TEM images of L-UCNPs (A), G-UCNPs (B), R-UCNPs (C), XRD of UCNPs (D), and fluorescence emission spectrum of UCNPs (E).

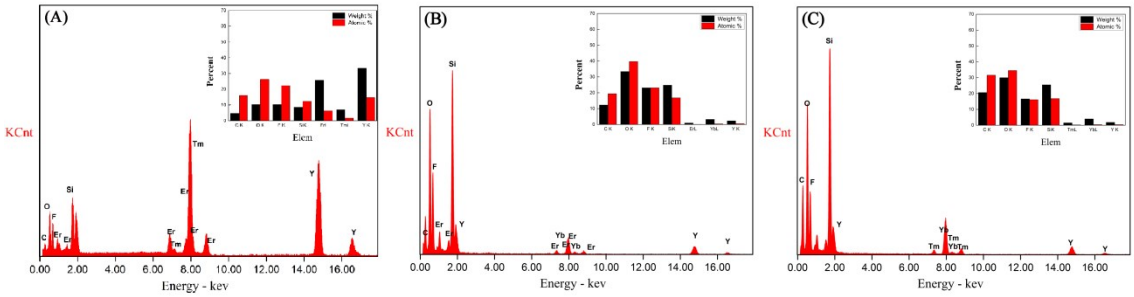


Figure S3 EDS of R-UCNPs@SiO_2-F (A), G-UCNPs@SiO_2-F (B), and L-UCNPs@SiO_2-F (C).

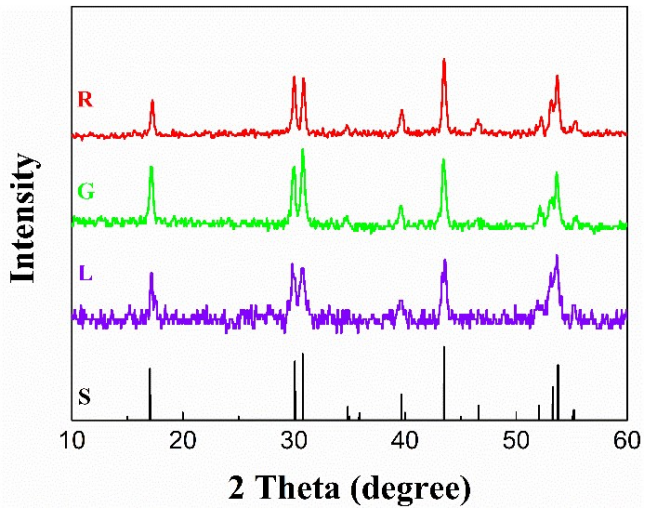


Figure S4 XRD patterns of L-UCNPs@SiO_2-F (a), G-UCNPs@SiO_2-F (b), R-UCNPs@SiO_2-F (c), and standard alignment card (s).

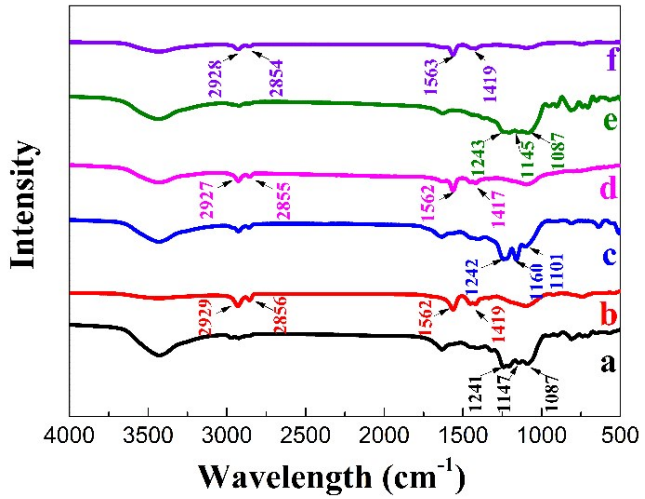


Figure S5 FI-TR spectra of G-UCNPs@SiO_2-F (a), G-UCNPs (b), L-UCNPs@SiO_2-F (c), L-UCNPs (d), R-UCNPs@SiO_2-F (e) and R-UCNPs (f).

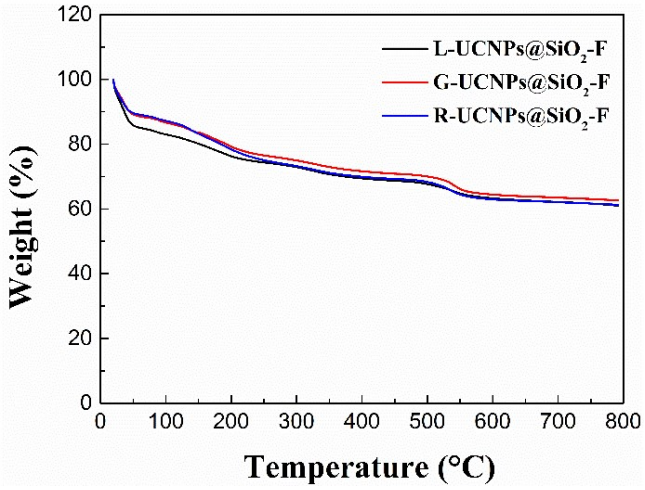


Figure S6 Thermogravimetric analysis of UCNPs@SiO_2-F materials.

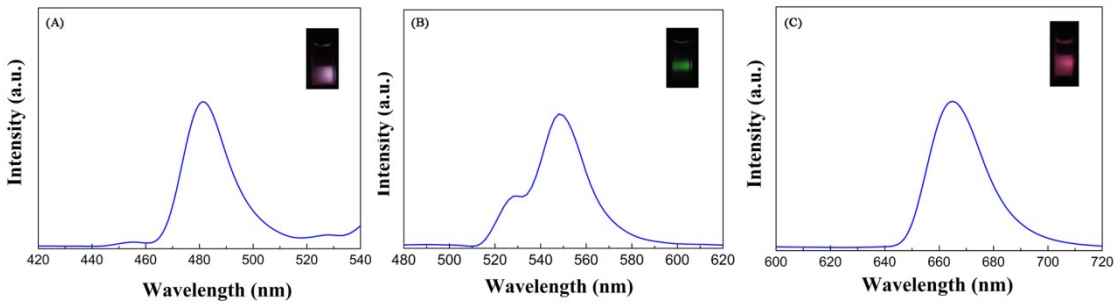


Figure S7 Fluorescence emission spectra of L-UCNPs@SiO_2-F (A), G-UCNPs@SiO_2-F (B), R-UCNPs@SiO_2-F (C), and the inset photos under 980 nm excitation wavelength.

