Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting information for

Enhanced fluorescence detection of enrofloxacin with curved-surface responsive inverse opal polymers and molecular imprinting

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1. Photographs of silica crystals

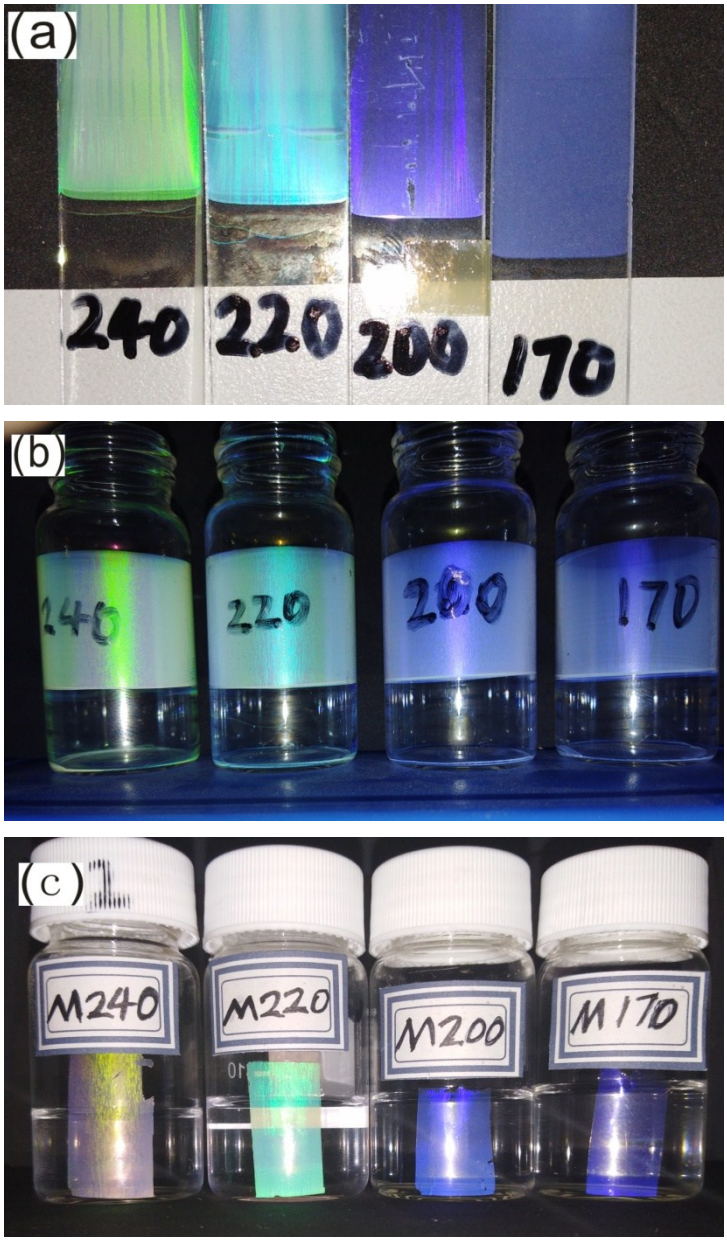

Figure S1 Photographs of silica crystals (a) on planar slides, (b) on the inner face of bottles, and (c) RIOPs in ACN/NAc (v/v, 50/50, pH5.5)

2. Photographs of silica crystals

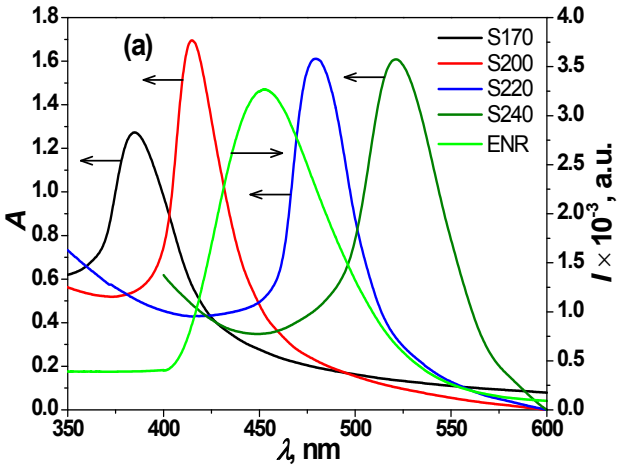

Figure S2 UV-VIS absorption spectra silica moldings on glass slides and ENR emission

