Supporting Information

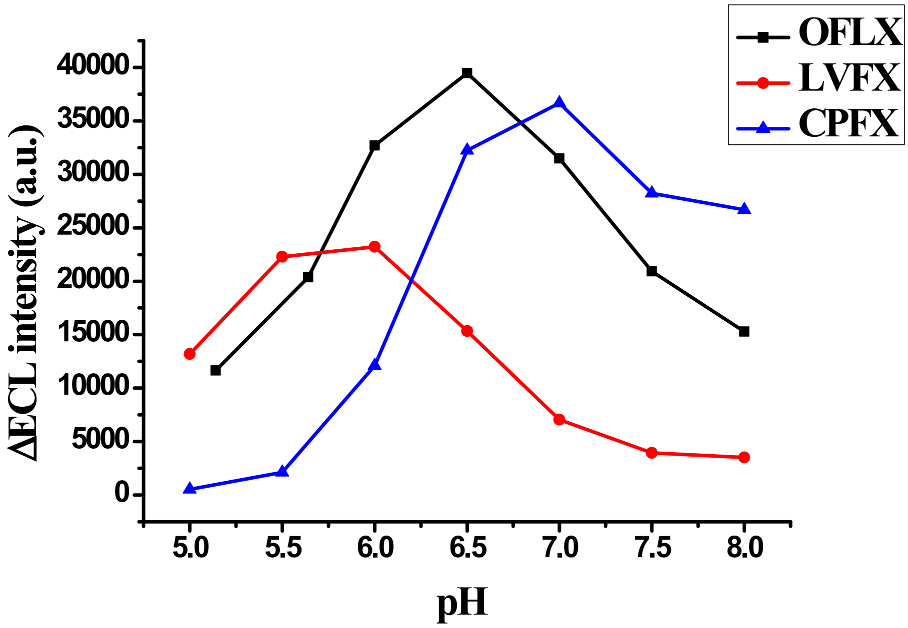


Fig. S1 Dependence of the ECL increase versus the pH with 1.0 × 10^{-5} mol/L **1** and 1.0 × 10^{-6} mol/L corresponding quinolone antibiotics in 0.10 mol/L phosphate buffer at GC electrode. $\Delta ECL = ECL_{after\ addition\ of\ analyte} - ECL_{before\ addition\ of\ analyte}$.

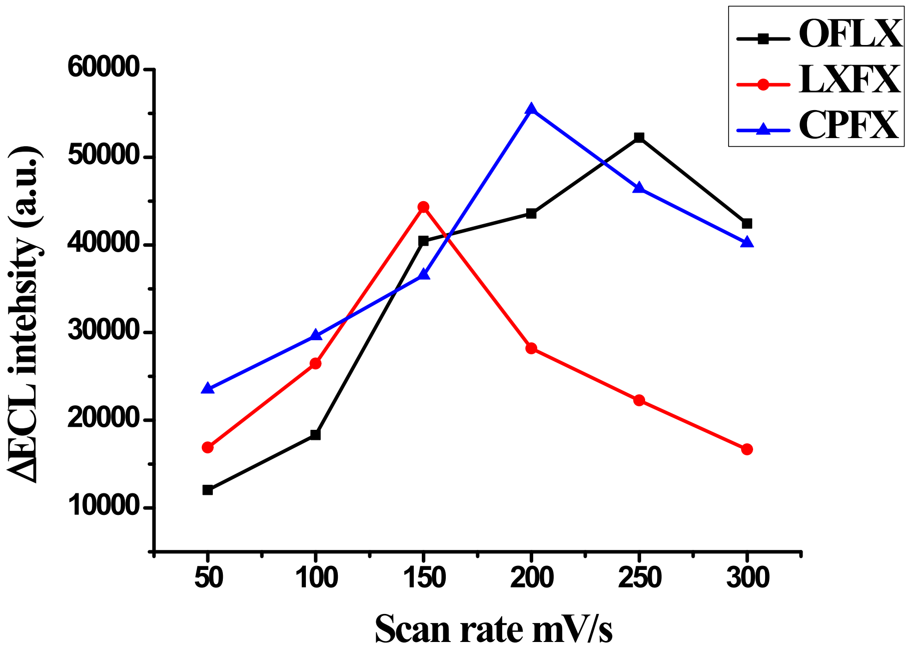


Fig. S2 The effect of different scan rate on ECL with 1.0 × 10^{-5} mol/L **1** and 1.0 × 10^{-6} mol/L corresponding quinolone antibiotics in 0.10 mol/L phosphate buffer (pH=6.5, 6.0 and 7.0 for OFLX, LVFX and CPFX, respectively) at GC electrode. $\Delta ECL = ECL_{after\ addition\ of\ analyte} - ECL_{before\ addition\ of\ analyte}$.