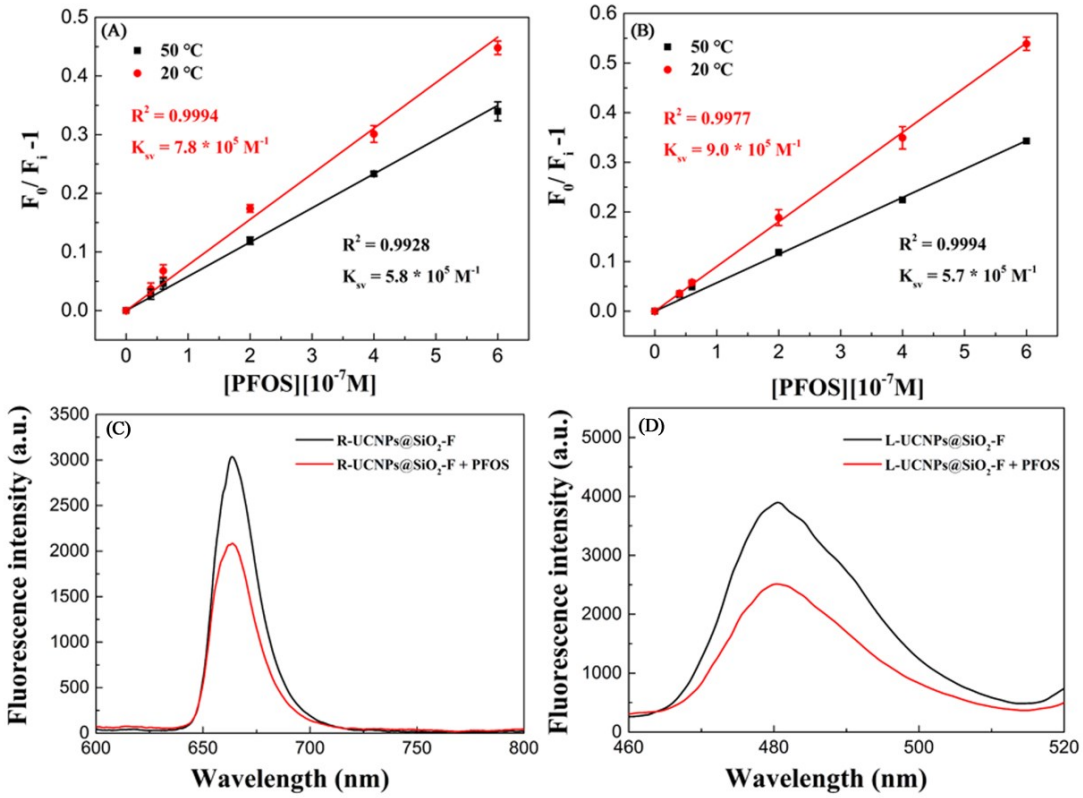


Figure S8 Stern-Volmer plots of F_0/F_i-1 vs [PFOS][10^{-7}M] (A) R-UCNPs@SiO_2-F and (B) L-UCNPs@SiO_2-F (The fluorescence quenching of UCNPs@SiO_2-F (0.40 mg mL^{-1}) to different amounts of perfluorooctane sulfonate potassium (PFOS, 0 - 6.0 × 10^{-7} M) were determined at 50 ℃ (black line) and at 20 ℃ (red line), respectively). Fluorescence emission spectrum of UCNPs@SiO_2-F materials treated with PFOS (6.0 × 10^{-7} M) (C) R-UCNPs@SiO_2-F and (D) L-UCNPs@SiO_2-F.

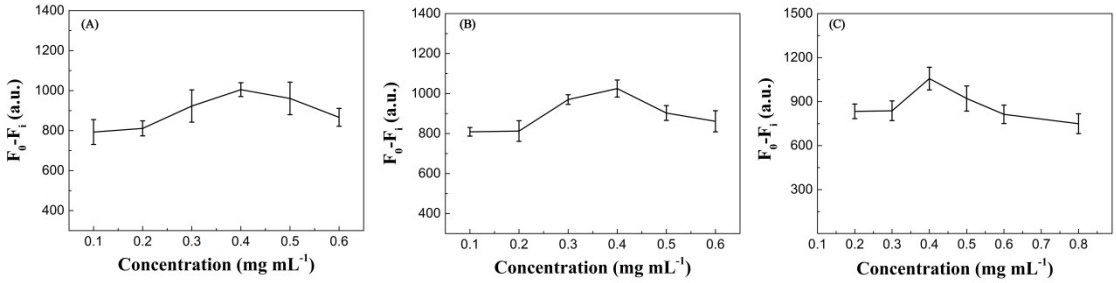


Figure S9 Optimization of assay conditions for the concentration of the three UCNPs@SiO_2-F probes treated with the model perfluorooctane sulfonate potassium (6.0×10^{-7} M). (A) L-UCNPs@SiO_2-F, (B) G-UCNPs@SiO_2-F, and (C) R-UCNPs@SiO_2-F.

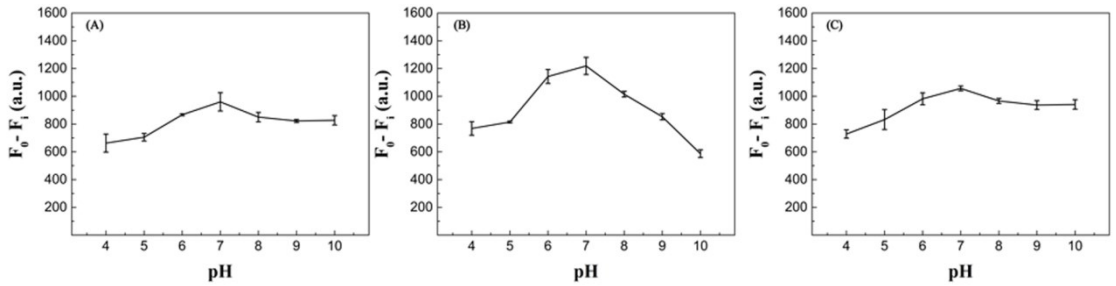


Figure S10 Optimization of assay conditions for pH of the three UCNPs@SiO_2-F probes treated with the model perfluorooctane sulfonate potassium (6.0×10^{-7} M). (A) L-UCNPs@SiO_2-F, (B) G-UCNPs@SiO_2-F, and (C) R-UCNPs@SiO_2-F.

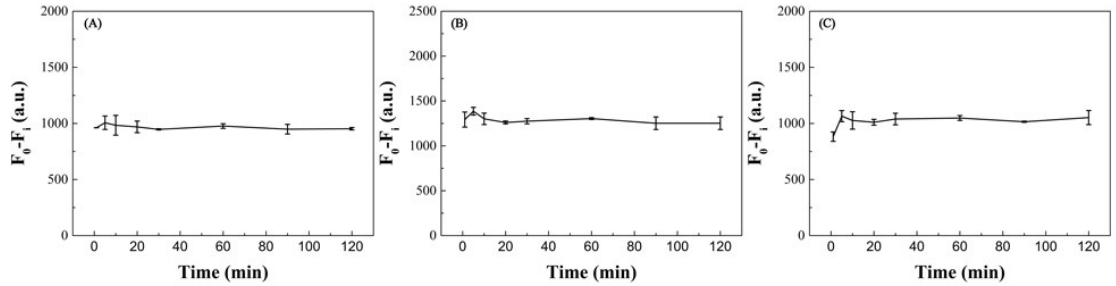


Figure S11 Optimization of assay conditions for the incubation time of the three UCNPs@SiO_2-F probes treated with the model perfluorooctane sulfonate potassium (6.0×10^{-7} M). (A) L-UCNPs@SiO_2-F, (B) G-UCNPs@SiO_2-F, and (C) R-UCNPs@SiO_2-F.

