Supplementary material

A novel molecularly imprinted electrochemiluminescence sensor based on cobalt nitride nanoarray electrode for sensitive detection of bisphenol S

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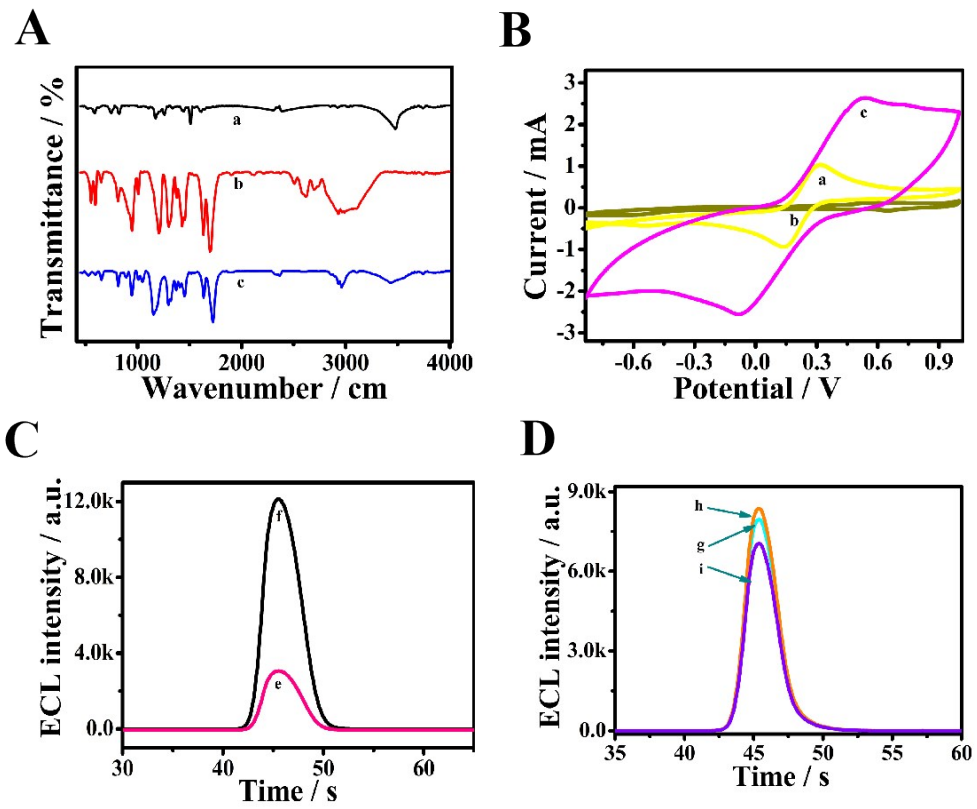

Fig.S1. (A) FT-IR spectra of (a) BPS, (b) MAA, (c) BPS-MIP; (B) Cyclic voltammograms of various electrodes in a 5 mmol/L $K_3[Fe(CN)_6]$ and 0.1 mol/L KNO_3 solution: (a) bare CC electrode, (b) $Ru(bpy)_3^{2+}$/Nafion/CC, (c) $Ru(bpy)_3^{2+}$/Nafion/CoN/CC, Scan rate: 0.1 V/s; (C) ECL responses of each electrode modification step in10 mL of PBS (pH 7.4) containing 55 mmol/L of TPrA: (e) $Ru(bpy)_3^{2+}$/Nafion/CC, (f) $Ru(bpy)_3^{2+}$/Nafion/CoN/CC; (D) ECL responses of each electrode modification step in 10 mL of PBS (pH7.4) containing 55 mmol/L of TPrA: (g) NIP/$Ru(bpy)_3^{2+}$/Nafion/CoN/CC, (h) Eluted NIP/$Ru(bpy)_3^{2+}$/Nafion CoN CC, (i) Rebinding MIP/$Ru(bpy)_3^{2+}$/ Nafion/CoN/CC.