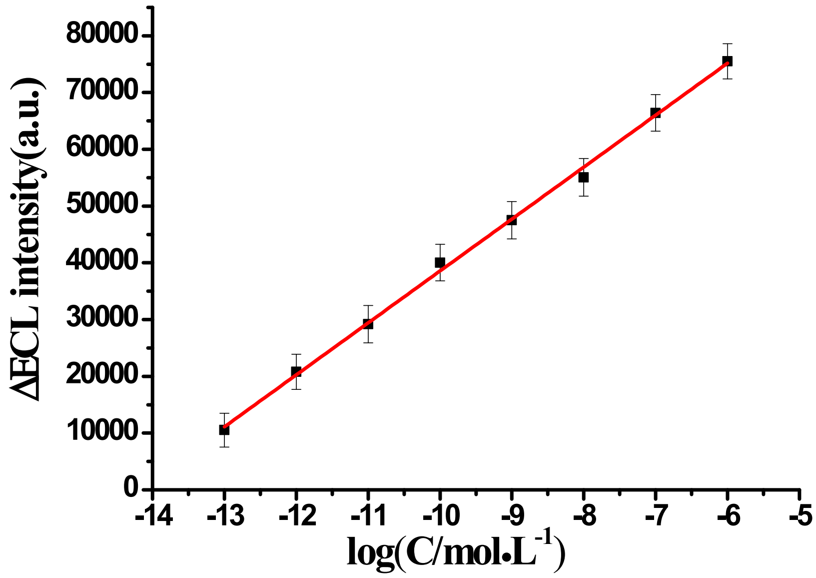


Fig. S3 Dependence of the ΔECL increase versus the logarithmic concentration of OFLX with 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 6.5) at GC electrode. ΔECL = $ECL_{\text{after addition of OFLX}} - ECL_{\text{before addition of OFLX}}$

A good linear calibration curve (Fig. S3) between the ΔECL (ΔECL=$ECL_{\text{after addition of OFLX}} - ECL_{\text{before addition of OFLX}}$) and the logarithmic concentration of OFLX (log[OFLX]) can be established over the concentration range from 1.0×10^{-13} to 1.0×10^{-6} mol/L for OFLX. The regression equation was ΔECL=129995.83+9144.17×log[OFLX] with a linear coefficient R^2=0.99. The quantitation limit for OFLX is 1.0×10^{-13} mol/L (3.61×10^{-11}g/L), which is much lower than the MRLs (the maximum residue in milk is 75 μg/kg for OFLX) set by the European Union (EU) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

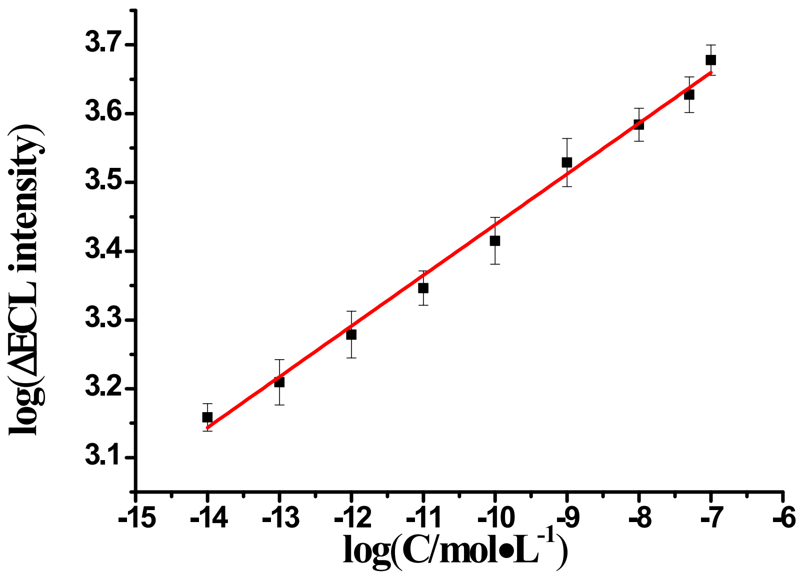


Fig. S4 Dependence of the logarithmic of ΔECL increase versus the logarithmic concentration of LVFX with 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 6.0) at GC electrode. $\Delta ECL = ECL_{\text{after addition of LVFX}} - ECL_{\text{before addition of LVFX}}$.

A good linear calibration curve (Fig. S4) between the logarithmic of ΔECL ($\Delta ECL = ECL_{\text{after addition of LVFX}} - ECL_{\text{before addition of LVFX}}$) and the logarithmic concentration of LVFX (log[LVFX]) can be established over the concentration range from 1.0×10^{-14} to 1.0×10^{-6} mol/L for LVFX. The regression equation was $\log\Delta ECL=4.18+0.08\times\log[LVFX]$ with a linear coefficient $R^2=0.99$. The quantitation limit for LVFX is 1.0×10^{-14} mol/L (3.61×10^{-12}g/L), which is much lower than the MRLs (the maximum residue in milk is 75 μg/kg for LVFX) set by the European Union (EU) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