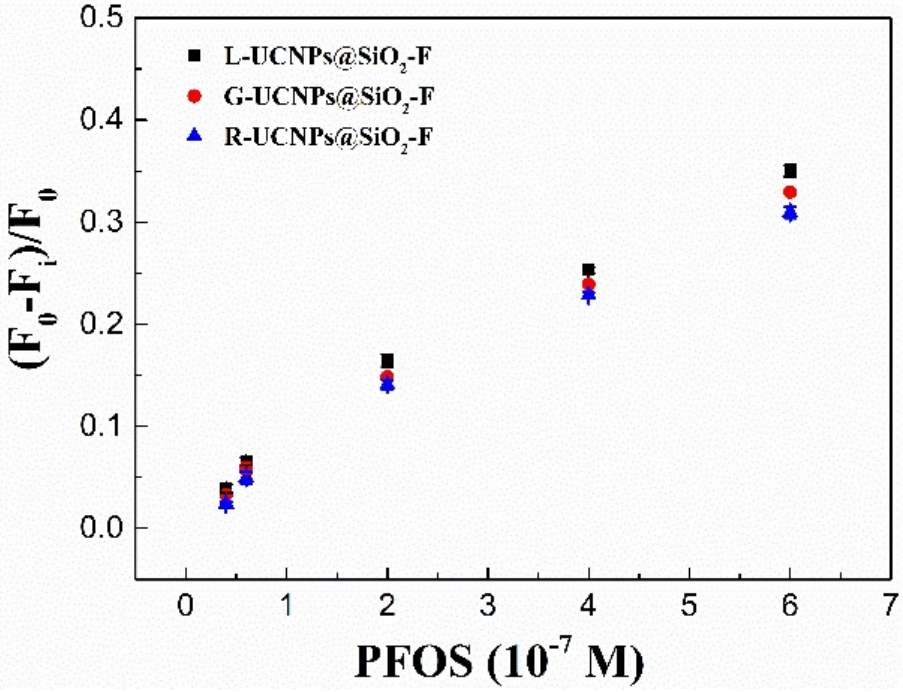


Figure S12 Relative fluorescence intensity variety ($(F_0-F_i)/F_0$) of the tricolor UCNPs@SiO_2-F probes toward different concentration of perfluorooctane sulfonate potassium (PFOS, 4.0×10^{-8} – 6.0×10^{-7} M).

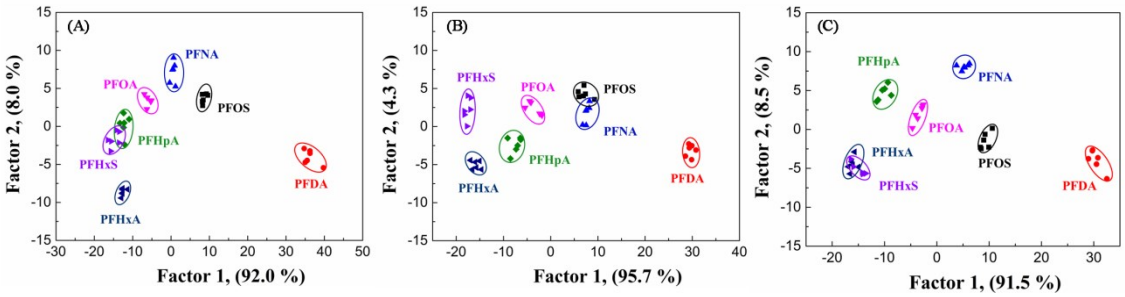


Figure S13 Canonical score plot for perfluorinated compounds (PFCPs) discrimination based on sensor array of (A) L-UCNPs@SiO_2-F + G-UCNPs@SiO_2-F, (B) L-UCNPs@SiO_2-F + R-UCNPs@SiO_2-F, and (C) G-UCNPs@SiO_2-F + R-UCNPs@SiO_2-F. (The detailed information of PFCPs was shown in Table S1).

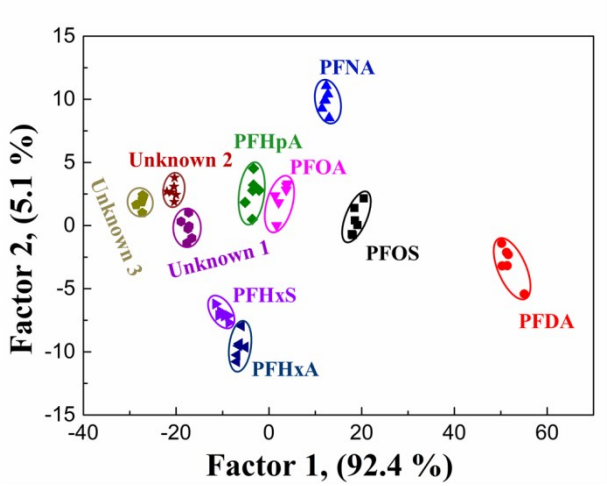


Figure S14 Canonical score plot for the response patterns of seven PFCPs and three kinds of unknown PFCPs samples including perfluoropentanoic acid, potassium nonafluoro-1-butanesulfonate, and heptafluorobutyric acid.

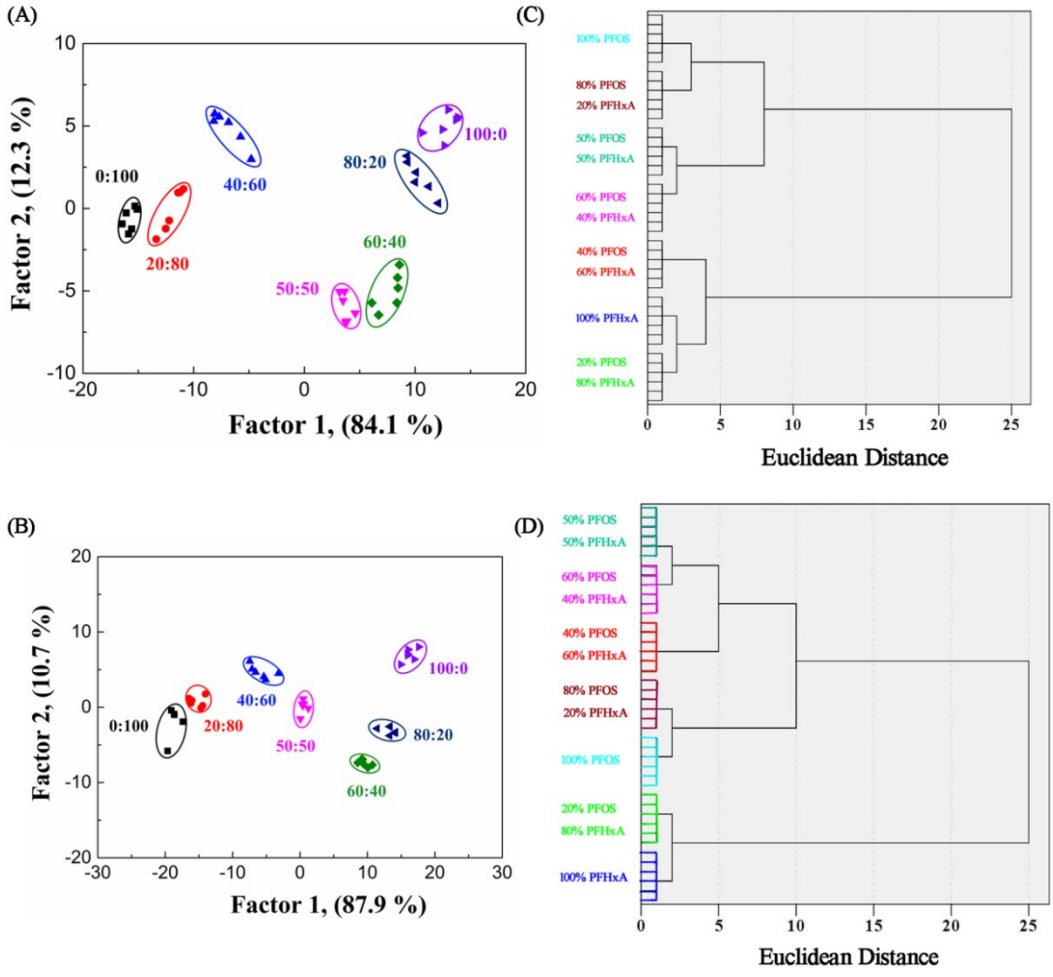


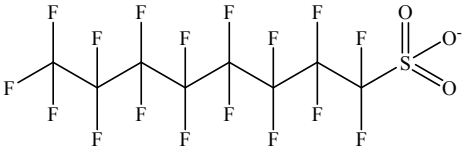
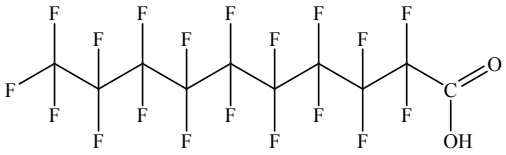
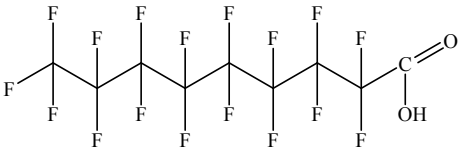
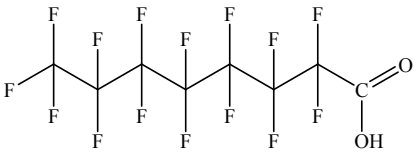
Figure S15 Canonical score plot for the response patterns of PFCPs mixtures of perfluorooctane sulfonate potassium (PFOS) and perfluorohexanoic acid (PFHxA) with different molar ratios obtained from LDA (six parallel measurements) in tap water (A) and food packing (B). Dendrogram generated by HCA of PFCPs mixtures in tap water (C) and food packing (D).