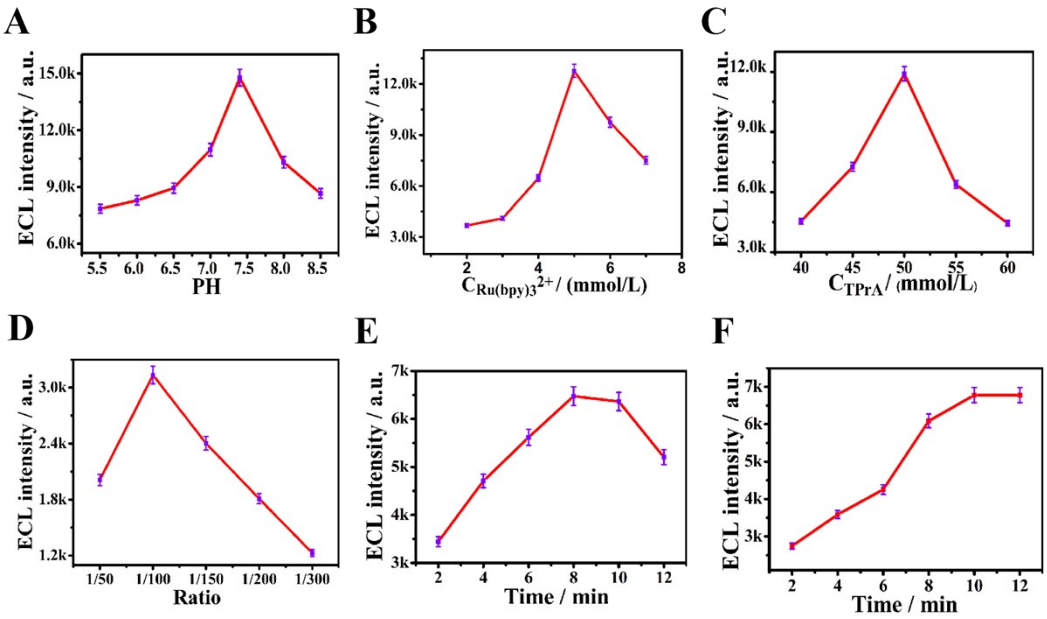

Fig.S2. (A) Effect of pH on ECL intensity, (B) Concentration of $Ru(bpy)_3^{2+}$ on ECL intensity, (C) Concentration of TPrA on ECL intensity, (D) Effect of ratio of template molecules to functional monomers on ECL intensity, (E) Effect of incubation time of template molecule on ECL intensity, (F) Effect of elution time on ECL intensity.

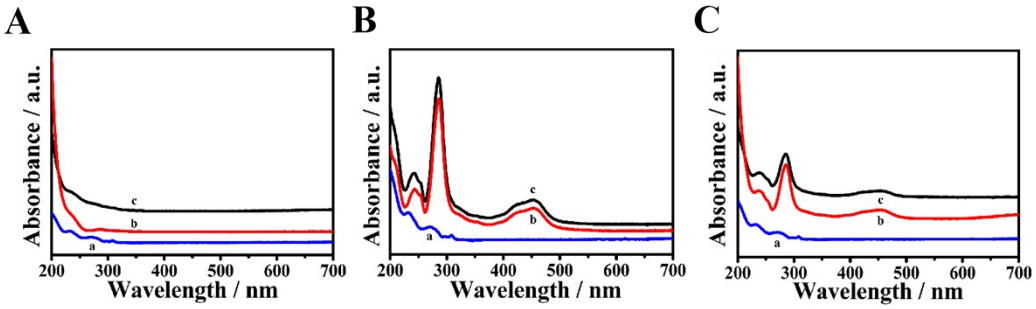

Fig.S3. (A) UV-Vis spectra of (a) BPS, (b) $Ru(bpy)_3^{2+}$+TPrA, (c) $Ru(bpy)_3^{2+}$+TPrA+BPS; (B) UV-Vis spectra of (a) BPS, (b) $Ru(bpy)_3^{2+}$, (c) $Ru(bpy)_3^{2+}$+BPS; (C) UV-Vis spectra of (a) BPS, (b) TPrA, (c) TPrA+BPS.

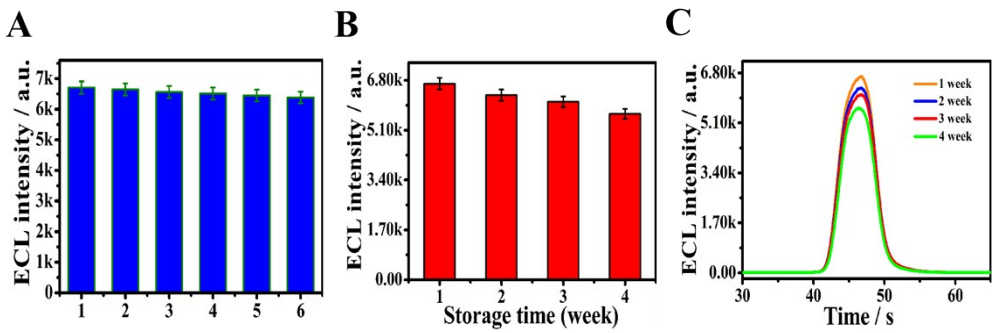

Fig.S4. (A) Repeatability of MIECL sensor incubated with1.0×10^{-6}mol/L BPS, (B) Long-term storage stability of the MIECL sensor incubated with 1.0×10^{-6}mol/L bisphenol S, (C) ECL-Time curves of long-term storage stability of the MIECL sensor.