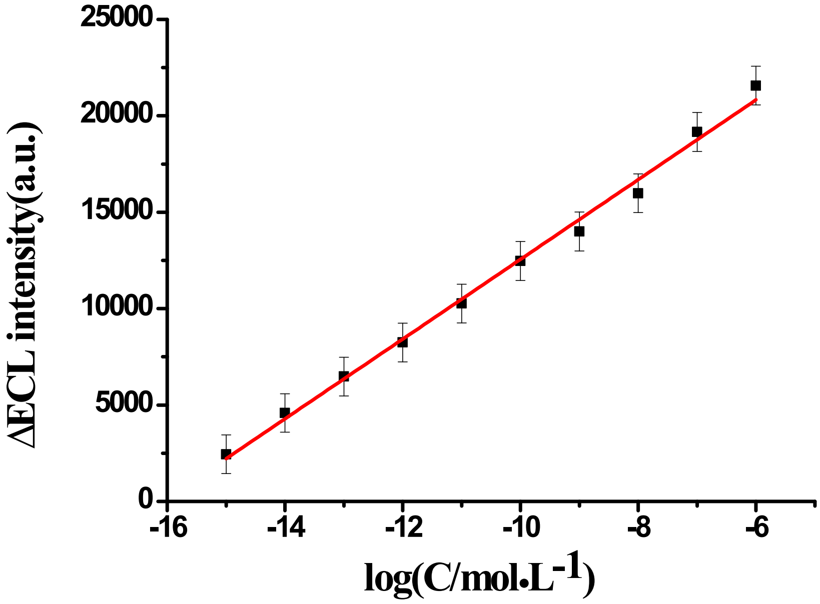


Fig. S5 Dependence of the ΔECL increase versus the logarithmic concentration of CPFX with 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 7.0) at GC electrode. $\Delta ECL = ECL_{\text{after addition of CPFX}} - ECL_{\text{before addition of the CPFX}}$.

A good linear calibration curve (Fig. S5) between ΔECL ($\Delta ECL = ECL_{\text{after addition of CPFX}} - ECL_{\text{before addition of the CPFX}}$) and the logarithmic concentration of CPFX (log[CPFX]) can be established over the concentration range from 1.0×10^{-15} to 1.0×10^{-6} mol/L for CPFX. The regression equation was ΔECL=33231+2067.67×log[CPFX] with a linear coefficient R^2=0.99. The CPFX quantitation limit is down to 1.0×10^{-15} mol/L (3.31×10^{-13}g/L), which is much lower than the MRLs (the maximum residue in milk is 100 μg/kg for CPFX) set by the European Union (EU) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

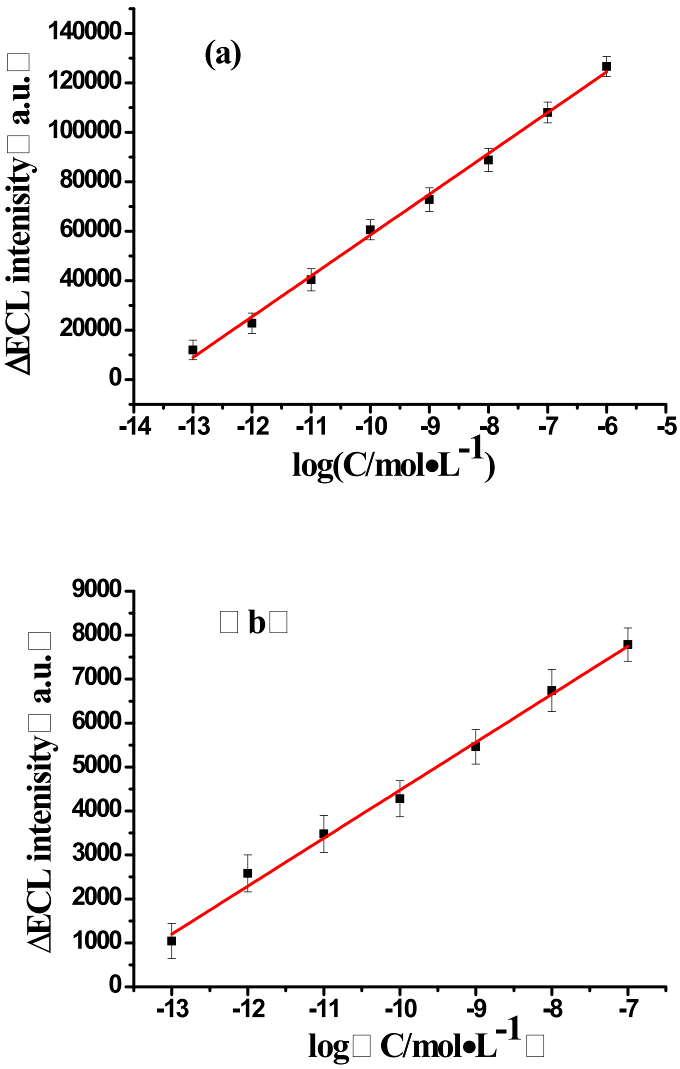


Fig. S6 Dependence of the ΔECL increase versus the logarithmic concentration of NFLX with 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 7.0) at Au electrode (a) and Pt electrode (b). $\Delta ECL = ECL_{\text{after addition of NFLX}} - ECL_{\text{before addition of NFLX}}$.

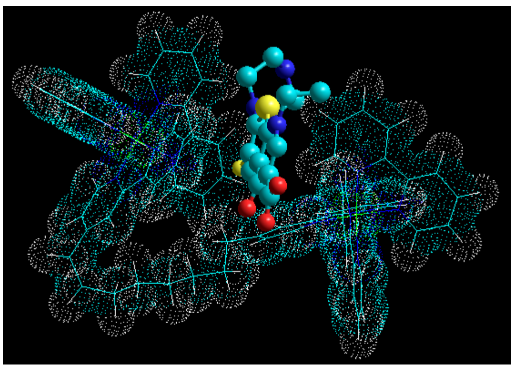
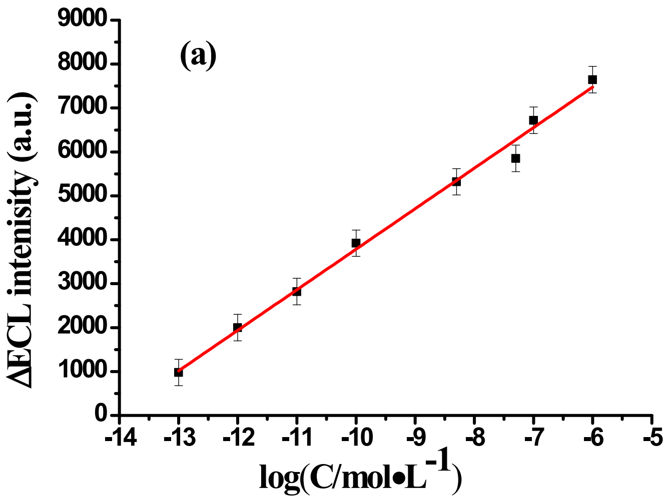


