Supplementary information

Developing a novel magnetic organic polymer for selective extraction and determination of 16 macrolides in water and honey samples

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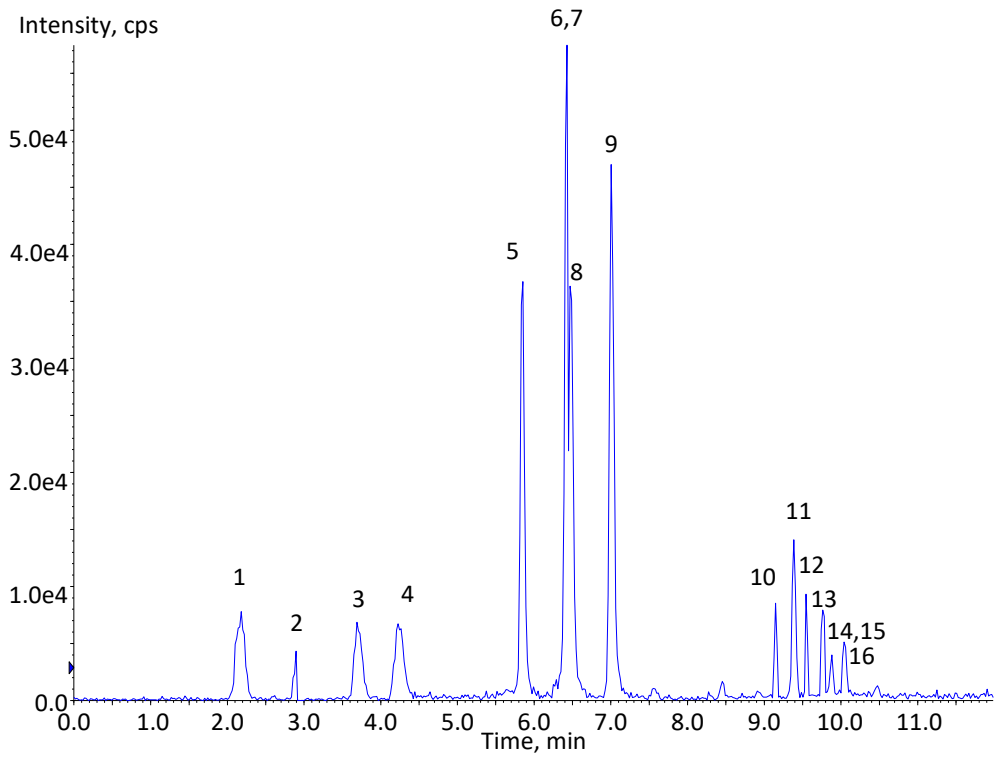

Fig. S1 The MRM chromatograms of 16 MALs (0.2 μg·L^{-1}). 1. Clindamycin, 2. Tilmicosin, 3. Oleandomycin, 4.Erythromycin, 5. Anhydroerythromycin A, 6. Clarithromycin 7. Roxithromycin, 8. Erythromycin A enol ether, 9. Oleandomycin triacetate, 10. Eprinomectin, 11. Avermectin, 12. Dolamectin, 13. Ememectin, 14. Serramectin, 15. Ivermectin 16. Moximycin