3. Setup of fluorescence measurement

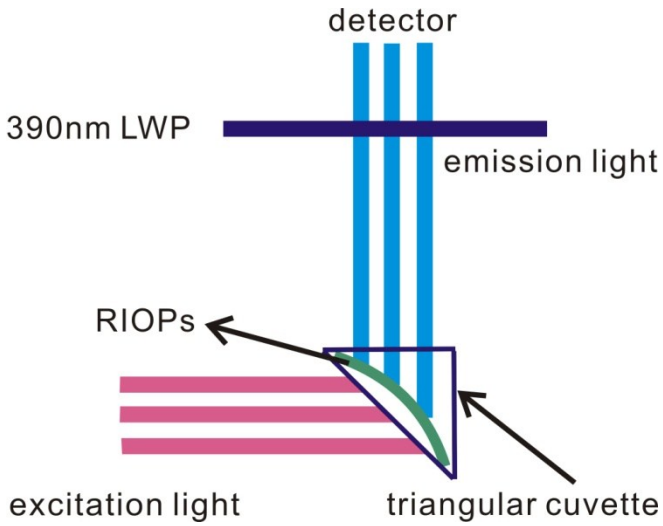

Figure S3 Scheme of fluorescence measurement **s**etup

4. Absorption of enrofloxacin

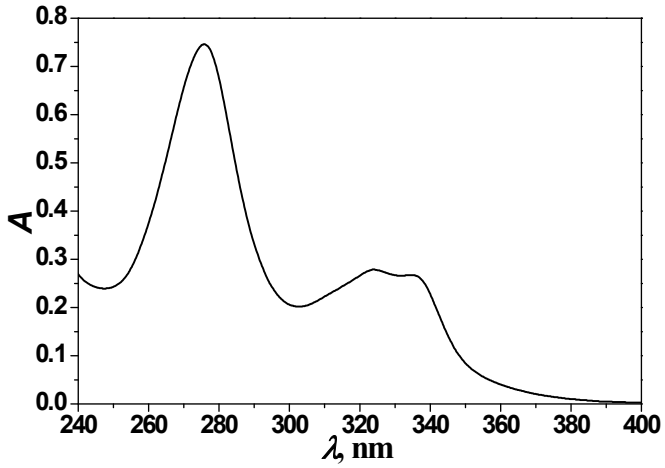

Figure S4 UV-Vis absorption of enrofloxacin in ACN/NAc (v/v, 50/50, pH5.5)

5. Absorption spectrum of MIM and NIM

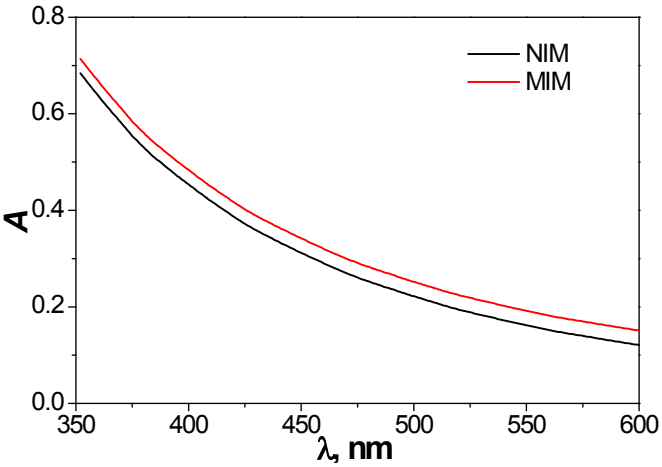

Figure S5 UV-Vis absorption of NIM and MIM in ACN/NAc (v/v, 50/50, pH5.5)

