Self-assembly of new O- and S-heterocycle-based protective layers for copper in acid solution

Li Feng[a], Xiaolei Ren[b], Yangyang Feng[a], Bochuan Tan[a], Shengtao Zhang[a*], Wenpo Li[a], Jie Liu[c]

[a] *School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.*

[b] *College of environment and resources, chongqing technology and business university, Chongqing 400067, China.*

[c] *College of Chemistry and Chemical Engineering, Yantai 264005,PR China.*

1. The characterization of target molecules

3,3'-(Furan-2-ylmethylene)bis(1H-indole) (FYBI): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 2H), 6.65 (s, 2H), 6.19 (s, 1H), 5.95 (d, *J* = 2.8 Hz, 1H), 5.83 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 143.4, 133.8, 132.5, 130.5, 129.4, 127.1, 127.0, 126.7, 118.5, 120.1, 33.7.

3,3'-(thiophen-2-ylmethylene)bis(1H-indole) (TYBI): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.16 (dd, *J* = 15.2, 7.2 Hz, 3H), 7.02 (t, *J* = 7.2 Hz, 2H), 6.91-6.90 (m, 2H), 6.81 (s, 2H), 6.15 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 136.7, 127.0, 125.3, 123.3, 122.2, 120.0, 119.94, 119.88, 119.5, 111.3, 94.8, 35.6.