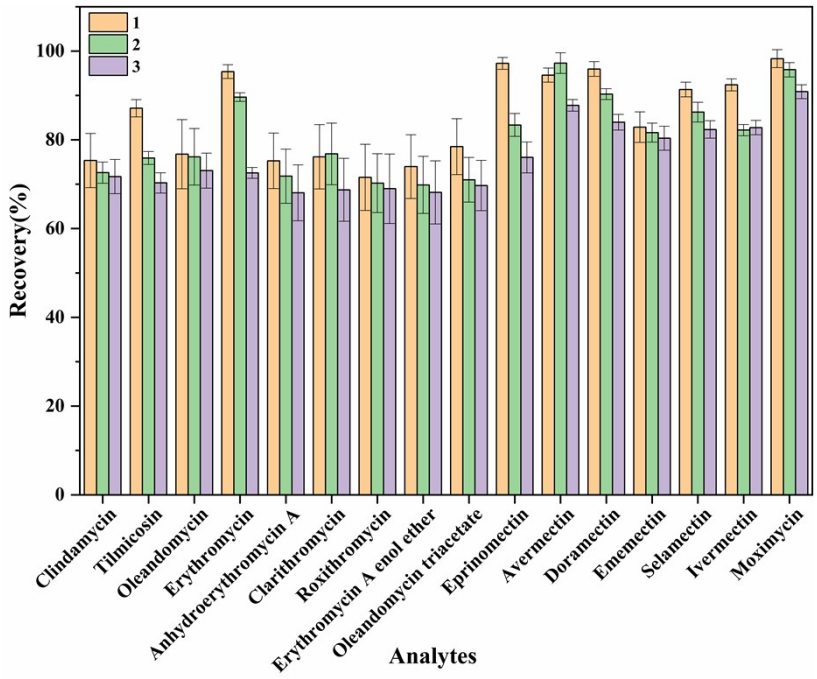

Fig. S2 The reusability of Fe_3O_4@SiO_2@Tb-PDAN.

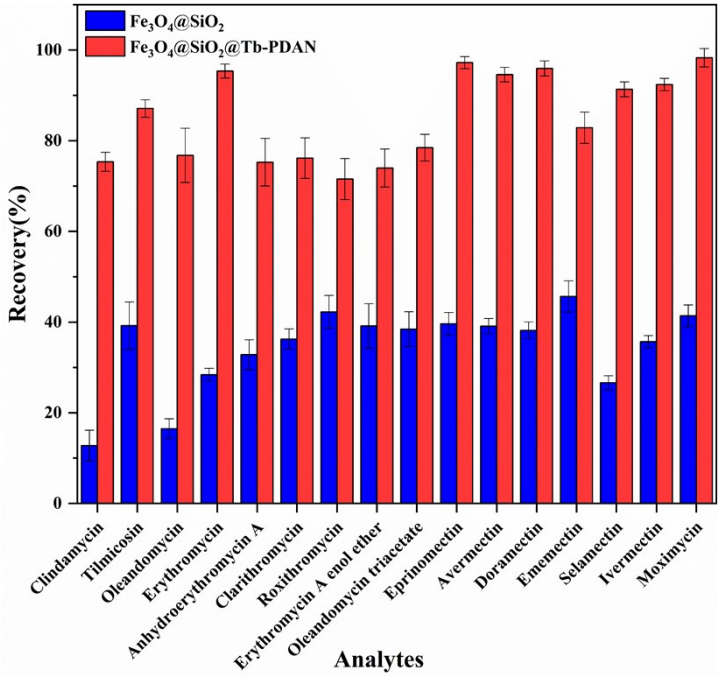

Fig. S3 Comparison of extraction efficiency among Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2@Tb-PDAN.

Table S1 The standard information of 16 MALs

Analytes	CAS	Molecular formula	Purity (%)
Clindamycin	18323-44-9	$C_{18}H_{33}ClN_2O_5S$	94.1
Tilmicosin	108050-54-0	$C_{46}H_{80}N_2O_{13}$	80.7
Oleandomycin	3922-90-5	$C_{35}H_{61}NO_{12}$	95.0
Erythromycin	114-07-8	$C_{37}H_{67}NO_{13}$	95.0
Anhydroerythromycin A	23893-13-2	$C_{37}H_{65}NO_{12}$	97.0
Clarithromycin	81103-11-9	$C_{38}H_{69}NO_{13}$	98.9
Roxithromycin	80214-83-1	$C_{41}H_{76}NO_{15}$	96.2
Erythromycin A enol ether	33396-29-1	$C_{37}H_{65}NO_{15}$	96.0
Oleandomycin triacetate	2751-09-9	$C_{41}H_{67}NO_{15}$	97.0
Eprinomectin	123997-26-2	$C_{50}H_{75}Cl_2N_2O_5$	99.5
Avermectin	71751-41-2	$C_{49}H_{74}O_{14}$	98.0
Doramectin	117704-25-3	$C_{50}H_{74}O_{14}$	96.0
Ememectin	119791-41-2	$C_{49}H_{77}NO_{13}$	98.3
Selamectin	220119-17-5	$C_{43}H_{63}NO_{11}$	96.5
Ivermectin	70288-86-7	$C_{48}H_{74}O_{14}$	98.5
Moximycin	113507-06-5	$C_{37}H_{53}NO_8$	96.0