6. Structures of enrofloxacin and analogues and absorption spectrum of ENR

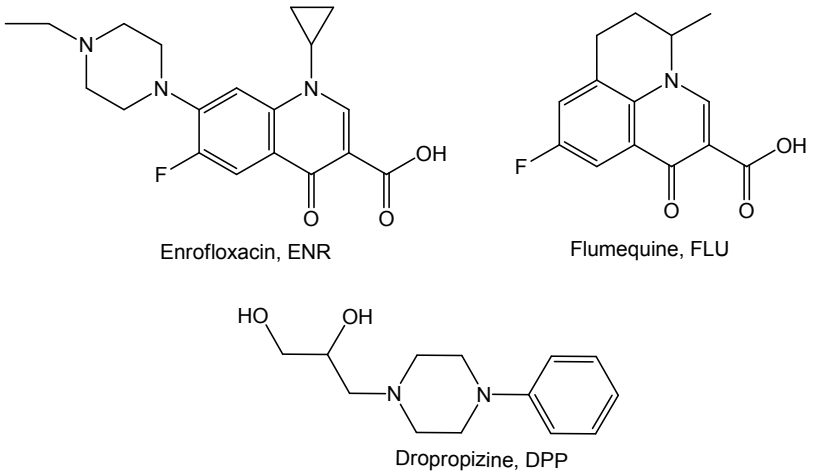

Figure S6 Structure of enrofloxacin (ENR), flumequine (FLU) and dropropizine (DPP)

7. Bulk polymer preparation

The polymer composition is the same as the RIOPs. After dissolving the monomers, oxygen was removed from the solution by purging it with nitrogen during 15 min. The glass tube was then sealed and polymerisation was allowed to proceed thermally by placing the tube in an oven set at 60 °C for 24 h. The MIP was crushed and sieved afterwards, and particles in the size range 74–200 μm were collected. Soxlet extraction was performed to fully remove templates with methanol containing 10% (v/v) acetic acid. Then they were washed several times with methanol to fully remove acetic acid. Afterwards, the polymers were vacuum dried at 60 °C for 24 hours. Non-imprinted polymers (NIP) were prepared and cleaned the same way as MIP but without the addition of DPP.

8. Batch sorption and sorption isotherm

In detail, about 20mg of polymer was weighed and filled into a 5mL polypropylene vial. Then 2mL DPP in ACN/NAc buffer was added. The vial was then sealed and incubated at 25 °C for 12h. After rebinding was over, the supernatants in each vial were filtered with a 0.22μm Nylon filter and the template in the supernatent was measured with UHPLC (Agilent 1290).