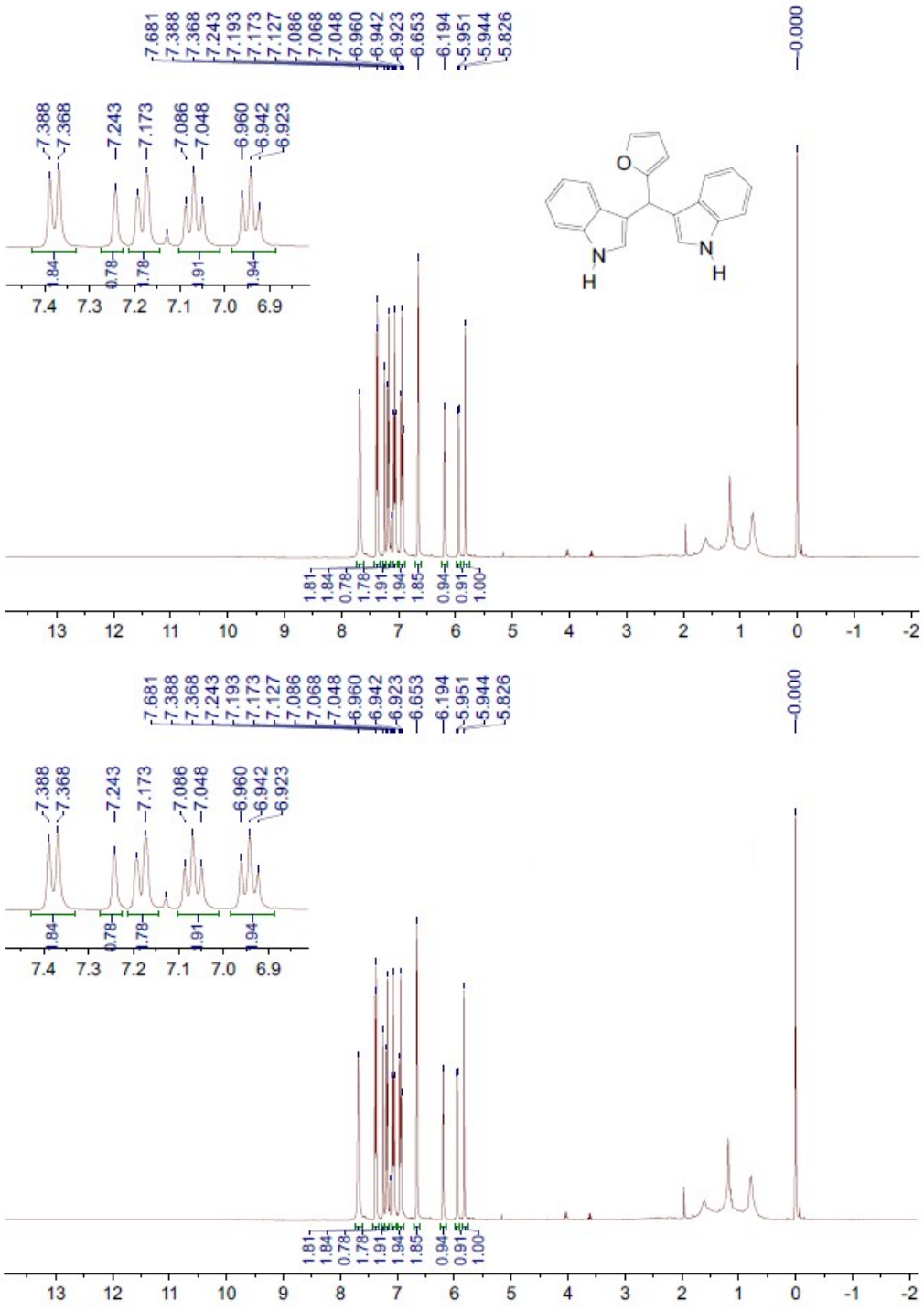

Fig. S.1 The ^{1}H & ^{13}C NMR spectra of FYBI.

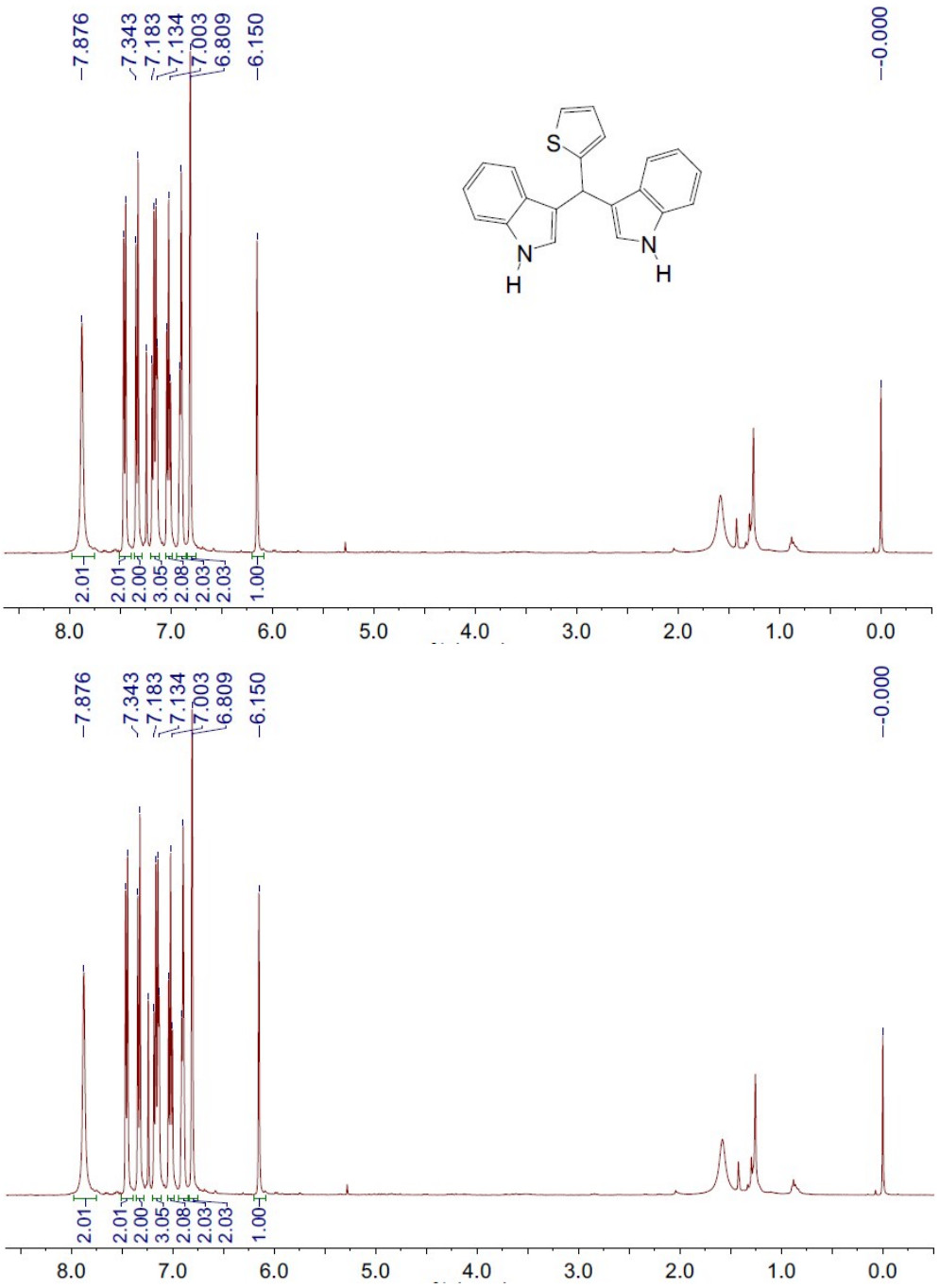

Fig. S2 The ^{1}H & ^{13}C NMR spectra of TYBI.