Table S1 Comparison of various methods for determination of BPS

Methods	Linear range (mol/L)	LOD (mol/L)	Reference
fluorescence aptasensor	5.0×10^{-8}-2.0×10^{-6}	2.0×10^{-9}	1
MIP-potentiometric sensor	1.0×10^{-7}-2.0×10^{-6}	4.0×10^{-8}	2
Electrochemical sensor	1.0×10^{-6}-1.0×10^{-4}	5.0×10^{-7}	3
DLLME-UHPLC-MS/MS	1.21×0^{-9}-1.6×10^{-7}	4.0×10^{-10}	4
MIP-Electrochemical sensor	1.0×10^{-8}-5.0×10^{-5}	1.1×10^{-8}	5
Electrochemical sensor	5.0×10^{-7}-5.0×10^{-5}	9.0×10^{-8}	6
Ratio derivate ultraviolet spectrometry	1.4×10^{-6}-1.0×10^{-4}	4.4×10^{-7}	7
Py-GC/MS	-	4.0×10^{-6}	8
MIP-Electrochemical sensor	1.0×10^{-7}-5.0×10^{-5}	3.0×10^{-8}	9
MIP-Electrochemiluminesence sensor	2.4×10^{-9}-5.0×10^{-5}	7.5×10^{-10}	this work

DLLME-UHPLC-MS/MS: dispersive liquid-liquid microextraction ultrahigh-performance liquid chromatography–tandem mass spectrometry.

Py-GC/MS: pyrolysis gas chromatography mass spectrometry.

Table S2 Comparison of this method with other reported ECL methods for detecting BPA

Methods	Linear range (mol/L)	LOD (mol/L)	Reference
Electrochemiluminesence sensor	4.4×10^{-8}-2.2×10^{-5}	2.9×10^{-6}	10
MIP-Electrochemiluminesence sensor	2.2×10^{-10}-1.1×10^{-7}	4.5×10^{-11}	11
Electrochemiluminesence sensor	2.6×10^{-7}-9.9×10^{-3}	8.3×10^{-8}	12
Electrochemiluminesence sensor	3.0×10^{-8}-1.0×10^{-6}	1.0×10^{-8}	13
Electrochemiluminesence sensor	5.0×10^{-8}-3.0×10^{-6}	2.0×10^{-8}	14
MIP-Electrochemiluminesence sensor	2.4×10^{-9}-5.0×10^{-5}	7.5×10^{-10}	This work

Table S3 Determination result and recovery of bisphenol S in the drinking water sample(n=5)

Sample number	Detected (10^{-6}mol/L)	Added (10^{-6}mol/L)	Total found by MIECL sensor (10^{-6}mol/L)	RSD (%)	Recovery[a] (%)	Total found by HPLC method(10^{-6}mol/L)	RSD (%)	Recovery[a] (%)
1	5.27	5.00	10.17	2.9	98.0	10.25	2.9	99.6
2		10.0	15.19	3.3	99.2	15.50	3.3	102.3
3		15.0	20.96	2.6	104.6	20.79	2.6	103.4

a The recovery is calculated through the equation1.

(1)
$$\text{Recovery}(\%) = \frac{\text{Found} - \text{detected}}{\text{Added}} \times 100\%$$

Table S4 *t*-Test about the drinking water analysis(n=5)

Sample	HPLC (10^{-6}mol/L)	Mean (10^{-6}mol/L)	RSD (%)	This method (10^{-6}mol/L)	Mean (10^{-6}mol/L)	RSD (%)	*t*-Test[b]	P
The drinking water	4.79,5.20,4.61,6.00,5.80	5.30	5.7	4.53,5.16,5.84,4.88, 5.95	5.27	6.3	1.912	0.95

[b] The *t* value is calculated through the equation2.

(2)
$$t = \frac{|\bar{\chi} - \mu|}{s}\sqrt{n}$$

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