

Supplementary Materials

Molecularly Imprinted Polymer-Coated CdTe Quantum Dots for Fluorometric Detection of Sulfonamide Antibiotics in Food Samples

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S.1. The structural formula of sulfadiazine (SDZ) can be found in Figure S1 below.

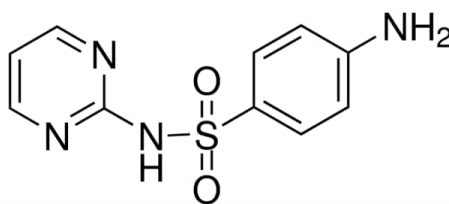


Figure S1. Structural formula of sulfadiazine.

S.2. A CdTe Fourier-transform infrared spectroscopy (FTIR) was also performed in order to understanding the QD@MIP synthesis process. The figure S2 shows the spectra of the pure MPA reagent and the CdTe quantum dot coated with MPA, their bands were studied according to reports in the literature. For the pure MPA reagent: as can be clearly observed, there is a long band in 1700 cm⁻¹, this band corresponds to the C=O stirring in the carboxylic acid; the big band on the 3200-2500 cm⁻¹ corresponds to the S-H stirring group and the bands on 1400 and 1250 cm⁻¹ are for the CH₂ groups. For the CdTe quantum dot: the 1556 cm⁻¹ corresponds to the COO⁻ formed when the MPA coats the nanocrystal, as previously explained in the previous section S.1, the MPA thiol group interacts with the CdTe crystal and the COO⁻ group at the opposite molecule side becomes the new CdTe coated surface. Comparing with the QD@MIP spectra shown in Figure 4, it is observed that these peaks disappear after polymerization, proving that, during the synthesis process, the printed polymer completely covers the entire surface of the quantum dot.

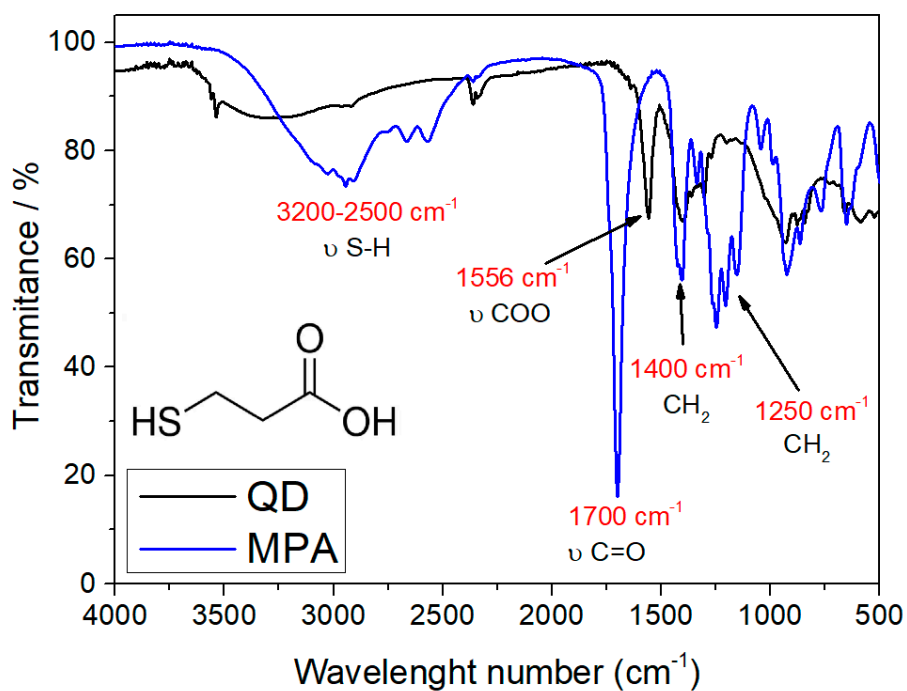


Figure S1. Infrared spectra of QdTe and MPA with their structural formula inserted.

Table S1. Repeatability values calculated for the QD@MIP and QD@NIP with the average (n=10), standard deviation and RSD values.

| Concentration (ppm) | MIP | | | NIP | | |
|---------------------|----------------|-------|---------|----------------|-------|---------|
| | Average (n=10) | Error | RSD (%) | Average (n=10) | Error | RSD (%) |
| 10 | 1.548 | 0.077 | 4.956 | 0.415 | 0.101 | 24.30 |
| 20 | 2.308 | 0.054 | 2.348 | 1.057 | 0.062 | 5.879 |
| 30 | 3.058 | 0.076 | 2.471 | 1.671 | 0.072 | 4.295 |
| 40 | 3.464 | 0.057 | 1.648 | 1.994 | 0.071 | 3.582 |
| 50 | 3.783 | 0.050 | 1.317 | 2.374 | 0.066 | 2.765 |
| 60 | 4.050 | 0.036 | 0.896 | 2.568 | 0.060 | 2.341 |

Table S2. Reproducibility values obtained for the QD@MIP and QD@NIP (with the average (n=3), standard deviation, and RSD values).

| Concentration (ppm) | MIP | | | NIP | | |
|---------------------|---------------|-------|---------|---------------|-------|---------|
| | Average (n=3) | Error | RSD (%) | Average (n=3) | Error | RSD (%) |
| 10 | 3.771 | 0.079 | 2.108 | 0.789 | 0.135 | 17.13 |
| 20 | 4.445 | 0.021 | 0.465 | 1.461 | 0.099 | 6.770 |
| 30 | 5.200 | 0.140 | 2.689 | 1.918 | 0.107 | 5.587 |
| 40 | 5.773 | 0.202 | 3.505 | 2.226 | 0.105 | 4.728 |
| 50 | 6.539 | 0.292 | 4.464 | 2.422 | 0.095 | 3.939 |
| 60 | 7.227 | 0.340 | 4.699 | 2.602 | 0.124 | 4.785 |

