Supporting Information

Chelation as a Strategy to Reinforce Cationic Copper Surface Protection in Acidic Solutions

Liang Cai,[1] Xue-Qing Feng,[1] Xin Hua, Xiao-Peng He,* Yi-Tao Long and Guo-Rong Chen*

Key Laboratory for Advanced Materials & Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Rd, Shanghai 200237, PR China

[1]*Equal Contribution*

Corresponding Authors.

xphe@ecust.edu.cn (X.-P. He)

mrs_guorongchen@ecust.ac.cn (G.-R. Chen)

Contents list

S1. Additional Figures

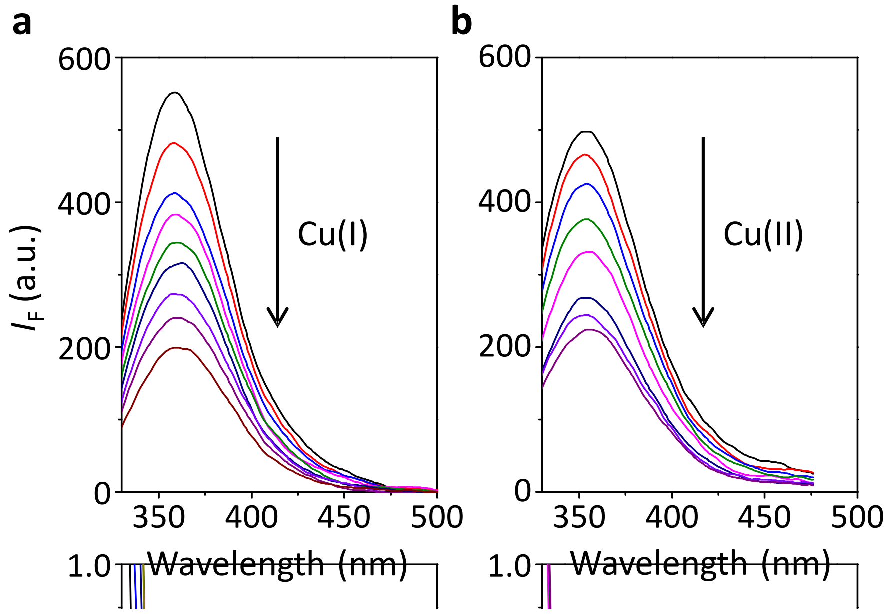

Figure S1. Fluorescence titration of **BTI1** (1.5×10^{-6} M) in the presence of increasing (a) Cu(I) (30-270 μM) and (b) Cu(II) (30-270 μM) in a mixed solution of 1 M HCl/DMSO (1:1, *v/v*) with an excitation wavelength of 282 nm.

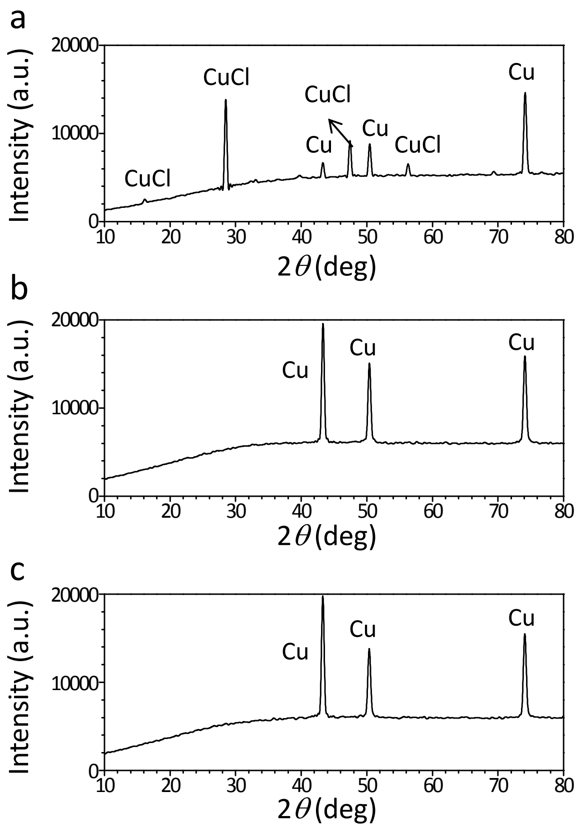

Figure S2. X-Ray Diffraction (XRD) of copper (Cu) surface after immersion in 1 M HCl for 3 days in the absence (a) and presence (b) of 3.2×10^{-4} M **BTI1**, and (c) bare copper surface.

