

## Supplementary Materials

### Single-sensing-unit 3D quantum dot sensors for identification and differentiation of mucopolysaccharides

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**Table S1** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (0.4 μM).

**Table S2** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (0.8 μM).

**Table S3** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (1.2 μM).

**Table S4** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (1.6 μM).

**Table S5** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (2.0 μM).

**Fig. S1.** (a) TEM image of MPA-capped Mn-doped ZnS QDs. (b) XRD patterns of Mn-doped ZnS QDs. (c) XPS analysis results of Mn-doped ZnS QDs. (d) Ultraviolet (1) and RTP emission (2) spectra of Mn-doped ZnS QDs. (e) EDX of the Mn-doped ZnS QDs.

**Fig. S2.** (a) phosphorescence of Mn-ZnS QDs was gradually enhanced and (b) fluorescence of Mn-ZnS QDs was gradually weakened after the addition of PDC (0,  $1.4 \times 10^{-5}$  wt.%,  $2.8 \times 10^{-5}$  wt.%,  $5.6 \times 10^{-5}$  wt.%,  $8.4 \times 10^{-5}$  wt.%).

**Fig. S3.** Ultraviolet imaging of 4 types of MPSs in the concentrations of (a) 0.4 μM, (b) 1.2 μM, (c) 2.0 μM.

**Fig. S4.** (a) Fingerprints and (b) LDA plots of the 3D Mn-ZnS<sup>+</sup> QDs sensors in response to different types of MPSs (concentration of each type of MPS was 1.6 μM); (c) the 3D sensors used to differentiate different concentrations of Hep (0.8, 1.6 μM) in human urine.

**Table S1** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (0.4 μM).

sample name	Sample number	Ph (I-I <sub>0</sub> )/I <sub>0</sub>	FL (I-I <sub>0</sub> )/I <sub>0</sub>	RLS (I-I <sub>0</sub> )/I <sub>0</sub>	Discrimination result	Actual results
Hep	1	-0.451	0.299	0.150	1	1
	2	-0.449	0.289	0.131	1	1
	3	-0.452	0.303	0.222	1	1
	4	-0.463	0.307	0.144	1	1
	5	-0.465	0.250	0.198	1	1
	6	-0.430	0.238	0.156	1	1
Hya	7	-0.593	0.129	0.385	2	2
	8	-0.579	0.083	0.468	2	2
	9	-0.582	0.056	0.444	2	2
	10	-0.587	0.083	0.420	2	2
	11	-0.574	0.070	0.411	2	2
	12	-0.574	0.056	0.457	2	2
Der	13	-0.227	0.175	0.179	3	3
	14	-0.223	0.148	0.128	3	3
	15	-0.224	0.148	0.187	3	3
	16	-0.226	0.148	0.133	3	3
	17	-0.227	0.177	0.115	3	3
	18	-0.225	0.179	0.122	3	3
Cho	19	-0.525	0.101	0.197	4	4
	20	-0.509	0.049	0.131	4	4
	21	-0.497	0.160	0.223	4	4
	22	-0.532	0.160	0.254	4	4
	23	-0.535	0.176	0.164	4	4
	24	-0.528	0.192	0.132	4	4

**Table S2** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (0.8 μM).

sample name	Sample number	Ph (I-I <sub>0</sub> )/I <sub>0</sub>	FL (I-I <sub>0</sub> )/I <sub>0</sub>	RLS (I-I <sub>0</sub> )/I <sub>0</sub>	Discrimination result	Actual results
Hep	1	-0.568	0.506	0.244	1	1
	2	-0.544	0.539	0.289	1	1
	3	-0.559	0.526	0.267	1	1
	4	-0.555	0.560	0.251	1	1
	5	-0.557	0.450	0.278	1	1
	6	-0.523	0.438	0.286	1	1
Hya	7	-0.702	0.157	0.504	2	2
	8	-0.714	0.167	0.589	2	2
	9	-0.685	0.097	0.589	2	2
	10	-0.702	0.111	0.534	2	2
	11	-0.709	0.127	0.519	2	2
	12	-0.701	0.155	0.528	2	2
Der	13	-0.388	0.400	0.115	3	3
	14	-0.387	0.407	0.304	3	3
	15	-0.381	0.444	0.227	3	3
	16	-0.393	0.420	0.147	3	3
	17	-0.384	0.456	0.078	3	3
	18	-0.376	0.487	0.173	3	3
Cho	19	-0.603	0.228	0.245	4	4
	20	-0.604	0.183	0.243	4	4
	21	-0.586	0.293	0.302	4	4
	22	-0.604	0.307	0.315	4	4
	23	-0.617	0.324	0.224	4	4
	24	-0.612	0.384	0.192	4	4