2. The open circuit potential

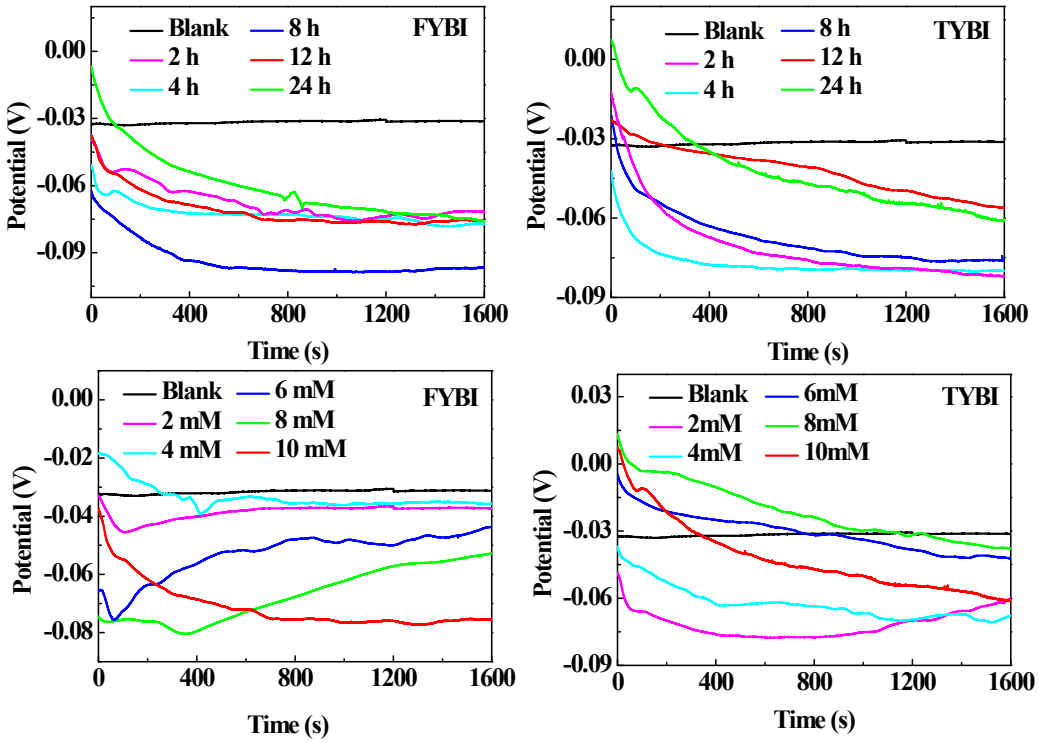

Fig. S3 The open circuit potential with various concentration and assemble time.

3. The equivalent circuit

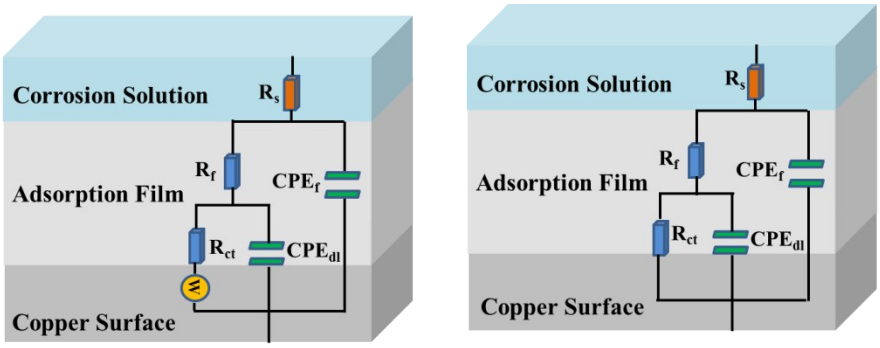

Fig. S4 The equivalent circuit fitting the EIS data.