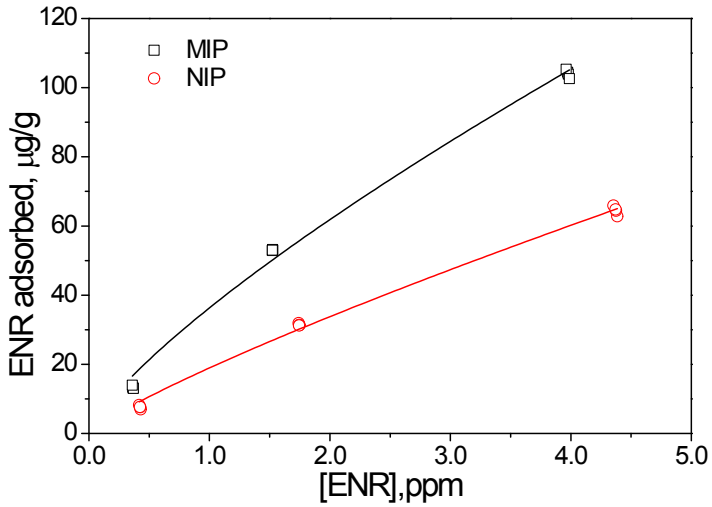

Figure S7. ENR adsorbed on MIP and NIP

9. Absorption and emission spectrums of enrofloxacin and analogues

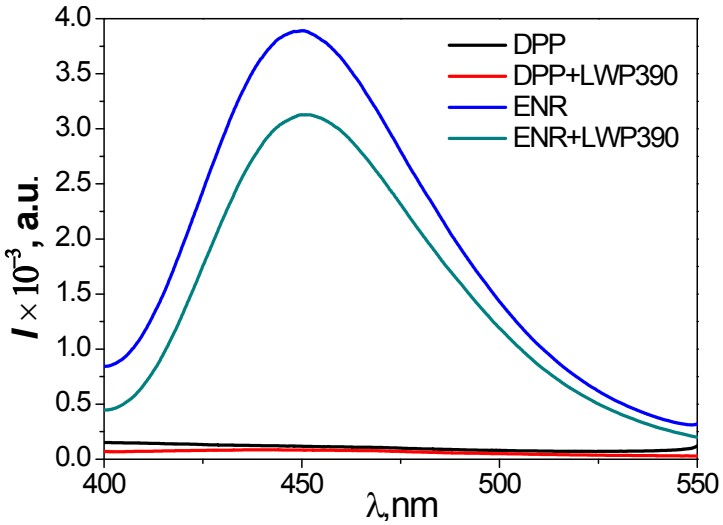

Figure S8 Emission of enrofloxacin (ENR, 500ppb) and dropropizine (DPP, 500ppb) ACN/NAc (v/v, 50/50, pH5.5) under the fluorescence measurement setup with a 390nm long-wave pass (LWP) filter

10. Absorption spectra of M220 in different solvents and buffers

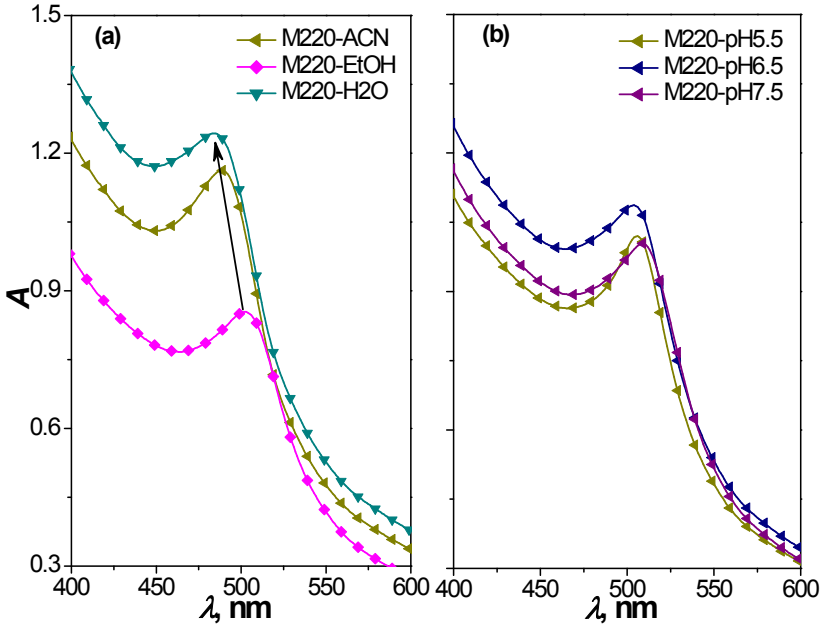

Figure S9 Absorption spectra of M220 in solvents (a) and ACN/buffers (b)

11. Response time of M220

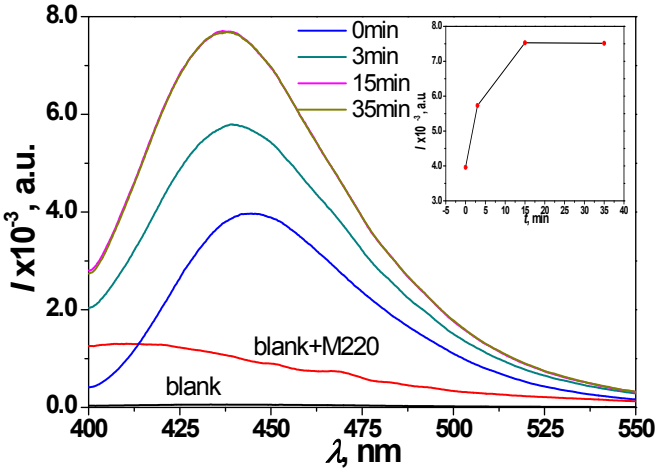

Figure S10 Emission of blank solution, ENR with M220, and blank solution with M220 (Inset: emission intensity at 443nm as a function of time after incubation with M220)