Fig. S7 Optimized molecular modeling of **1** (stick) and NFLX (ball) with Ru-, N-, C- and H-atom in green, blue, cyan and white color, respectively.



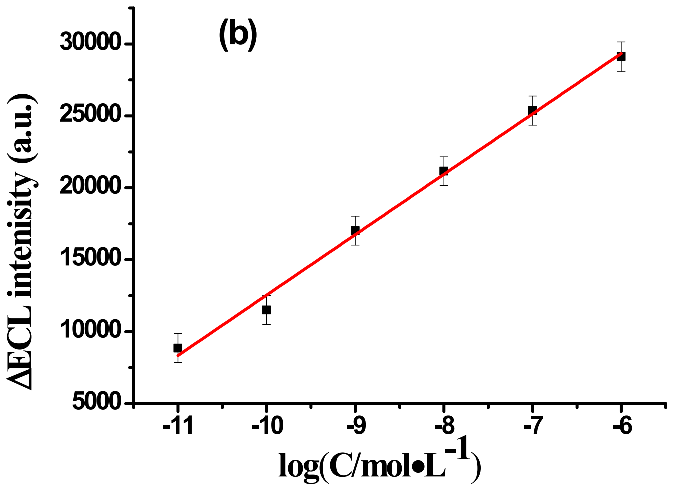
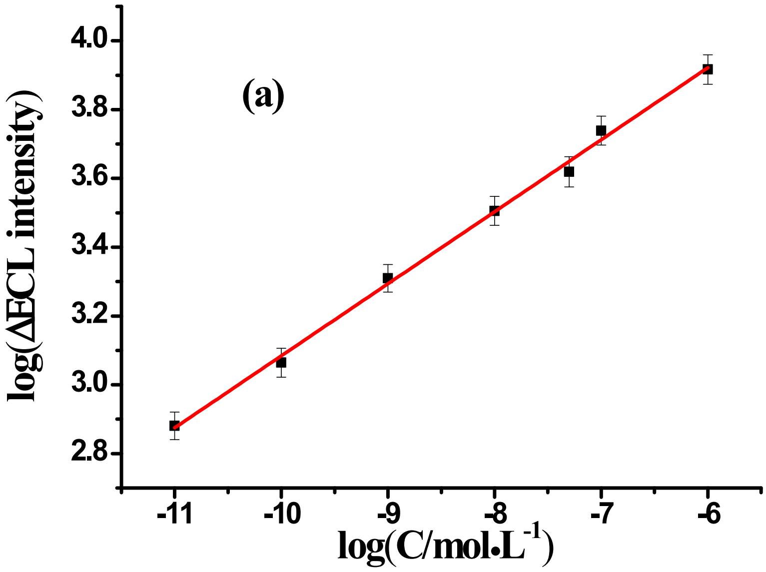


Fig. S8 (a) Dependence of the ΔECL increase versus the logarithmic concentration of NFLX with 5.0×10^{-5} mol/L mol/L **1** in 0.10 mol/L phosphate buffer (pH = 7.0) at GC electrode. (b) Dependence of the ΔECL increase versus the logarithmic concentration of NFLX with 1.0×10^{-4} mol/L $Ru(bpy)_3^{2+}$ in 0.1.0 mol/L phosphate buffer (pH = 7.0) at GC electrode. ΔECL = $ECL_{\text{after addition of NFLX}} - ECL_{\text{before addition of NFLX}}$