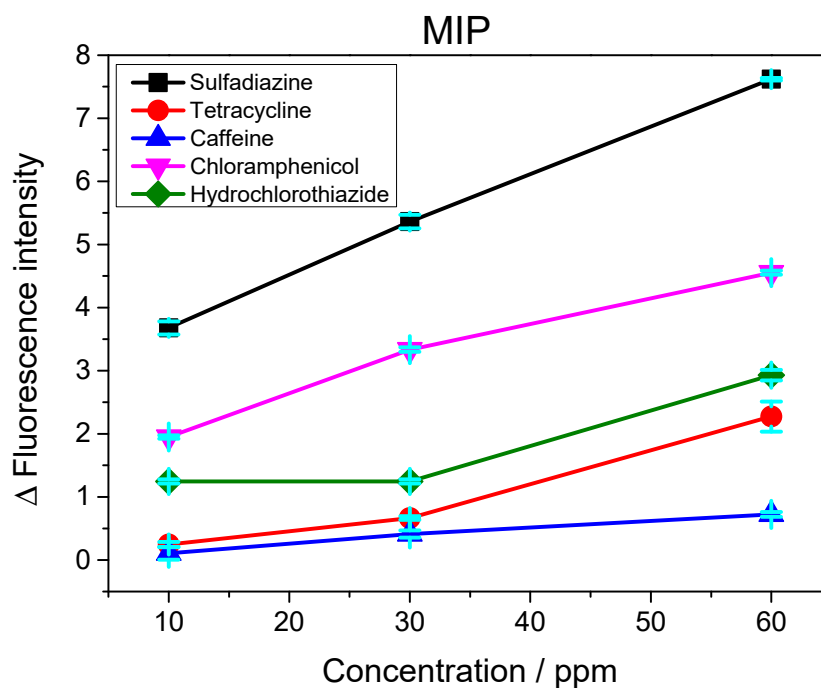


Figure S3. Plot of curves of fluorescence variation as a function of concentration (10, 30 and 60 ppm) of sulfadiazine and interferences for the QD@MIP sensor.

Table S3. Comparison of the proposed QD@MIP sensor with the sensors previously reported in the literature using the SDZ as analyte.

| Probe | LOD (ppm) | Sample | Method | Ref. |
|------------------------------------|----------------------|---|--------------------------|------|
| QD@MIP (CdTe) | 0.002 | sea water | fluorescence | [33] |
| ZnO-Co ₃ O ₄ | 3.0 10 ⁻⁴ | pork meat, human urine, and river water | photoelectrochemical | [34] |
| MIPs@CQDs@PN | 1.0 | tap water | fluorescence | [35] |
| CQD@MIP | 0.01 | tap water and milk | ratiometric fluorescence | [36] |
| MIPs@QDs@PMMA-Ns | 0.06 | tap water | fluorescence | [37] |
| QD@MIP (CdTe) | 3.33 | milk, honey and egg | fluorescence | - |

CQD = Carbon quantum dot; PNs = poly(methyl methacrylate) nanoparticles; PMMA-Ns = poly(methyl methacrylate) nanospheres

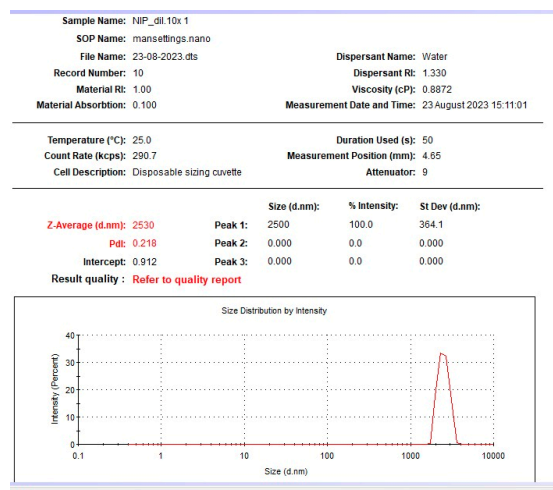
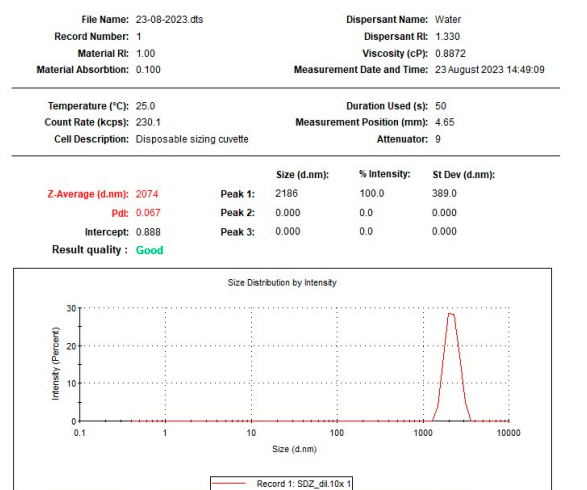


Figure S4. DLS spectras for Both QD@MIP and QD@NIP are given below in which Z-average (d.nm) for QD@MIP is 2074 while for QD@NIP is 2530.