Table S2 Mass spectrometry conditions of 16 MALs

Analytes	RT[a] (min)	Precursor ion(m/z)	Ion mode	DP[b]（V）	Product ion(m/z)	CE[c]（eV）
Clindamycin	2.20	425.3	$[M+H]^+$	95.9/137.6	126.2*/277.3	34.2/26.9
Tilmicosin	2.83	869.6	$[M+H]^+$	70.9/67.4	696.5*/174.0	59.7/58.3
Oleandomycin	3.77	688.4	$[M+H]^+$	102.8/106.9	544.5*/158.2	23.0/34.9
Erythromycin	4.33	734.5	$[M+H]^+$	11.1/10.5	158.2*/576.6	38.1/27.6
Anhydroerythromycin A	5.93	716.5	$[M+H]^+$	88.1/107.0	558.4*/158.3	22.5/38.1
Clarithromycin	6.47	748.5	$[M+H]^+$	104.0/116.1	158.1*/590.4	35.7/27.1
Roxithromycin	6.47	837.6	$[M+H]^+$	109.3/119.1	679.5*/158.2	30.2/40.2
Erythromycin A enol ether	6.54	716.5	$[M+H]^+$	101.7/106.0	558.4*/158.2	24.3/38.1
Oleandomycin triacetate	7.13	772.4	$[M-COCH_3+2H]^+$	124.2/127.3	158.2*/586.4	30.7/27.0
Eprinomectin	9.13	914.5	$[M+H]^+$	200.2/164.1	186.0*/330.2	23.2/20.6
Avermectin	9.38	890.5	$[M+NH_4]^+$	84.0/99.9	305.1*,567.3	34.5/19.3
Doramectin	9.55	916.5	$[M+NH_4]^+$	80.7/95.1	331.3*/593.3	34.3/19.4
Ememectin	9.79	886.4	$[M+H]^+$	65.9/65.9	158.2*/126.1	42.1/40.1
Selamectin	9.85	770.5	$[M+H]^+$	14.1/14.0	608.5*/626.0	28.1/24.1
Ivermectin	9.87	892.7	$[M+NH_4]^+$	97.2/101.0	569.5*/307.0	20.1/30.8
Moximycin	10.02	640.3	$[M+H]^+$	30.9/66.1	528.4*/498.0	12.6/18.8

* Quantitative ion; [a] Retention time; [b] Declustering potential; [c] Collision energy

Table S3 Matrix effects of 16 MALs

Analytes	Matrix effect(%)	
	Water Sample	Honey Sample
Clindamycin	101.93	109.21
Tilmicosin	107.13	80.02
Oleandomycin	94.75	105.18
Erythromycin	110.51	106.18
Anhydroerythromycin A	91.81	100.06
Clarithromycin	100.14	113.56
Roxithromycin	99.97	118.03
Erythromycin A enol ether	99.89	102.26
Oleandomycin triacetate	109.26	90.83
Eprinomectin	85.90	93.81
Avermectin	116.41	118.93
Doramectin	106.75	89.68
Ememectin	94.62	96.06
Selamectin	117.58	91.41
Ivermectin	113.61	119.71
Moximycin	113.67	118.96