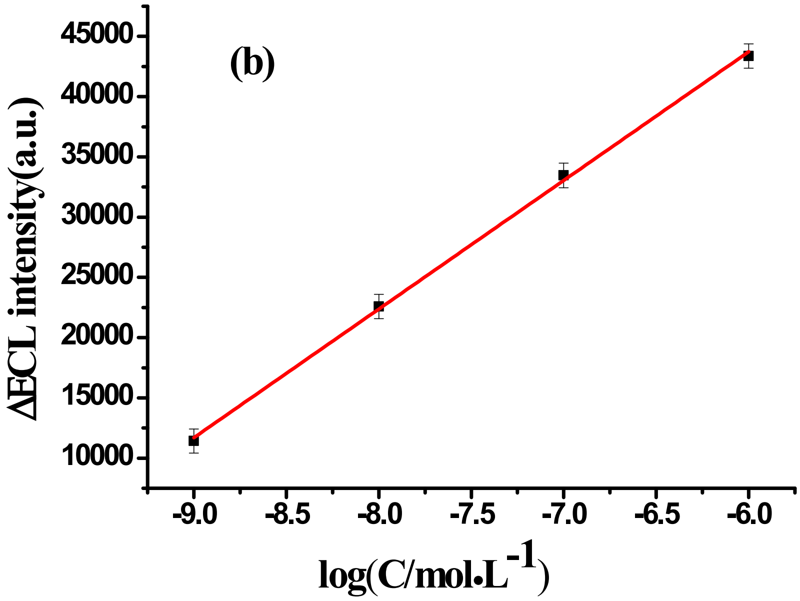
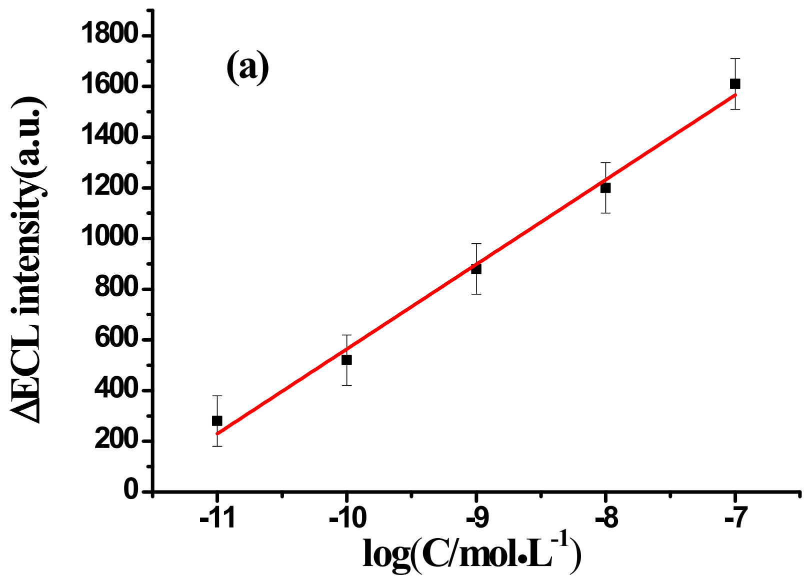


Fig. S9 (a) Dependence of the logarithmic ΔECL increase versus the logarithmic concentration of OFLX with 5.0×10^{-5} mol/L **1** in 0.10 mol/L phosphate buffer (pH = 6.5) at GC electrode. (b) Dependence of the ΔECL increase versus the logarithmic concentration of OFLX with 1.0×10^{-4} mol/L $Ru(bpy)_3^{2+}$ in 0.10 mol/L phosphate buffer (pH = 6.5) at GC electrode. $\Delta ECL = ECL_{\text{after addition of OFLX}} - ECL_{\text{before addition of OFLX}}$



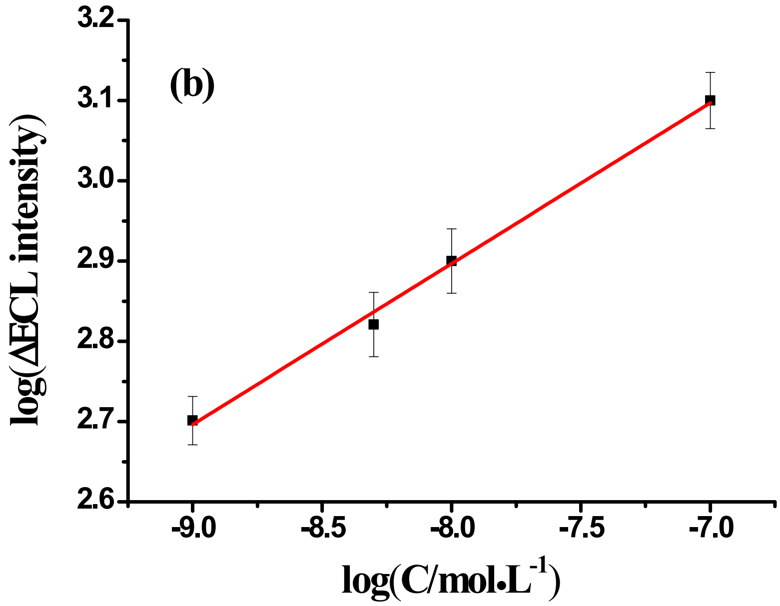
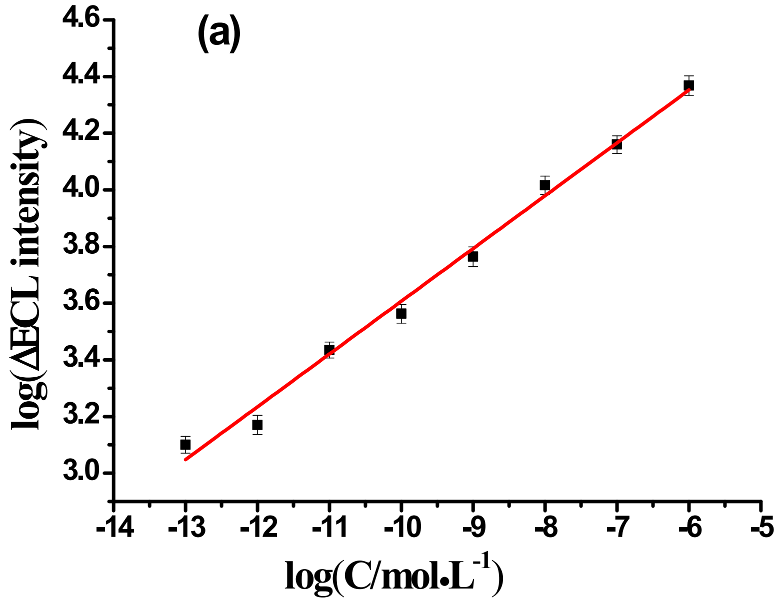