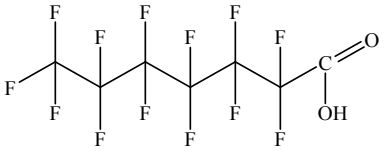
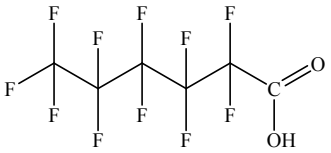
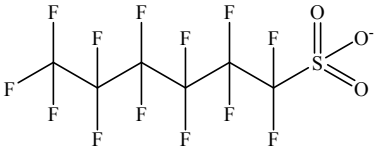
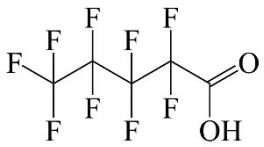
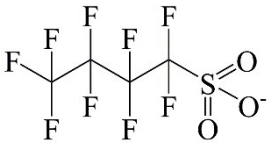
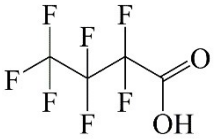
Table S1. Comparison of the lifetime and fluorescence quantum yields.

	Lifetime (ns)	Quantum yields
G-UCNPs	17.81	2.15%
G-UCNPs treated with PFOS	11.42	0.09%
G-UCNPs@SiO_2-F	17.57	1.60%
G-UCNPs@SiO_2-F treated with PFOS	10.81	0.05%

Structural information of PFCPs

Table S2. Information of PFCPs

Compound	Structural Formula	MW (g/mol)
Perfluorooctane sulfonate potassium (PFOS)		538.15
Perfluorodecanoic acid (PFDA)		514.09
Perfluorononanoic acid (PFNA)		464.08
Perfluorooctanoic acid (PFOA)		414.20

Perfluoroheptanoic acid (PFHpA)		364.06
Perfluorohexanoic acid (PFHxA)		314.05
Perfluorohexanesulfonic acid potassium (PFHxS)		438.00
Perfluoropentanoic acid (PFPA)		264.00
Potassium nonafluoro-1-butanesulfonate (PFBS)		338.19
Heptafluorobutyric acid (PFBA)		214.04

Fluorescence Response Pattern and Linear Discriminant Analysis

Table S3. Training matrix of fluorescence response pattern obtained from an array of the three UCNPs@SiO_2-F probes against 7 PFCPs (6.0×10^{-7} M) in water. LDA was carried out and resulting in 3 factors of the canonical scores and group generation. Jackknifed classification matrix showed the 100% correct classification. The detailed information of PFCPs was shown in Table S1.

Analytes	Fluorescence Response Pattern			Results LDA			Group
	C1	C2	C3	F1	F2	F3	
PFOS	0.347	0.330	0.308	9.957	2.834	2.928	1
PFOS	0.346	0.329	0.301	8.548	1.594	5.320	1
PFOS	0.342	0.325	0.301	8.064	2.476	3.798	1
PFOS	0.339	0.324	0.299	8.120	1.561	3.839	1
PFOS	0.337	0.323	0.295	7.437	0.816	4.700	1
PFOS	0.335	0.322	0.294	7.659	0.558	4.084	1
PFDA	0.403	0.427	0.392	41.131	-6.989	-0.103	2
PFDA	0.402	0.418	0.390	38.150	-4.021	-0.608	2
PFDA	0.401	0.418	0.387	37.884	-4.695	-0.118	2
PFDA	0.399	0.413	0.387	36.908	-3.267	-1.207	2
PFDA	0.393	0.413	0.387	37.911	-4.347	-2.450	2
PFDA	0.390	0.411	0.381	36.966	-5.092	-1.701	2
PFNA	0.341	0.305	0.303	3.088	10.748	-0.260	3
PFNA	0.337	0.304	0.302	3.408	9.925	-0.916	3
PFNA	0.333	0.302	0.298	2.902	9.477	-1.017	3
PFNA	0.332	0.301	0.298	2.779	9.439	-1.135	3
PFNA	0.323	0.300	0.295	3.686	7.686	-2.512	3
PFNA	0.320	0.295	0.292	2.294	8.422	-2.736	3
PFOA	0.290	0.272	0.256	-4.687	3.997	0.061	4
PFOA	0.290	0.272	0.255	-4.943	3.933	0.282	4
PFOA	0.289	0.271	0.254	-5.028	3.668	0.414	4
PFOA	0.289	0.269	0.248	-6.617	3.273	2.063	4
PFOA	0.289	0.267	0.247	-7.304	3.825	2.056	4
PFOA	0.281	0.266	0.242	-7.046	1.567	1.948	4
PFHpA	0.257	0.245	0.231	-10.153	3.035	-2.846	5
PFHpA	0.256	0.242	0.231	-11.130	4.501	-3.637	5
PFHpA	0.250	0.240	0.227	-11.161	3.175	-3.970	5
PFHpA	0.246	0.238	0.225	-11.313	2.680	-4.319	5
PFHpA	0.246	0.235	0.220	-12.911	2.354	-2.664	5
PFHpA	0.235	0.234	0.218	-11.431	0.393	-4.809	5
PFHxA	0.207	0.226	0.189	-13.292	-8.256	-2.070	6
PFHxA	0.203	0.221	0.189	-13.893	-7.080	-3.688	6
PFHxA	0.202	0.221	0.185	-14.541	-8.133	-2.294	6
PFHxA	0.200	0.220	0.185	-14.356	-8.195	-3.031	6
PFHxA	0.199	0.220	0.180	-15.002	-9.126	-1.687	6
PFHxA	0.195	0.218	0.180	-14.856	-8.996	-3.002	6
PFHxS	0.239	0.232	0.193	-16.862	-3.703	5.057	7
PFHxS	0.238	0.230	0.191	-17.661	-3.609	5.315	7
PFHxS	0.232	0.229	0.191	-16.692	-4.601	3.745	7
PFHxS	0.225	0.222	0.185	-18.632	-4.067	3.302	7
PFHxS	0.223	0.219	0.184	-19.179	-3.395	2.557	7
PFHxS	0.218	0.219	0.184	-18.201	-4.366	1.311	7

Table S4. Summary of the jackknifed classification matrix for seven kinds of PFCPs.

	PFOS	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFHxS	% correct
PFOS	6	0	0	0	0	0	0	100
PFDA	0	6	0	0	0	0	0	100
PFNA	0	0	6	0	0	0	0	100
PFOA	0	0	0	6	0	0	0	100
PFHpA	0	0	0	0	6	0	0	100
PFHxA	0	0	0	0	0	6	0	100
PFHxS	0	0	0	0	0	0	6	100
Total	6	6	6	6	6	6	6	100

The detailed information of PFCPs was shown in Table S1.