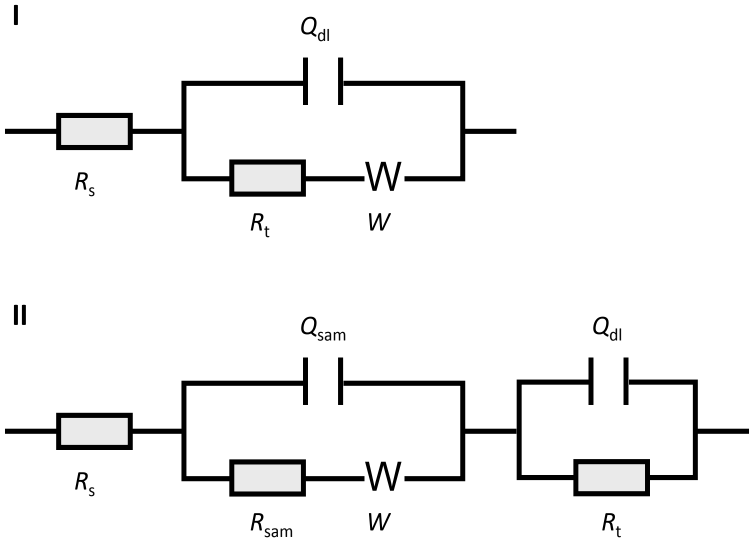

Figure S3. Equivalent circuit models used to fit the obtained electrochemical impedance spectroscopy (EIS) data, where R_s is the solution resistance, R_t the charge transfer resistance corresponding to the corrosion reaction at the copper/solution interface, R_{sam} the polarization resistance of transfer resistance of electrons through the protective molecular layer (if any) on copper surface, W the Warburg impedance, L the inductance, Q_{dl} the constant phase elements as a surrogate for the double-layer capacitance, and Q_{sam} the capacitance of the molecular film formed on copper.

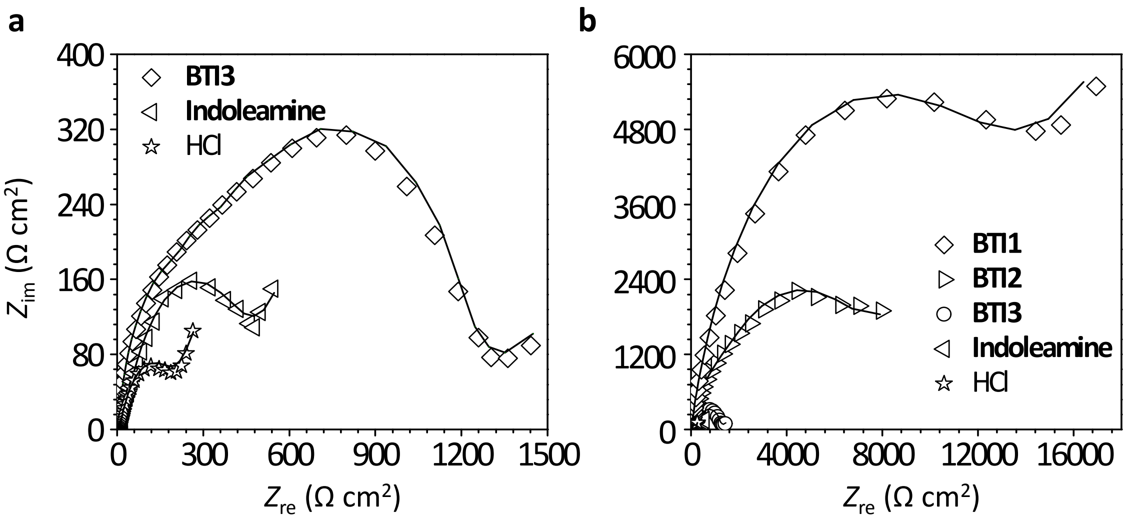

Figure S4. The experimental (dots) and fitted (line) Nyquist (a, b) plots for copper in 1 M HCl in the absence or presence of different corrosion inhibitors (10^{-3} M). Note that Fig. a is an enlarged area of the high frequency of Fig. b.