Fig. 10 (a) Dependence of the ΔECL increase versus the logarithmic concentration of LVFX with 5.0×10^{-5} mol/L **1** in 0.10 mol/L phosphate buffer (pH = 6.0) at GC electrode. (b) Dependence of the logarithmic of ΔECL increase versus the logarithmic concentration of LXFX with 1.0×10^{-4} mol/L $Ru(bpy)_3^{2+}$ in 0.10 mol/L phosphate buffer (pH = 6.0) at GC electrode. $\Delta ECL = ECL_{\text{after addition of LVFX}} - ECL_{\text{before addition of LVFX}}$



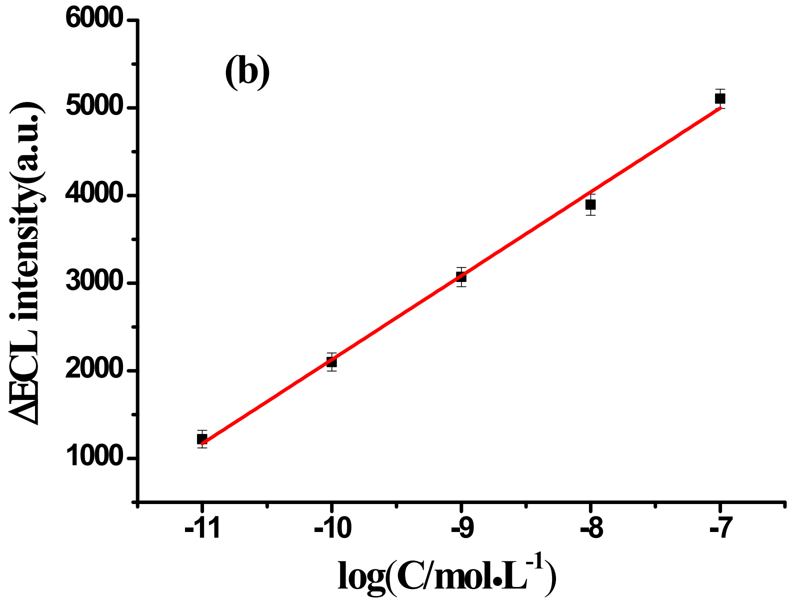


Fig. S11 (a) Dependence of the logarithmic of ΔECL increase versus the logarithmic concentration of CPFX with 5.0×10^{-5} mol/L **1** in 0.10 mol/L phosphate buffer (pH = 7.0) at GC electrode. (b) Dependence of the ΔECL increase versus the logarithmic concentration of CPFX with 1.0×10^{-4} mol/L $Ru(bpy)_3^{2+}$ in 0.10 mol/L phosphate buffer (pH = 7.0) at GC electrode. $\Delta ECL = ECL_{\text{after addition of CPFX}} - ECL_{\text{before addition of CPFX}}$

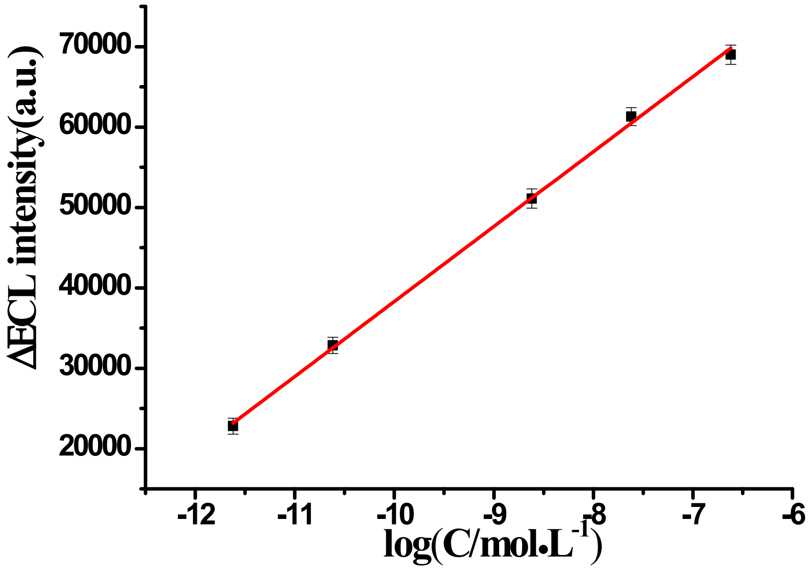


Fig. S12 Dependence of the ΔECL increase versus the logarithmic concentration of the OFLX in milk samples with 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 6.5) at GC electrode. $\Delta\text{ECL} = ECL_{\text{after addition of the milk samples}} - ECL_{\text{before addition of the milk samples}}$

A good linear calibration curve (Fig. S12) between the ΔECL ($\Delta\text{ECL}=ECL_{\text{after addition of the milk samples}}-ECL_{\text{before addition of the milk samples}}$) and the logarithmic concentration of OFLX (log[OFLX]) can be established over the concentration range from 2.4×10^{-12} to 2.4×10^{-7} mol/L for OFLX. The regression equation was ΔECL=133907.44 + 9568.60×log[OFLX] with a linear coefficient R^2=0.99. The OFLX quantitation limit is down to 2.4×10^{-12} mol/L (8.67×10^{-10}g/L), which is much lower than the MRLs (the maximum residue in milk is 75 μg/kg for ofloxacin) set by the European Union (EU) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