Table S5. Training matrix of fluorescence response pattern obtained from an array of the three UCNPs@SiO_2-F probes against 7 PFCPs and three kinds of unknown PFCPs samples including PFPA, PFBS, and PFBA (6.0×10^{-7} M) in water. LDA was carried out and resulting in 3 factors of the canonical scores and group generation. Jackknifed classification matrix showed the 100% correct classification. The detailed information of PFCPs was shown in Table S1.

Analytes	Fluorescence Response Pattern			Results LDA			Group
	C1	C2	C3	F1	F2	F3	
PFOS	0.347	0.330	0.308	20.464	2.148	3.933	1
PFOS	0.346	0.329	0.301	19.111	0.032	6.402	1
PFOS	0.342	0.325	0.301	18.443	1.389	4.977	1
PFOS	0.339	0.324	0.299	18.543	0.408	4.823	1
PFOS	0.337	0.323	0.295	17.873	-0.682	5.665	1
PFOS	0.335	0.322	0.294	18.087	-0.759	4.920	1
PFDA	0.403	0.427	0.392	55.060	-5.418	-4.303	2
PFDA	0.402	0.418	0.390	51.623	-2.303	-3.950	2
PFDA	0.401	0.418	0.387	51.387	-3.181	-3.535	2
PFDA	0.399	0.413	0.387	50.183	-1.403	-4.329	2
PFDA	0.393	0.413	0.387	51.249	-2.120	-6.001	2
PFDA	0.390	0.411	0.381	50.284	-3.193	-5.258	2
PFNA	0.341	0.305	0.303	12.370	11.066	2.771	3
PFNA	0.337	0.304	0.302	12.711	10.405	1.854	3
PFNA	0.333	0.302	0.298	12.162	9.927	1.695	3

PFNA	0.332	0.301	0.298	12.021	9.914	1.570	3
PFNA	0.323	0.300	0.295	12.998	8.516	-0.383	3
PFNA	0.320	0.295	0.292	11.418	9.276	-0.343	3
PFOA	0.290	0.272	0.256	4.059	3.302	2.404	4
PFOA	0.290	0.272	0.255	3.793	3.153	2.653	4
PFOA	0.289	0.271	0.254	3.718	2.826	2.749	4
PFOA	0.289	0.269	0.248	2.086	1.818	4.606	4
PFOA	0.289	0.267	0.247	1.307	2.364	4.777	4
PFOA	0.281	0.266	0.242	1.670	0.012	4.159	4
PFHpA	0.257	0.245	0.231	-2.132	2.794	-0.461	5
PFHpA	0.256	0.242	0.231	-3.319	4.523	-0.922	5
PFHpA	0.250	0.240	0.227	-3.325	3.211	-1.562	5
PFHpA	0.246	0.238	0.225	-3.497	2.778	-2.033	5
PFHpA	0.246	0.235	0.220	-5.140	1.841	-0.155	5
PFHpA	0.235	0.234	0.218	-3.574	0.485	-3.039	5
PFHxA	0.207	0.226	0.189	-5.122	-9.635	-1.720	6
PFHxA	0.203	0.221	0.189	-5.937	-7.945	-3.176	6
PFHxA	0.202	0.221	0.185	-6.521	-9.518	-1.822	6
PFHxA	0.200	0.220	0.185	-6.363	-9.353	-2.655	6
PFHxA	0.199	0.220	0.180	-6.954	-10.781	-1.331	6
PFHxA	0.195	0.218	0.180	-6.884	-10.245	-2.747	6
PFHxS	0.239	0.232	0.193	-8.767	-7.132	7.326	7
PFHxS	0.238	0.230	0.191	-9.637	-7.159	7.699	7
PFHxS	0.232	0.229	0.191	-8.632	-7.686	5.692	7
PFHxS	0.225	0.222	0.185	-10.824	-7.112	5.502	7
PFHxS	0.223	0.219	0.184	-11.502	-6.212	4.883	7
PFHxS	0.218	0.219	0.184	-10.468	-6.813	3.233	7
Unknown 1	0.199	0.191	0.177	-17.292	1.030	-1.523	8
Unknown 1	0.195	0.190	0.174	-17.212	-0.052	-1.750	8
Unknown 1	0.194	0.190	0.173	-17.434	-0.253	-1.567	8
Unknown 1	0.188	0.189	0.172	-16.609	-0.995	-3.205	8
Unknown 1	0.187	0.187	0.168	-17.661	-1.393	-2.297	8
Unknown 1	0.186	0.183	0.168	-18.920	0.323	-2.824	8
Unknown 2	0.187	0.178	0.171	-20.337	3.787	-3.925	9
Unknown 2	0.185	0.177	0.169	-20.449	3.079	-3.789	9
Unknown 2	0.182	0.177	0.168	-20.008	2.436	-4.513	9
Unknown 2	0.180	0.176	0.166	-20.396	1.870	-4.196	9
Unknown 2	0.178	0.173	0.165	-20.978	2.641	-4.842	9
Unknown 2	0.176	0.171	0.162	-21.988	2.687	-4.396	9
Unknown 3	0.179	0.162	0.150	-27.216	2.398	0.436	10
Unknown 3	0.176	0.161	0.150	-26.989	2.313	-0.337	10
Unknown 3	0.169	0.158	0.147	-27.237	2.092	-1.557	10
Unknown 3	0.169	0.157	0.146	-27.405	1.860	-1.460	10
Unknown 3	0.166	0.157	0.144	-27.297	1.003	-1.670	10

Unknown 3	0.165	0.154	0.142	-28.596	1.635	-1.151	10

Table S6. Fluorescence response patterns using the sensor array against the PFCPs mixtures of perfluorooctane sulfonate potassium (PFOS) and perfluorohexanoic acid (PFHxA) with different ratios (100:0, 80:20, 60:40, 50:50, 40:60, 20:80, and 0:100, respectively). LDA was carried out and resulting in 3 factors of the canonical scores and group generation. The concentration PFOS and PFHxA were 6.0×10^{-7} M.

PFOS:PFHxA	Fluorescence Response Pattern			Results LDA			Group
	C1	C2	C3	F1	F2	F3	
0:100	0.207	0.226	0.189	-12.966	3.017	-2.760	1
0:100	0.203	0.221	0.189	-13.453	3.515	-3.794	1
0:100	0.202	0.221	0.185	-13.831	3.191	-3.160	1
0:100	0.200	0.220	0.185	-14.110	3.694	-3.483	1
0:100	0.199	0.220	0.180	-14.438	3.340	-2.883	1
0:100	0.195	0.218	0.180	-14.912	4.126	-3.520	1
80:20	0.264	0.242	0.219	-5.738	-3.320	-2.113	2
80:20	0.253	0.241	0.210	-6.346	-4.420	-0.729	2
80:20	0.253	0.236	0.198	-7.267	-6.233	0.369	2
80:20	0.250	0.234	0.194	-7.858	-6.071	0.552	2
80:20	0.250	0.233	0.193	-7.982	-6.361	0.605	2
80:20	0.244	0.233	0.191	-8.707	-5.080	0.386	2
60:40	0.268	0.280	0.227	-3.214	-3.644	1.892	3
60:40	0.265	0.267	0.227	-3.562	-2.856	1.682	3
60:40	0.264	0.267	0.227	-3.612	-2.825	1.717	3
60:40	0.264	0.266	0.221	-4.097	-3.425	2.310	3
60:40	0.252	0.264	0.221	-5.367	-0.856	1.336	3
60:40	0.246	0.258	0.221	-6.082	-0.032	-0.070	3
50:50	0.278	0.308	0.267	1.134	2.183	2.767	4
50:50	0.277	0.305	0.263	0.862	1.693	2.896	4
50:50	0.273	0.299	0.262	0.139	2.041	1.872	4
50:50	0.272	0.296	0.258	-0.236	1.442	2.015	4
50:50	0.272	0.296	0.257	-0.348	1.435	1.959	4
50:50	0.271	0.290	0.257	-0.520	1.042	1.063	4
40:60	0.294	0.345	0.285	4.742	3.642	7.171	5
40:60	0.293	0.338	0.282	4.269	3.115	6.413	5
40:60	0.292	0.326	0.277	3.732	1.526	4.964	5
40:60	0.292	0.320	0.277	3.561	0.987	4.054	5
40:60	0.290	0.311	0.276	3.114	0.606	2.575	5
40:60	0.289	0.309	0.267	2.407	-0.293	3.536	5
20:80	0.318	0.329	0.332	10.100	1.999	-1.985	6