**Table S3** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (1.2 μM).

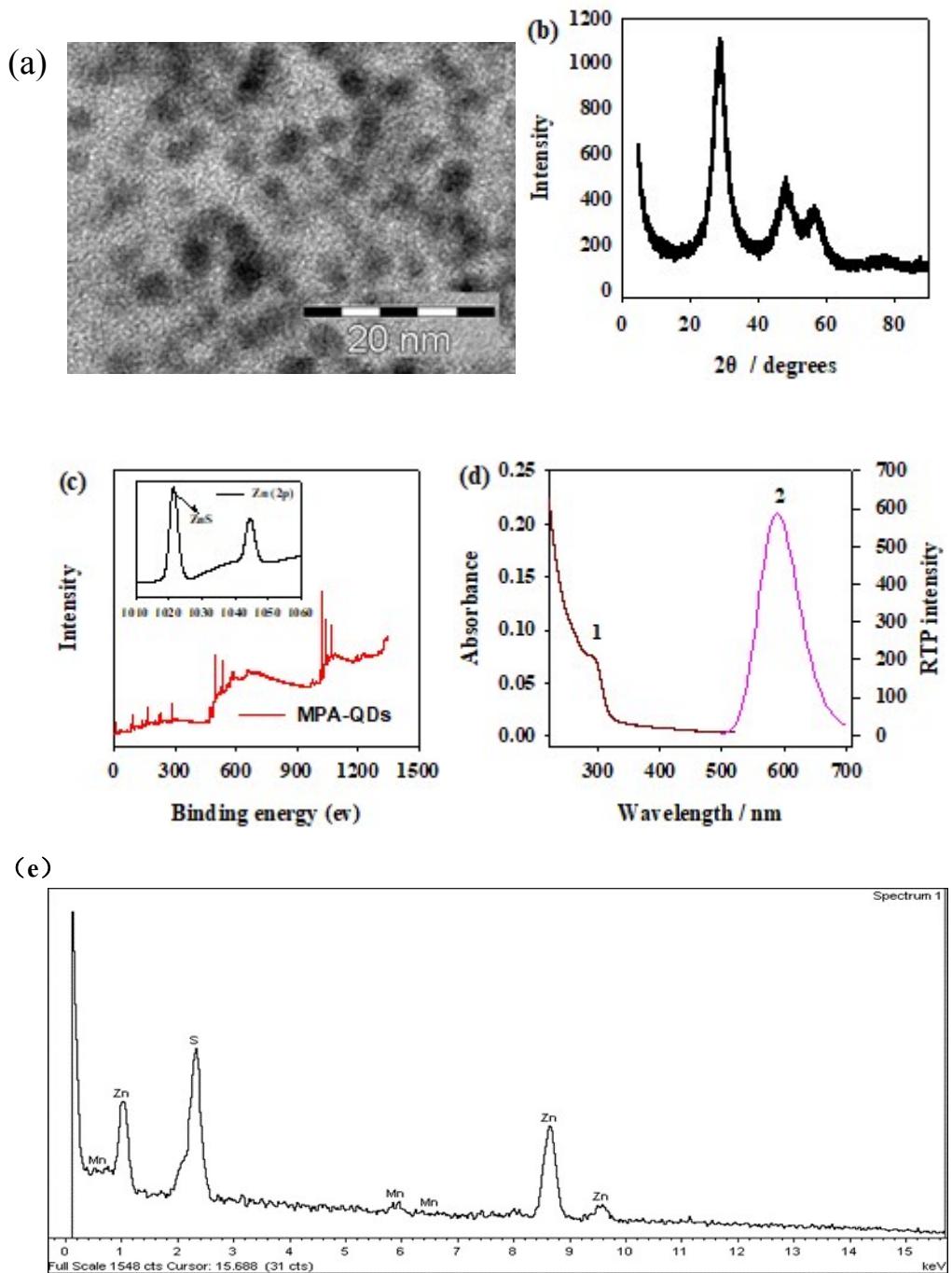
sample name	Sample number	Ph (I-I <sub>0</sub> )/I <sub>0</sub>	FL (I-I <sub>0</sub> )/I <sub>0</sub>	RLS (I-I <sub>0</sub> )/I <sub>0</sub>	Discrimination result	Actual results
Hep	1	-0.600	0.649	0.331	1	1
	2	-0.599	0.684	0.397	1	1
	3	-0.600	0.658	0.318	1	1
	4	-0.609	0.680	0.321	1	1
	5	-0.613	0.575	0.394	1	1
	6	-0.589	0.538	0.346	1	1
Hya	7	-0.776	0.343	0.593	2	2
	8	-0.765	0.278	0.629	2	2
	9	-0.765	0.347	0.621	2	2
	10	-0.771	0.306	0.565	2	2
	11	-0.767	0.296	0.543	2	2
	12	-0.763	0.296	0.543	2	2
Der	13	-0.461	0.525	0.153	3	3
	14	-0.461	0.519	0.167	3	3
	15	-0.462	0.531	0.131	3	3
	16	-0.462	0.531	0.150	3	3
	17	-0.451	0.544	0.165	3	3
	18	-0.468	0.577	0.226	3	3
Cho	19	-0.626	0.443	0.517	4	4
	20	-0.644	0.439	0.393	4	4
	21	-0.632	0.533	0.437	4	4
	22	-0.635	0.573	0.495	4	4
	23	-0.642	0.541	0.403	4	4
	24	-0.647	0.562	0.383	4	4