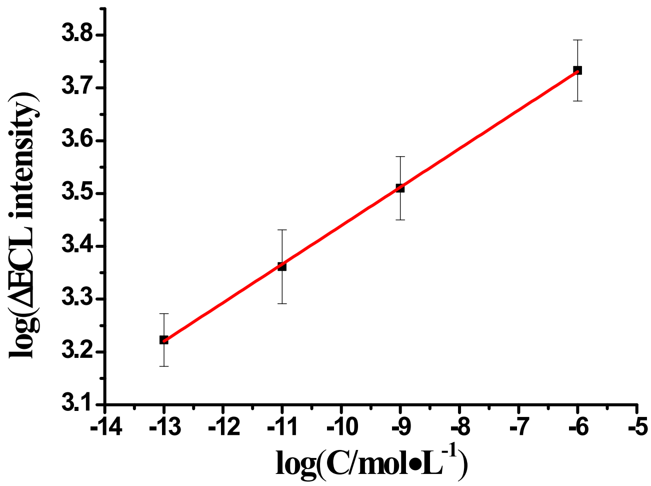


Fig. S13 Dependence of the logarithmic of ΔECL increase versus the logarithmic concentration of the LVFX in milk samples with 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 6.0) at GC electrode. $\Delta ECL = ECL_{\text{after addition of the milk samples}} - ECL_{\text{before addition of the milk samples}}$

A good linear calibration curve (Fig. S13) between the logarithmic of ΔECL ($\Delta ECL = ECL_{\text{after addition of the milk samples}} - ECL_{\text{before addition of the milk samples}}$) and the logarithmic concentration of LVFX (log[LVFX]) can be established over the concentration range from 1.0×10^{-13} to 1.0×10^{-6} mol/L for LVFX. The regression equation was $\log\Delta ECL = 4.17 + 0.07\times\log[LVFX]$ with a linear coefficient $R^2=0.99$. The LVFX quantitation limit is down to 1.0×10^{-13} mol/L (3.61×10^{-11}g/L), which is much lower than the MRLs (the maximum residue in milk is 75 μg/kg for LVFX) set by the European Union (EU) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

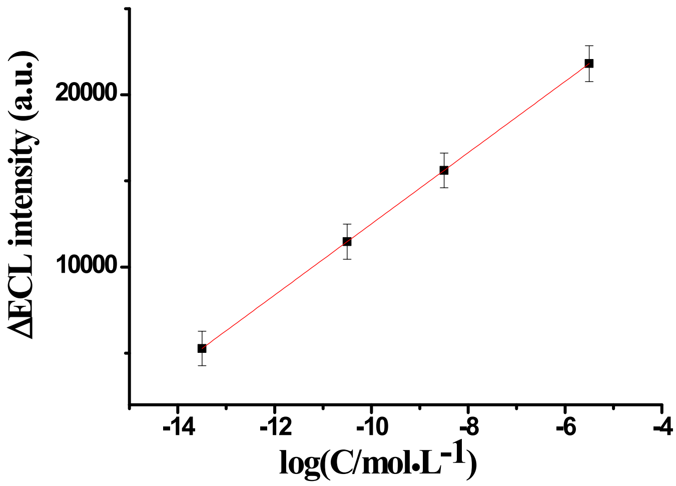


Fig. S14 Dependence of the ΔECL increase versus the logarithmic concentration of the CPFX in milk samples with 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 7.0) at GC electrode. $\Delta ECL = ECL_{\text{after addition of the milk samples}} - ECL_{\text{before addition of the milk samples}}$

A good linear calibration curve (Fig. S14) between the ΔECL ($\Delta ECL = ECL_{\text{after addition of the milk samples}} - ECL_{\text{before addition of the milk samples}}$) and the logarithmic concentration of CPFX (log[CPFX]) can be established over the concentration range from 3.0×10^{-14} to 3.0×10^{-6} mol/L for CPFX. The regression equation was ΔECL=33182.31 + 2067.56×log[CPFX] with a linear coefficient R^2=0.99. The CPFX quantitation limit is down to 3.00×10^{-14} mol/L (9.94×10^{-12}g/L), which is much lower than the MRLs (the maximum residue in milk is 100 μg/kg for CPFX) set by the European Union (EU) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

Table S1 Recoveries of the OFLX , LVFX and CPFX added into milk samples detected by 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH=6.5, 6.0 and 7.0 for OFLX, LVFX and CPFX, respectively) at GC electrode.[a]