20:80	0.312	0.327	0.331	9.432	2.927	-2.441	6
20:80	0.307	0.327	0.329	8.688	3.956	-2.375	6
20:80	0.304	0.325	0.325	8.101	3.995	-2.165	6
20:80	0.301	0.325	0.314	7.043	3.651	-0.717	6
20:80	0.298	0.324	0.309	6.673	2.933	-0.040	6
100:0	0.347	0.330	0.352	14.520	-2.681	-3.221	7
100:0	0.346	0.329	0.351	14.393	-2.852	-3.201	7
100:0	0.342	0.325	0.351	13.854	-2.271	-4.142	7
100:0	0.339	0.324	0.349	13.390	-1.776	-4.116	7
100:0	0.337	0.323	0.339	12.532	-2.566	-2.819	7
100:0	0.335	0.322	0.335	11.961	-2.495	-2.400	7

Table S7. Fluorescence response pattern obtained from an array of the tricolor UCNPs@SiO_2-F probes against perfluorooctane sulfonate potassium at different concentrations (4.0×10^{-8} – 6.0×10^{-7} M). LDA was carried out and resulting in 3 factors of the canonical scores and group generation. Jackknifed classification matrix showed the 100% correct classification.

Concentration (10^{-7} M)	Fluorescence Response Pattern			Results LDA			Group
	C1	C2	C3	F1	F2	F3	
20	0.628	0.610	0.553	209.603	4.793	0.051	1
20	0.627	0.606	0.552	208.923	2.942	-0.188	1
20	0.624	0.605	0.549	207.912	3.708	-0.228	1
20	0.619	0.599	0.542	205.950	3.302	-0.719	1
20	0.619	0.595	0.541	205.821	1.353	-1.091	1
20	0.616	0.593	0.536	205.284	1.654	-1.544	1
6.0	0.347	0.328	0.321	65.146	-4.465	1.513	2
6.0	0.346	0.327	0.318	65.700	-4.773	0.986	2
6.0	0.342	0.322	0.310	64.664	-4.812	0.276	2
6.0	0.339	0.322	0.306	63.747	-3.485	0.098	2
6.0	0.337	0.321	0.293	65.759	-2.914	-1.787	2
6.0	0.335	0.320	0.293	64.136	-2.075	-1.398	2
4.0	0.262	0.249	0.252	22.031	-4.071	2.414	3
4.0	0.258	0.246	0.237	22.739	-3.275	0.581	3
4.0	0.256	0.245	0.231	22.863	-2.652	-0.091	3
4.0	0.255	0.249	0.231	22.579	0.053	0.356	3
4.0	0.254	0.242	0.228	22.729	-3.251	-0.555	3
4.0	0.249	0.242	0.225	19.711	-0.893	0.106	3
2.0	0.161	0.158	0.166	-28.554	-2.064	3.088	4
2.0	0.160	0.154	0.164	-29.547	-3.122	2.947	4
2.0	0.156	0.152	0.158	-30.328	-2.155	2.520	4

2.0	0.155	0.149	0.152	-29.447	-3.307	1.432	4
2.0	0.155	0.149	0.149	-28.743	-3.087	0.904	4
2.0	0.154	0.146	0.143	-27.849	-4.109	-0.168	4
0.6	0.061	0.077	0.074	-76.434	5.626	3.173	5
0.6	0.057	0.074	0.060	-76.091	6.251	1.558	5
0.6	0.057	0.073	0.056	-75.089	5.850	0.795	5
0.6	0.055	0.072	0.054	-75.480	6.122	0.674	5
0.6	0.052	0.070	0.052	-77.155	6.860	0.814	5
0.6	0.052	0.065	0.043	-75.252	4.244	-0.988	5
0.4	0.032	0.046	0.032	-86.712	3.859	0.042	6
0.4	0.031	0.044	0.027	-86.519	3.962	-0.603	6
0.4	0.029	0.044	0.023	-86.185	4.309	-1.120	6
0.4	0.028	0.043	0.021	-86.725	4.968	-1.157	6
0.4	0.027	0.042	0.018	-86.990	4.750	-1.460	6
0.4	0.026	0.039	0.017	-87.462	4.113	-1.614	6

Table S8. Fluorescence response pattern obtained from an array of the tricolor UCNPs@SiO_2-F probes against perfluorohexanoic acid at different concentrations (4.0×10^{-8} – 6.0×10^{-7} M). LDA was carried out and resulting in 3 factors of the canonical scores and group generation. Jackknifed classification matrix showed the 100% correct classification.

Concentration (10^{-7} M)	Fluorescence Response Pattern			Results LDA			Group
	C1	C2	C3	F1	F2	F3	
20	0.386	0.456	0.398	100.707	4.755	0.151	1
20	0.383	0.452	0.394	99.409	5.254	0.296	1
20	0.381	0.446	0.394	98.965	3.848	-2.212	1
20	0.379	0.444	0.393	98.317	3.353	-1.830	1
20	0.376	0.442	0.390	97.377	3.236	-1.391	1
20	0.375	0.437	0.385	96.227	5.024	-2.656	1
6.0	0.168	0.205	0.183	20.439	1.225	2.906	2
6.0	0.167	0.205	0.180	19.734	2.734	3.214	2
6.0	0.163	0.199	0.179	18.845	0.545	2.187	2
6.0	0.163	0.198	0.179	18.740	0.571	2.224	2
6.0	0.162	0.196	0.176	18.009	1.939	1.683	2
6.0	0.160	0.192	0.174	17.340	1.290	0.850	2
4.0	0.120	0.160	0.156	6.535	-9.415	6.336	3
4.0	0.119	0.157	0.156	6.174	-10.450	5.665	3
4.0	0.118	0.155	0.156	6.023	-10.610	4.932	3
4.0	0.117	0.154	0.155	5.592	-11.151	5.090	3
4.0	0.115	0.152	0.154	5.073	-11.605	5.494	3

4.0	0.114	0.151	0.150	4.227	-10.030	5.385	3
2.0	0.074	0.075	0.100	-13.145	-7.807	-7.950	4
2.0	0.072	0.075	0.097	-13.946	-7.429	-6.883	4
2.0	0.070	0.073	0.096	-14.344	-7.924	-7.257	4
2.0	0.069	0.073	0.095	-14.870	-7.736	-6.356	4
2.0	0.068	0.072	0.091	-15.735	-5.708	-5.708	4
2.0	0.066	0.072	0.091	-16.054	-6.514	-4.913	4
0.6	0.047	0.053	0.057	-25.409	1.223	-2.059	5
0.6	0.046	0.048	0.057	-25.835	0.050	-3.825	5
0.6	0.045	0.047	0.057	-25.927	-0.012	-3.777	5
0.6	0.044	0.047	0.057	-26.092	-0.313	-3.494	5
0.6	0.044	0.046	0.053	-26.897	1.537	-3.229	5
0.6	0.042	0.046	0.050	-27.617	2.431	-2.344	5
0.4	0.017	0.026	0.025	-36.746	2.726	2.807	6
0.4	0.023	0.026	0.022	-36.295	7.455	-0.042	6
0.4	0.018	0.026	0.022	-37.219	5.148	2.559	6
0.4	0.016	0.026	0.021	-37.668	4.930	3.489	6
0.4	0.016	0.026	0.020	-37.744	5.029	3.457	6
0.4	0.011	0.024	0.020	-38.655	2.981	4.978	6

Table S9. Detection and identification of unknown PFCPs samples (6.0×10^{-7} M in tap water). All unknown samples could be assigned to the corresponding LDA group defined by the training matrix. According to the verification, 21 unknown samples were classified, representing an accuracy of 100%. The detailed information of PFCPs was shown in Table S1.