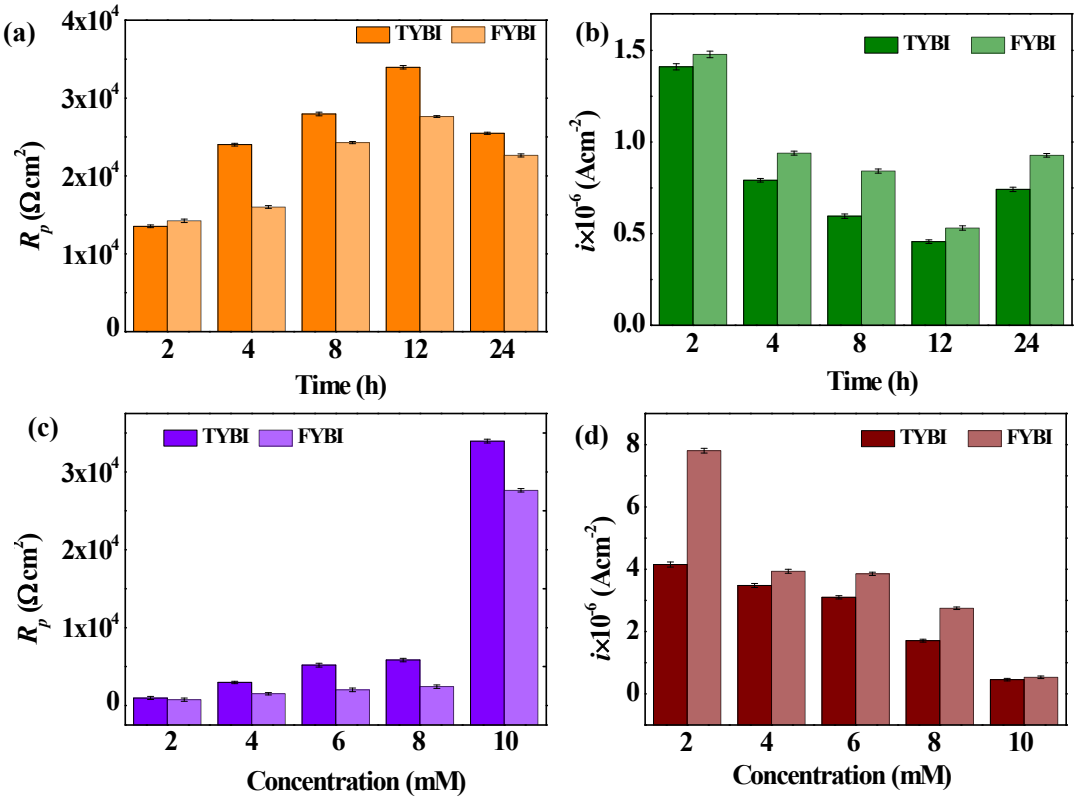

Fig. S5 Values of polarization resistance (R_p) and current density (i_{corr}) at different times and concentrations (Error bars represent mean ± SD for n = 3, *p < 0.05).

4. Adsorption study

The form of these isotherms is listed as followings (1)−(5):

Temkin adsorption isotherm: $KC = exp(2a\theta)$ (1)

Frumkin adsorption isotherm: $ln\left[\frac{\theta}{(1-\theta)C}\right] = lnK + 2a\theta$ (2)

Flory-Huggins adsorption isotherm: $ln\frac{\theta}{C} = xln(1-\theta) + ln(xK_{ads})$ (3)

EI-Awady adsorption isotherm: $ln\frac{\theta}{C} = xln(1-\theta) + \ln\left(xK_{ads}\right)$ (4)

Langmuir adsorption isotherm: $\frac{C}{\theta} = \frac{1}{K_{ads}} + c$ (5)