Sample	Added (mol/L)	Detected (mol/L)	Average (mol/L)	Recovery	RSD
	2.4×10^{-12}	2.39×10^{-12}			
	2.4×10^{-12}	2.29×10^{-12}	2.38×10^{-12}	99.02%	2.29%
	2.4×10^{-12}	2.45×10^{-12}			
	2.4×10^{-11}	2.50×10^{-11}			
The milk	2.4×10^{-11}	2.39×10^{-11}	2.43×10^{-11}	101.25%	2.30%
samples	2.4×10^{-11}	2.40×10^{-11}			
containing	2.4×10^{-8}	2.45×10^{-8}			
OFLX	2.4×10^{-8}	2.50×10^{-8}	2.45×10^{-8}	101.90%	2.29%
	2.4×10^{-8}	2.39×10^{-8}			
	2.4×10^{-7}	2.50×10^{-7}			
	2.4×10^{-7}	2.45×10^{-7}	2.48×10^{-7}	103.40%	1.24%
	2.4×10^{-7}	2.50×10^{-7}			
	1.0×10^{-13}	1.02×10^{-13}			
	1.0×10^{-13}	1.02×10^{-13}	1.03×10^{-13}	100.27%	1.05%
	1.0×10^{-13}	1.04×10^{-13}			
The milk	1.0×10^{-11}	1.01×10^{-11}			
samples	1.0×10^{-11}	1.00×10^{-11}	1.00×10^{-11}	100.00%	0.58%
containing	1.0×10^{-11}	1.00×10^{-11}			
LVFX	1.0×10^{-9}	0.99×10^{-9}			
	1.0×10^{-9}	1.00×10^{-9}	0.99×10^{-9}	99.00%	1.34%
	1.0×10^{-9}	0.97×10^{-9}			
	1.0×10^{-6}	1.00×10^{-6}			
	1.0×10^{-6}	1.01×10^{-6}	1.01×10^{-6}	101.30%	1.50%
	1.0×10^{-6}	1.03×10^{-6}			
	3.0×10^{-14}	3.03×10^{-14}			
	3.0×10^{-14}	3.012×10^{-14}	3.01×10^{-14}	100.32%	0.75%
	3.0×10^{-14}	2.98×10^{-14}			
	3.0×10^{-11}	3.02×10^{-11}			
	3.0×10^{-11}	2.90×10^{-11}	2.96×10^{-11}	98.50%	2.04%
The milk	3.0×10^{-11}	2.95×10^{-11}			
samples	3.0×10^{-9}	2.99×10^{-9}			
containing	3.0×10^{-9}	3.00×10^{-9}	2.96×10^{-9}	98.60%	1.86%
CPFX	3.0×10^{-9}	2.90×10^{-9}			
	3.0×10^{-6}	3.09×10^{-6}			
	3.0×10^{-6}	3.02×10^{-6}	3.03×10^{-6}	101.00%	1.83%
	3.0×10^{-6}	2.98×10^{-6}			

[a] Average of three samples, each sample was measured repeatedly for at least 7 times, and the averaged readings were used.

The relative deviations of less than 2.30% and the recoveries of 98.50-103.40% for OFLX, LVFX and CPFX showed the fine accuracy, further demonstrated the potential application of this method for the determination of quinolone antiotics residues in milk.

Table S2 Precision studies results of the milk sample containing OFLX were detected by 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 7.0)[a]

Sample	No.	Concentration (mol/L)	Intraday precision ECL intensity(a.u.)	Interday precision ECL intensity(a.u.)
	1	1.0×10^{-9}	122480	124598
	2	1.0×10^{-9}	118733	130851
	3	1.0×10^{-9}	120779	122897
NFLX	4	1.0×10^{-9}	123214	125332
	5	1.0×10^{-9}	122765	124883
	6	1.0×10^{-9}	122729	124847
Mean			121783.33	125568.00
SD			1714.83	2721.40
RSD(%)			1.40	2.10

[a] Average of three samples, each sample was measured repeatedly for at least 7 times, and the averaged readings were used.

Table S3 Precision studies results of the milk sample containing OFLX were detected by 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 6.5)[a]

Sample	No.	Concentration (mol/L)	Intraday precision ECL intensity(a.u.)	Interday precision ECL intensity(a.u.)
	1	1.0×10^{-9}	59250	59580
	2	1.0×10^{-9}	59380	59480
	3	1.0×10^{-9}	58970	58980
OFLX	4	1.0×10^{-9}	59230	59460
	5	1.0×10^{-9}	59340	59490
	6	1.0×10^{-9}	59310	58980
Mean			59246.60	59238.33
SD			146.24	290.20
RSD(%)			0.24	0.48

[a] Average of three samples, each sample was measured repeatedly for at least 7 times, and the averaged readings were used.

Table S4 Precision studies results of milk sample containing LVFX were detected by 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 6.0)[a]

Sample	No.	Concentration (mol/L)	Intraday precision ECL intensity(a.u.)	Interday precision ECL intensity(a.u.)
	1	1.0×10^{-9}	15920	16100
	2	1.0×10^{-9}	15970	15980
	3	1.0×10^{-9}	15890	14990
LVFX	4	1.0×10^{-9}	15960	15890
	5	1.0×10^{-9}	14980	15970
	6	1.0×10^{-9}	15890	15930
Mean			15768.33	15810.00
SD			146.24	407.87
RSD(%)			0.24	2.50

[a] Average of three samples, each sample was measured repeatedly for at least 7 times, and the averaged readings were used.

Table S5 Precision studies Results of milk sample containing CPFX precision studies were detected by 1.0×10^{-4} mol/L **1** in 0.10 mol/L phosphate buffer (pH 7.0)[a]

Sample	No.	Concentration (mol/L)	Intraday precision ECL intensity(a.u.)	Interday precision ECL intensity(a.u.)
	1	1.0×10^{-9}	26590	26280
	2	1.0×10^{-9}	26670	26290
	3	1.0×10^{-9}	26580	25980
CPFX	4	1.0×10^{-9}	26790	26780
	5	1.0×10^{-9}	26560	26260
	6	1.0×10^{-9}	26430	26270
Mean			26603.33	26310.00
SD			119.90	258.90
RSD(%)			0.45	0.98

[a] Average of three samples, each sample was measured repeatedly for at least 7 times, and the averaged readings were used.