12. Emission spectrums of enrofloxacin with and without M220

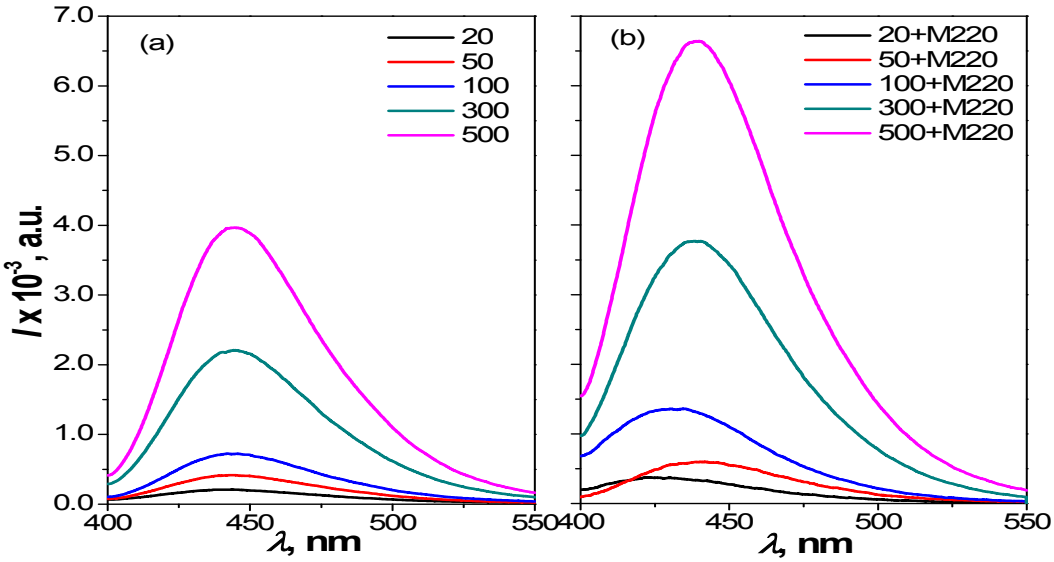

Figure S11 ENR emission without (a) and with (b) M220 in ACN:NAc (50:50, v/v)

13. Limit of detection of ENR

Table S1 Limit of detection of ENR

	M220 with blank solution		Blank solution	
	I, a.u.	[ENR], ppb	*I*, a.u.	[ENR], ppb
1	560.7	45.8	37.1	5.74
2	557.8	45.6	38.6	5.93
3	553.1	45.2	39.8	6.09
3	560.9	45.8	39.8	6.08
5	567.1	46.3	41.5	6.31
6	561.0	45.9	41.1	6.25
σ	4.61	0.35	1.61	0.21

DL	—	0.082	—	0.080

14. Comparison of imprinted RIOP and other analytical systems

Table S2 Comparison between current analytical systems for antibiotics determination

No.	Target	Sensing platform	Limit of Detection	Ref.
1	Amoxicillin	Surface Plasmon resonance	73 pM	[1]
2	Amoxicillin	Quartz crystal microbalance	0.2 nM	[2]
3	Sulfamethizole	Surface acoustic wave	1.7 nM	[3]
4	Levofloxacin	Electrochemical	530 nM	[4]
5	Flumequine	Surface Acoustic Wave	1000 nM	[5]
6	Sulfadimethoxine	Electrochemical	70000 nM	[6]
7	Enrofloxacin	Raman Scattering	1.5 nM	[7]
8	Enrofloxacin	Fluorescence	228 nM	this work

Reference

[1] A.G. Ayankojo, J. Reut, A. Öpik, A. Furchner, V. Syritski, Hybrid molecularly imprinted polymer for amoxicillin detection, Biosens. Bioelectron. 118 (2018) 102–107. doi:10.1016/J.BIOS.2018.07.042.

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