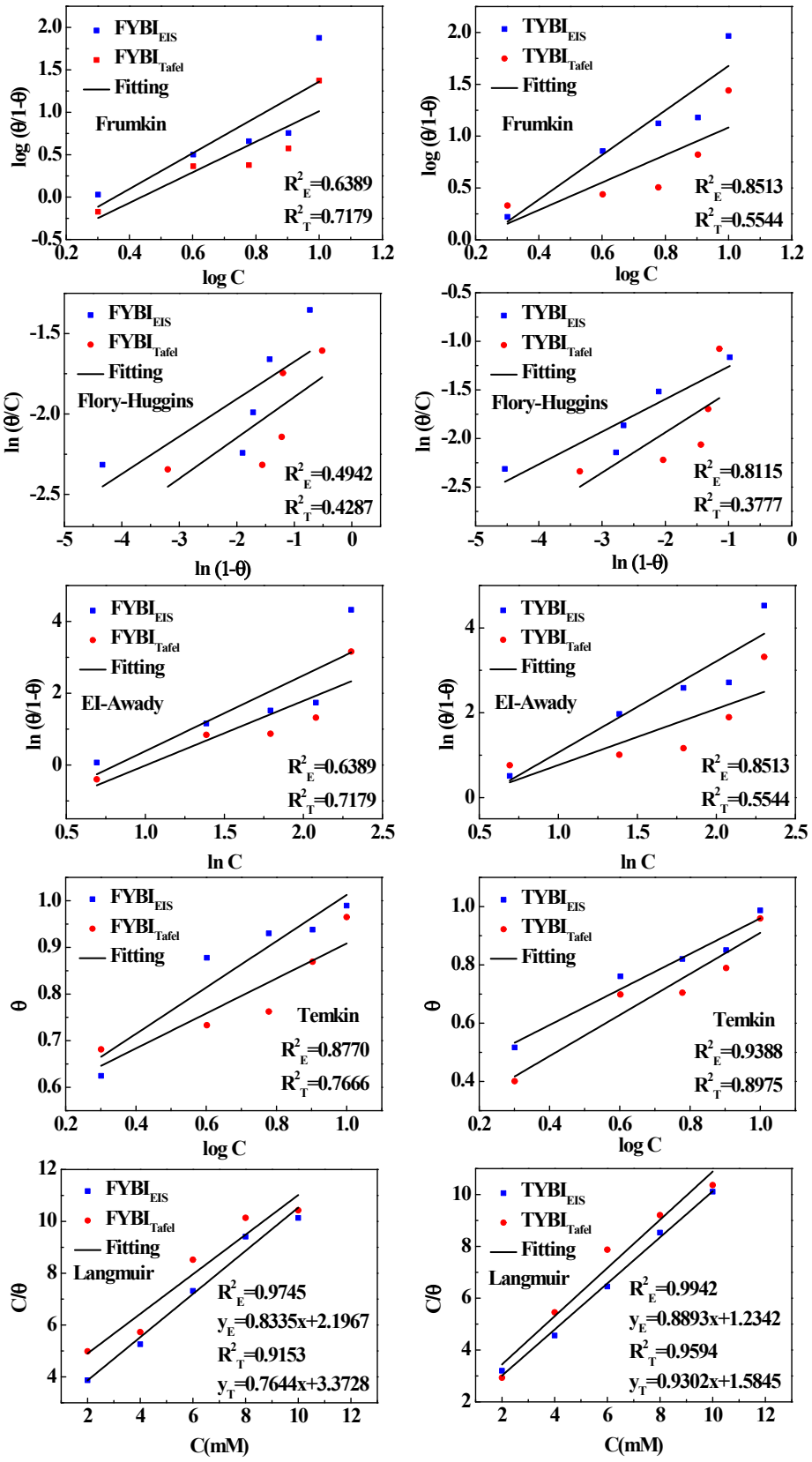

Fig. S6 The various adsorption isotherms of FYBI and TYBI on copper surface.

5. XPS high-resolution spectra

Table 6 The relevant chemical state, binding energy and FWMH from high-resolution XPS spectra.

Sample	Chemical state	Binding energy (eV)	FWHM	Sample	Chemical state	Binding energy (eV)	FWHM
FYBI SAMs				TYBI SAMs			
C1s	C-C/C-H	284.57	1.0	C1s	C-C/C-H	284.40	1.0
	C-N	285.35	1.0		C-S	284.98	1.0
	C-O	286.15	1.0		C-N	285.65	1.0
Cu2p	Cu(0)/Cu(I)	933.17	1.2	Cu2p	Cu(0)/Cu(I)	932.99	1.6
	Cu(II)	934.18	1.2				
N1s	N-H	399.39	0.9	N1s	N-H	398.82	0.9
	N-C	400.06	0.9		N-C	399.80	0.9
	N:Cu	400.70	0.9		N:Cu	400.50	0.9
O1s	C-O-C	531.75	2.0	S2p	S:Cu2p3/2	162.20	1.0
	CuO/Cu_2O	533.43	2.0		S:Cu2p1/2	163.30	1.0
					C-S-C2p3/2	164.25	1.0
					C-S-C2p1/2	165.35	1.0
					SO_4^{2-}	168.40	1.0