**Table S4** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (1.6 μM).

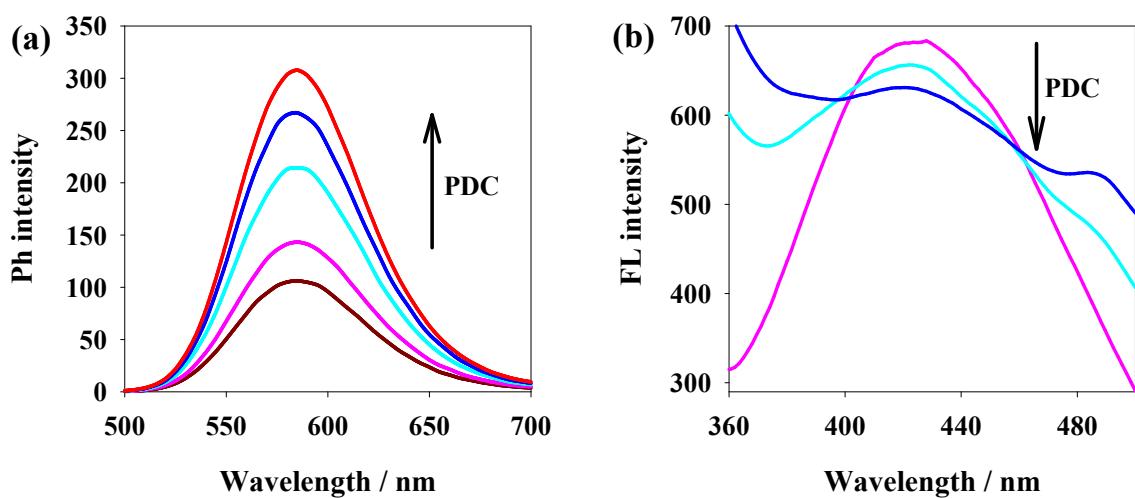
sample name	Sample number	Ph (I-I <sub>0</sub> )/I <sub>0</sub>	FL (I-I <sub>0</sub> )/I <sub>0</sub>	RLS (I-I <sub>0</sub> )/I <sub>0</sub>	Discrimination result	Actual results
Hep	1	-0.618	0.987	0.419	1	1
	2	-0.617	1.039	0.420	1	1
	3	-0.623	0.934	0.369	1	1
	4	-0.628	1.053	0.332	1	1
	5	-0.618	0.913	0.283	1	1
	6	-0.608	0.925	0.346	1	1
Hya	7	-0.830	0.429	0.467	2	2
	8	-0.830	0.389	0.605	2	2
	9	-0.834	0.403	0.637	2	2
	10	-0.823	0.431	0.565	2	2
	11	-0.823	0.423	0.558	2	2
	12	-0.826	0.423	0.567	2	2
Der	13	-0.485	0.688	0.179	3	3
	14	-0.487	0.630	0.292	3	3
	15	-0.488	0.654	0.149	3	3
	16	-0.498	0.617	0.204	3	3
	17	-0.484	0.696	0.140	3	3
	18	-0.494	0.679	0.223	3	3
Cho	19	-0.670	0.658	0.511	4	4
	20	-0.664	0.610	0.455	4	4
	21	-0.650	0.707	0.535	4	4
	22	-0.671	0.747	0.518	4	4
	23	-0.673	0.770	0.328	4	4
	24	-0.676	0.781	0.407	4	4