Samples #	Fluorescence Response Pattern			Analytes	
	C1	C2	C3	Identification	Verification
1	0.338	0.326	0.295	PFOS	PFOS
2	0.402	0.415	0.388	PFDA	PFDA
3	0.326	0.299	0.294	PFNA	PFNA
4	0.288	0.271	0.252	PFOA	PFOA
5	0.255	0.242	0.222	PFHpA	PFHpA
6	0.201	0.223	0.185	PFHxA	PFHxA
7	0.221	0.219	0.186	PFHxS	PFHxS
8	0.337	0.327	0.298	PFOS	PFOS
9	0.401	0.414	0.391	PFDA	PFDA
10	0.321	0.305	0.297	PFNA	PFNA
11	0.290	0.270	0.255	PFOA	PFOA
12	0.256	0.234	0.230	PFHpA	PFHpA
13	0.203	0.225	0.187	PFHxA	PFHxA

14	0.234	0.223	0.188	PFHxS	PFHxS
15	0.340	0.328	0.307	PFOS	PFOS
16	0.403	0.423	0.391	PFDA	PFDA
17	0.325	0.302	0.295	PFNA	PFNA
18	0.282	0.268	0.246	PFOA	PFOA
19	0.249	0.240	0.218	PFHpA	PFHpA
20	0.207	0.221	0.186	PFHxA	PFHxA
21	0.232	0.224	0.186	PFHxS	PFHxS

Table S10. Detection and identification of unknown PFCPs samples (6.0×10^{-7} M in food packing). All unknown samples could be assigned to the corresponding LDA group defined by the training matrix. According to the verification, 19 unknown samples were classified, representing an accuracy of 90.5 %. The detailed information of PFCPs was shown in Table S1.

Samples	Fluorescence Response Pattern			Analytes	
#	C1	C2	C3	Identification	Verification
1	0.343	0.326	0.300	PFOS	PFOS
2	0.397	0.413	0.391	PFDA	PFDA
3	0.329	0.301	0.294	PFNA	PFNA
4	0.288	0.269	0.248	PFOA	PFOA
5	0.255	0.242	0.231	PFHpA	PFHpA
6	0.203	0.218	0.185	PFHxA	PFHxA
7	0.235	0.223	0.187	PFHxS	PFHxS
8	0.342	0.327	0.304	PFOS	PFOS
9	0.400	0.411	0.385	PFDA	PFDA
10	0.334	0.300	0.299	PFNA	PFNA
11	0.288	0.271	0.255	PFOA	PFOA
12	0.290	0.267	0.248	PFOA	PFHpA
13	0.238	0.223	0.185	PFHxS	PFHxA
14	0.224	0.221	0.185	PFHxS	PFHxS
15	0.346	0.323	0.308	PFOS	PFOS
16	0.401	0.413	0.387	PFDA	PFDA
17	0.338	0.301	0.293	PFNA	PFNA
18	0.283	0.272	0.250	PFOA	PFOA
19	0.257	0.238	0.220	PFHpA	PFHpA
20	0.204	0.218	0.180	PFHxA	PFHxA
21	0.226	0.223	0.185	PFHxS	PFHxS

Table S11. Detection and identification of unknown PFCPs samples (6.0×10^{-7} M in

river water). All unknown samples could be assigned to the corresponding LDA group defined by the training matrix. According to the verification, 20 unknown samples were classified, representing an accuracy of 95.2 %. The detailed information of PFCPs was shown in Table S1.

Samples	Fluorescence Response Pattern			Analytes	
#	C1	C2	C3	Identification	Verification
1	0.338	0.325	0.305	PFOS	PFOS
2	0.395	0.416	0.391	PFDA	PFDA
3	0.328	0.296	0.294	PFNA	PFNA
4	0.289	0.272	0.250	PFOA	PFOA
5	0.256	0.240	0.227	PFHpA	PFHpA
6	0.202	0.226	0.185	PFHxA	PFHxA
7	0.221	0.220	0.190	PFHxS	PFHxS
8	0.337	0.330	0.296	PFOS	PFOS
9	0.393	0.418	0.389	PFDA	PFDA
10	0.332	0.304	0.302	PFNA	PFNA
11	0.290	0.269	0.253	PFOA	PFOA
12	0.253	0.240	0.219	PFHpA	PFHpA
13	0.198	0.221	0.185	PFHxA	PFHxA
14	0.222	0.229	0.190	PFHxS	PFHxS
15	0.345	0.324	0.300	PFOS	PFOS
16	0.399	0.417	0.384	PFDA	PFDA
17	0.329	0.301	0.300	PFNA	PFNA
18	0.290	0.269	0.242	PFOA	PFOA
19	0.243	0.240	0.228	PFHpA	PFHpA
20	0.203	0.225	0.188	PFHxA	PFHxA
21	0.204	0.223	0.189	PFHxA	PFHxS

Table S12. Detection and identification of unknown PFCPs samples (6.0×10^{-7} M in surface seawater). All unknown samples could be assigned to the corresponding LDA group defined by the training matrix. According to the verification, 18 unknown samples were classified, representing an accuracy of 85.7 %. The detailed information of PFCPs was shown in Table S1.

Samples	Fluorescence Response Pattern			Analytes	
#	C1	C2	C3	Identification	Verification

1	0.345	0.323	0.307	PFOS	PFOS
2	0.400	0.414	0.386	PFDA	PFDA
3	0.327	0.297	0.295	PFNA	PFNA
4	0.288	0.269	0.255	PFOA	PFOA
5	0.251	0.243	0.230	PFHpA	PFHpA
6	0.200	0.220	0.185	PFHxA	PFHxA
7	0.207	0.221	0.187	PFHxA	PFHxS
8	0.338	0.329	0.296	PFOS	PFOS
9	0.401	0.424	0.387	PFDA	PFDA
10	0.335	0.297	0.293	PFNA	PFNA
11	0.289	0.270	0.255	PFOA	PFOA
12	0.251	0.238	0.218	PFHpA	PFHpA
13	0.218	0.223	0.189	PFHxS	PFHxA
14	0.220	0.229	0.191	PFHxS	PFHxS
15	0.338	0.322	0.296	PFOS	PFOS
16	0.402	0.413	0.384	PFDA	PFDA
17	0.324	0.300	0.302	PFNA	PFNA
18	0.287	0.272	0.245	PFOA	PFOA
19	0.239	0.238	0.223	PFHpA	PFHpA
20	0.200	0.226	0.187	PFHxA	PFHxA
21	0.239	0.234	0.225	PFHpA	PFHxS

Table S13. Fluorescence response patterns using the sensor array against the PFCPs mixtures of perfluorooctane sulfonate potassium (PFOS) and perfluorohexanoic acid (PFHxA) in tap water with different ratios (100:0, 80:20, 60:40, 50:50, 40:60, 20:80, and 0:100, respectively). LDA was carried out and resulting in 3 factors of the canonical scores and group generation. The concentration PFOS and PFHxA were 6.0×10^{-7} M.