Table S4 Analytical performance of the proposed method for analysis of MALs

Analytes	Linear Range ($\mu g \cdot L^{-1}$)	Linearity equation	r	Water sample		Honey sample	
				LODs ($\mu g \cdot L^{-1}$)	LOQs ($\mu g \cdot L^{-1}$)	LODs ($\mu g \cdot kg^{-1}$)	LOQs ($\mu g \cdot kg^{-1}$)
Clindamycin	0.1-200	Y=190061.0X+30610.4	0.9999	0.011	0.037	0.367	1.222
Tilmicosin	0.1-200	Y=4185.8X+74.3	0.9992	0.001	0.003	0.001	0.003
Oleandomycin	0.1-200	Y=118229.0X+29043.2	0.9996	0.002	0.007	0.003	0.009
Erythromycin	0.1-200	Y=144979.0X+29470.2	0.9998	0.011	0.037	0.006	0.021
Anhydroerythromycin A	0.1-200	Y=232197.0X+103703.0	0.9996	0.001	0.003	0.017	0.056
Clarithromycin	0.1-200	Y=256965.0X+370068.0	0.9997	0.003	0.009	0.004	0.014
Roxithromycin	0.1-200	Y=244337.0X+317678.0	0.9993	0.002	0.005	0.011	0.037
Erythromycin A enol ether	0.1-200	Y=152140.0X+140922.0	0.9991	0.001	0.002	0.008	0.028
Oleandomycin triacetate	0.1-200	Y=470647.0X+623192.0	0.9997	0.001	0.004	0.007	0.023
Eprinomectin	0.1-200	Y=885.9X+2302.8	0.9992	0.005	0.017	0.002	0.006
Avermectin	0.1-200	Y=8479.8X+3263.5	0.9999	0.008	0.028	0.007	0.025
Doramectin	0.1-200	Y=4869.1X+463.6	0.9991	0.012	0.038	0.001	0.003
Ememectin	0.1-200	Y=101868.0X+110624	0.9997	0.001	0.005	0.002	0.007
Selamectin	0.1-200	Y=19167.3X+1716.1	0.9999	0.008	0.025	0.006	0.020
Ivermectin	0.1-200	Y=7459.3X+5422.1	0.9994	0.008	0.026	0.013	0.043
Moximycin	0.1-200	Y=62952.8X+65484.1	0.9993	0.001	0.002	0.004	0.014

Table S5 Adsorption rate of loading of Tb-PDAN in different concentration to Fe_3O_4@SiO_2

Analytes	Adsorption rate (%)		
	Low[a]	Medium[b]	High[c]
Clindamycin	26.73	71.74	74.29
Tilmicosin	54.20	87.28	84.57
Oleandomycin	38.48	78.81	75.81
Erythromycin	50.39	95.49	94.14
Anhydroerythromycin A	48.60	72.03	71.34
Clarithromycin	55.23	74.69	70.89
Roxithromycin	61.25	71.86	72.35
Erythromycin A enol ether	58.65	73.98	70.82
Oleandomycin triacetate	62.48	78.19	79.94
Eprinomectin	56.16	94.90	96.32
Avermectin	58.09	95.96	94.33
Doramectin	57.16	93.90	92.10
Ememectin	54.66	81.14	80.14
Selamectin	38.53	90.95	92.38
Ivermectin	59.68	95.24	92.95
Moximycin	58.40	96.10	95.18

[a] Tb (26.0 mg), PDAN (37.5 mg), Fe_3O_4@SiO_2 (100 mg); [b] Tb (51.9 mg), PDAN (75.0 mg), Fe_3O_4@SiO_2 (100 mg);[c] Tb (103.8 mg), PDAN (150.0 mg), Fe_3O_4@SiO_2 (100 mg)

Table S6 Adsorption of different types of analytes with Fe_3O_4@SiO_2@Tb-PDAN

Analytes		Log K_{ow}[a]	Recovery (%)
MALs	Clindamycin	1.83	75.33
	Tilmicosin	4.95	87.11
	Oleandomycin	1.23	76.76
	Erythromycin	2.83	95.37
	Anhydroerythromycin A	3.93	75.27
	Clarithromycin	3.16	76.17
	Roxithromycin	3.73	71.54
	Erythromycin A enol ether	3.81	73.96
	Oleandomycin triacetate	3.36	78.46

	Eprinomectin	6.22	97.23
	Avermectin	6.51	94.58
	Doramectin	7.16	95.96
	Ememectin	6.84	82.86
	Selamectin	6.61	91.33
	Ivermectin	6.83	92.38
	Moximycin	8.43	98.29
QNs	Ofloxacin	0.84	27.86
	Tosufloxacin	1.22	31.23
β-LAs	Ticarcillin	0.69	2.51
	Amoxicillin	0.61	3.16
	Ceftizoxime	0.59	5.26
SAs	Sulfathiazole	0.05	0.84
	Sulfapyridine	0.03	1.49
	Sulfacetamide	0.07	0.71

[a] $LogK_{ow}$: octanol/water partition coefficient.