**Table S5** Results of Array Sensors Based on Mn-ZnS<sup>+</sup> QDs in Response to Four Mucopolysaccharides (2.0 μM).

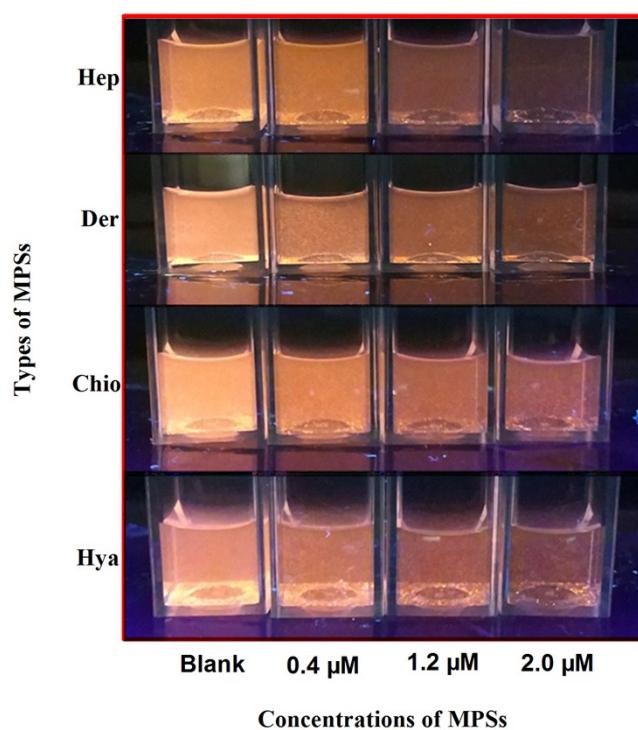
sample name	Sample number	Ph (I-I <sub>0</sub> )/I <sub>0</sub>	FL (I-I <sub>0</sub> )/I <sub>0</sub>	RLS (I-I <sub>0</sub> )/I <sub>0</sub>	Discrimination result	Actual results
Hep	1	-0.643	1.234	0.522	1	1
	2	-0.640	1.289	0.483	1	1
	3	-0.650	1.237	0.509	1	1
	4	-0.650	1.280	0.473	1	1
	5	-0.649	1.188	0.550	1	1
	6	-0.631	1.150	0.521	1	1
Hya	7	-0.839	0.600	0.711	2	2
	8	-0.855	0.597	0.742	2	2
	9	-0.846	0.611	0.790	2	2
	10	-0.859	0.583	0.809	2	2
	11	-0.861	0.690	0.837	2	2
	12	-0.864	0.620	0.787	2	2
Der	13	-0.513	0.863	0.332	3	3
	14	-0.504	0.852	0.253	3	3
	15	-0.517	0.852	0.251	3	3
	16	-0.514	0.852	0.215	3	3
	17	-0.511	0.886	0.265	3	3
	18	-0.506	0.923	0.220	3	3
Cho	19	-0.693	0.924	0.520	4	4
	20	-0.691	0.854	0.452	4	4
	21	-0.686	0.907	0.509	4	4
	22	-0.694	0.907	0.482	4	4
	23	-0.697	0.905	0.418	4	4
	24	-0.698	0.945	0.380	4	4