PFOS:PFHxA	Fluorescence Response Pattern			Results LDA			Group
	C1	C2	C3	F1	F2	F3	
0:100	0.168	0.200	0.167	-15.103	-0.050	1.472	1
0:100	0.166	0.200	0.164	-15.298	0.141	1.016	1
0:100	0.163	0.195	0.163	-16.089	-0.273	2.114	1
0:100	0.159	0.194	0.147	-15.597	-1.246	-1.267	1
0:100	0.158	0.192	0.146	-15.875	-1.549	-0.879	1
0:100	0.154	0.191	0.145	-16.461	-0.936	-0.818	1
80:20	0.198	0.222	0.203	-10.915	1.179	3.274	2
80:20	0.196	0.220	0.201	-11.223	0.990	3.329	2
80:20	0.192	0.219	0.193	-11.398	0.962	1.875	2
80:20	0.186	0.210	0.181	-12.210	-0.735	1.699	2
80:20	0.185	0.208	0.180	-12.524	-1.224	2.080	2

80:20	0.181	0.202	0.178	-13.378	-1.865	3.237	2
60:40	0.225	0.255	0.219	-4.799	2.981	-2.311	3
60:40	0.218	0.255	0.214	-5.761	4.350	-3.232	3
60:40	0.212	0.253	0.214	-6.849	5.226	-2.784	3
60:40	0.207	0.250	0.210	-7.686	5.560	-2.926	3
60:40	0.203	0.249	0.206	-8.105	5.753	-3.454	3
60:40	0.202	0.247	0.202	-8.188	5.305	-3.786	3
50:50	0.287	0.268	0.248	4.597	-6.354	0.453	4
50:50	0.281	0.267	0.247	3.631	-5.036	0.316	4
50:50	0.278	0.265	0.245	3.177	-5.052	0.404	4
50:50	0.278	0.265	0.240	3.501	-5.590	-0.552	4
50:50	0.278	0.263	0.232	3.844	-6.837	-1.604	4
50:50	0.276	0.262	0.229	3.715	-6.900	-1.992	4
40:60	0.310	0.294	0.275	8.586	-3.414	-0.852	5
40:60	0.310	0.291	0.274	8.422	-4.194	-0.279	5
40:60	0.309	0.290	0.270	8.463	-4.823	-0.617	5
40:60	0.308	0.286	0.266	8.364	-5.719	-0.763	5
40:60	0.301	0.277	0.262	6.715	-6.461	1.097	5
40:60	0.297	0.276	0.260	6.096	-5.723	0.806	5
20:80	0.331	0.321	0.306	12.097	0.320	-1.559	6
20:80	0.326	0.321	0.306	11.235	1.334	-1.502	6
20:80	0.319	0.318	0.301	10.086	2.193	-1.922	6
20:80	0.313	0.318	0.297	9.278	3.186	-2.594	6
20:80	0.313	0.317	0.295	9.317	2.809	-2.666	6
20:80	0.312	0.316	0.284	9.997	1.595	-4.927	6
100:0	0.352	0.345	0.355	13.864	5.528	2.523	7
100:0	0.351	0.343	0.355	13.698	5.378	2.779	7
100:0	0.347	0.342	0.353	12.998	5.995	2.765	7
100:0	0.346	0.336	0.352	12.481	4.792	4.116	7
100:0	0.346	0.334	0.347	12.655	3.809	3.696	7
100:0	0.335	0.327	0.341	10.641	4.596	4.233	7

Table S14. Fluorescence response patterns using the sensor array against the PFCPs mixtures of perfluorooctane sulfonate potassium (PFOS) and perfluorohexanoic acid (PFHxA) in food packing with different ratios (100:0, 80:20, 60:40, 50:50, 40:60, 20:80, and 0:100, respectively). LDA was carried out and resulting in 3 factors of the canonical scores and group generation. The concentration PFOS and PFHxA were 6.0 $\times 10^{-7}$ M.

PFOS:PFHxA	Fluorescence Response Pattern	Results LDA	Group

	C1	C2	C3	F1	F2	F3	
0:100	0.159	0.180	0.129	-17.375	-1.929	-0.130	1
0:100	0.159	0.176	0.129	-17.260	-1.923	-1.121	1
0:100	0.153	0.173	0.125	-18.637	-1.010	-0.331	1
0:100	0.151	0.168	0.124	-18.687	-0.903	-1.357	1
0:100	0.150	0.168	0.124	-19.093	-0.419	-0.991	1
0:100	0.149	0.167	0.105	-19.628	-5.813	-0.189	1
80:20	0.178	0.206	0.159	-14.028	1.769	1.603	2
80:20	0.176	0.205	0.153	-14.435	0.214	1.892	2
80:20	0.175	0.203	0.150	-14.714	-0.104	1.795	2
80:20	0.170	0.202	0.147	-16.035	0.910	2.990	2
80:20	0.167	0.193	0.144	-16.176	0.526	1.265	2
80:20	0.164	0.187	0.144	-16.447	1.174	0.119	2
60:40	0.223	0.236	0.223	-3.205	4.493	-3.386	3
60:40	0.216	0.234	0.212	-5.091	3.660	-1.750	3
60:40	0.215	0.233	0.211	-5.375	4.058	-1.654	3
60:40	0.208	0.231	0.206	-7.110	5.070	-0.451	3
60:40	0.207	0.219	0.205	-6.582	4.656	-3.522	3
60:40	0.203	0.219	0.205	-7.446	6.109	-2.834	3
50:50	0.253	0.284	0.238	1.224	-0.144	2.698	4
50:50	0.249	0.279	0.237	0.470	1.096	2.419	4
50:50	0.248	0.275	0.235	0.582	0.456	1.440	4
50:50	0.248	0.275	0.234	0.410	0.224	1.637	4
50:50	0.247	0.274	0.234	0.300	0.396	1.630	4
50:50	0.247	0.274	0.227	0.058	-1.538	1.956	4
40:60	0.295	0.308	0.265	10.745	-7.655	-1.087	5
40:60	0.289	0.308	0.260	9.217	-6.854	0.362	5
40:60	0.289	0.307	0.260	9.301	-6.957	0.030	5
40:60	0.288	0.291	0.259	10.057	-8.018	-3.855	5
40:60	0.286	0.290	0.257	9.455	-7.553	-3.492	5
40:60	0.282	0.290	0.253	8.564	-7.374	-2.707	5
20:80	0.315	0.339	0.299	14.175	-3.288	1.523	6
20:80	0.313	0.336	0.297	14.034	-3.386	1.164	6
20:80	0.311	0.336	0.296	13.346	-2.541	1.633	6
20:80	0.310	0.333	0.296	13.286	-2.566	1.225	6
20:80	0.309	0.330	0.292	13.297	-3.779	0.522	6
20:80	0.302	0.328	0.285	11.407	-2.815	2.044	6
100:0	0.329	0.355	0.350	17.602	8.025	0.379	7
100:0	0.327	0.354	0.342	16.939	6.366	1.109	7
100:0	0.320	0.343	0.340	16.049	7.663	-0.477	7
100:0	0.320	0.343	0.337	15.957	6.904	-0.405	7
100:0	0.319	0.339	0.337	15.910	7.114	-1.095	7
100:0	0.315	0.336	0.328	14.942	5.687	-0.603	7

Table S15. Comparison of different detection methods

Methods	Limit of detection (M)	Multiplexing ability	Sample source	Acquisition time (h)	Reference
Molecularly imprinted fluorescence sensor	10^{-8}	1	Water	0.5	[1]
Three-signal Assay	10^{-8}	1	Tap water	0.5	[2]
Fluorescence Detection	10^{-10}	1	Water samples	1.0	[3]
Fluorescent Visual Detection	10^{-8}	1	Environmental water	0.5	[4]
Fluorescence Detection	10^{-4}	2	-	-	[5]
UCNPs@SiO_2-F sensor array	10^{-7}	7	Tap water Food packing	0.5 1.0	This work

Reference:

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