

*Supporting Information*

**A regenerable electrochemical sensor for electro-inactive  
cyclovirobuxine D detection of in biological samples**

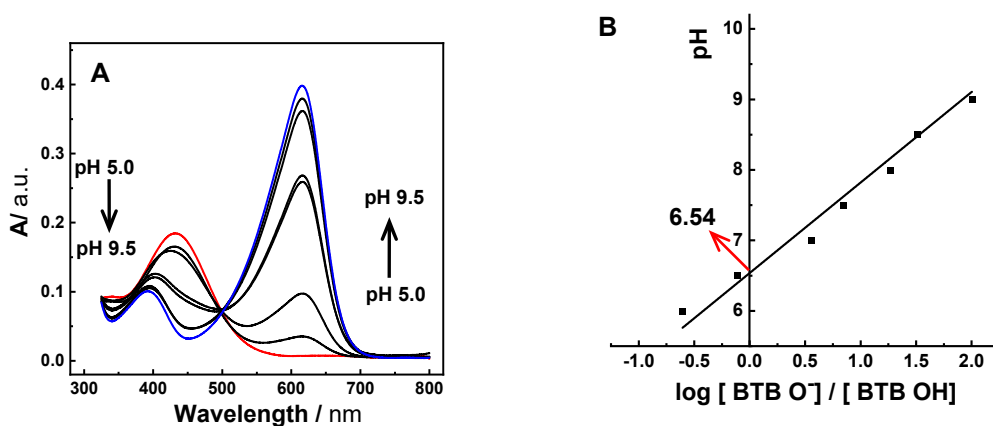
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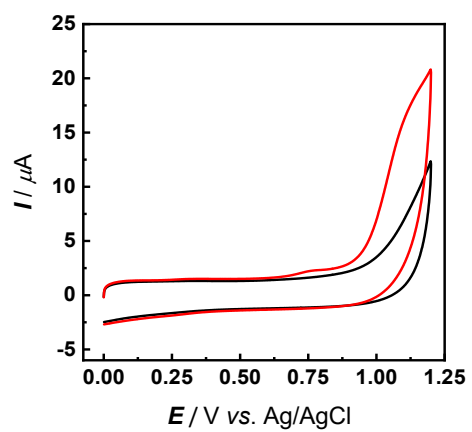
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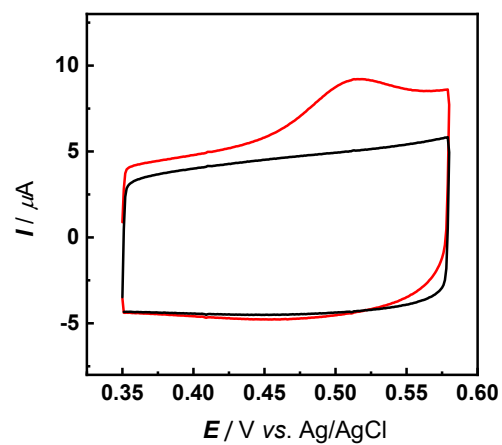
**Fig. S1.** Calculation of  $pK_a$  of BTB in aqueous solution: A) UV-vis absorption of 20  $\mu\text{M}$  BTB recorded at different pH ranged from 5.0 to 9.5 (the arrow indicated the increasing direction of pH). B) The calculation of  $pK_a$  of BTB.

Fig. S1A shows BTB absorbance at pH ranged from pH 5.0 to 9.0, two distinct absorption bands are apparent, one is at 435 nm which is characteristic for protonated form of BTB (BTB-OH) and another at 620 nm which is attributed to deprotonated form of BTB (BTB-O<sup>-</sup>). If pH of the medium is either in acidic with a pH less than 5.0 or in basic with a pH higher than 9.0, one of forms predominates and can be assumed to be 100% of total BTB and the other can be assumed to be 0% of total BTB. Thus, we can calculate the extinction coefficient ratio for two forms at 435nm and 620 nm according to Lambert-Beer law.

By rearranging the Henderson-Hasselbalch equation [35], we obtained the relationship between  $pK_a$  and pH which was described as following:  $\text{pH} = pK_a + \log[\text{BTB-O}^-]/[\text{BTB-OH}]$ . Thus, the pH is plotted vs. log term, the intercept is  $pK_a$ , as Fig. S1B displayed, the  $pK_a$  was read to be 6.54 from the intercept.



**Fig. S2.** CVs obtained at the SWNTs-modified GC electrode in 0.1 M PBS of pH 7.4 in the absence (black curve) and presence (red curve) of 500  $\mu\text{M}$  CVB-D. Scan rate, 50  $\text{mVs}^{-1}$ .



**Fig. S3.** CVs obtained in 0.1M PBS of pH 7.4 for the SWNTs-modified GC electrode before (black curve) and after (red curve) being immersed in 500  $\mu\text{M}$  BTB aqueous solution for 30 min. Scan rate, 50  $\text{mVs}^{-1}$ .

**Table S1.** Spike-and-recoveries for plasma (n=3) and liver homogenates(n=3)

Sample	Spiked ( $\mu\text{mol/L}$ )	found ( $\mu\text{mol/L}$ )	Recovery (%)	RSD (%)
Plasma	0.1	0.098	98.0	3.8
	2.0	2.03	101.5	1.4
	45	43.80	97.3	0.27
Liver homogenates	0.1	0.104	104.0	4.6
	2.0	1.94	97.0	5.1
	45	45.55	101.2	1.8