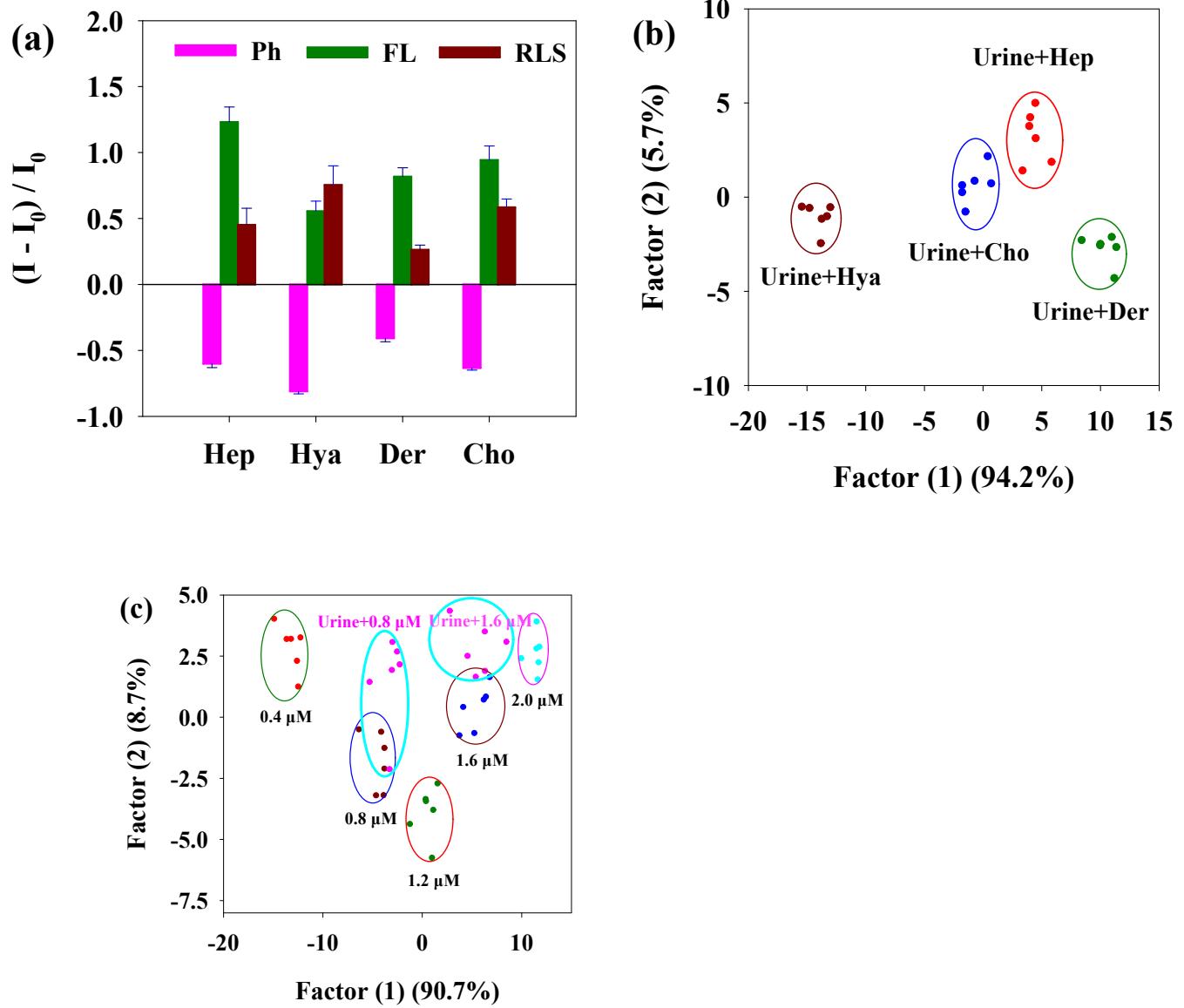
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**Fig. S3.** Ultraviolet imaging of 4 types of MPSs in the concentrations of (a) 0.4  $\mu$ M, (b) 1.2  $\mu$ M, (c) 2.0  $\mu$ M.



**Fig. S4.** (a) Fingerprints and (b) LDA plots of the 3D Mn-ZnS<sup>+</sup> QDs sensors in response to different types of MPSs (concentration of each type of MPS was 1.6  $\mu\text{M}$ ); (c) the 3D sensors used to differentiate different concentrations of Hep (0.8, 1.6  $\mu\text{M}$ ) in human urine.