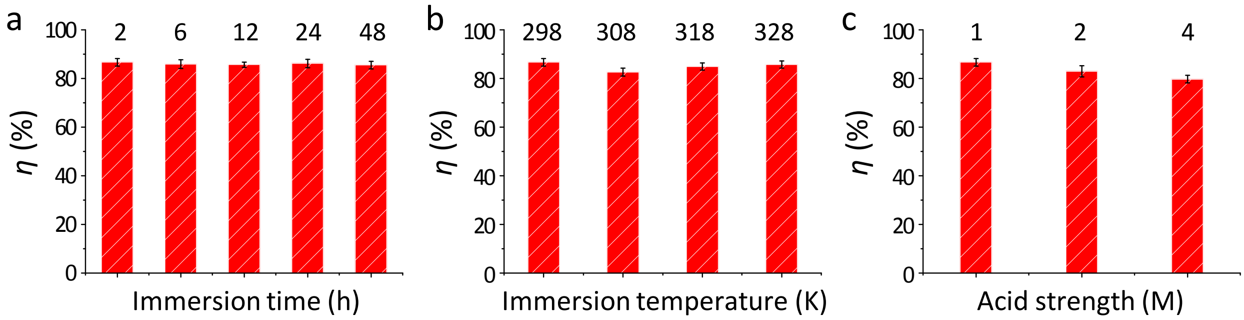

Figure S5. Histograms (determined by EIS) depicting the corrosion inhibitive efficiency (η) of **BTI1** (10^{-3} M) for copper in HNO_3 under different conditions. (a) Increasing immersion time. (b) Increasing temperature. (c) Increasing HNO_3 concentration.

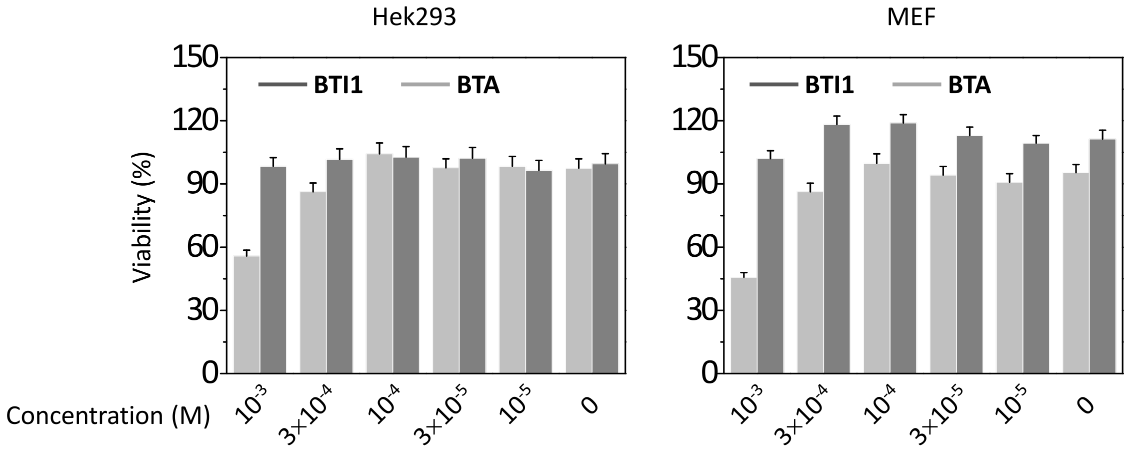

Figure S6. Cell viability of two healthy cell lines, Hek293 (human kidney cell line) and MEF (Mouse Embryonic Fibroblast cell line), after treatment with **BTI1** or **BTA** with different concentrations for 72 h, determined by a typical MTS cell viability assay (for a reference, see: *Chem. Sci.*, 2016, **7**, 4004).

S2. Additional Tables

Table S1. Parameters obtained from polarization and isothermal analyses for copper in 1 M HCl in the absence (blank) or presence of **BTI1** with different concentrations at 25 °C

Medium	1 M HCl	E_{corr} (mV *vs.* SCE)	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	i_{corr} (μA cm^{-2})	η (%)
	blank	-251.8	296.9	65.4	20.2	n.a.[a]
	1.0×10^{-5}	-233.1	193.6	59.6	2.1	89.6
	3.2×10^{-5}	-231.5	191.3	73.4	2.0	90.1
BTI1 (M)	1.0×10^{-4}	-247.4	192.7	79.4	1.7	91.6
	3.2×10^{-4}	-242.1	196.2	84.9	1.5	92.6
	1.0×10^{-3}	-259.6	228.4	87.1	1.2	94.1
	blank	-201.3	60.9	110.1	14.1	n.a.
	1.0×10^{-5}	-209.0	n.a.	75.9	9.7	31
	3.2×10^{-5}	-213.8	58.6	150.3	9.7	31.2
BTA (M)	1.0×10^{-4}	-221.1	56.3	180.4	9.3	34.2
	3.2×10^{-4}	-223.2	51.9	210.6	8.8	37.3
	1.0×10^{-3}	-225.2	50.1	278.3	7.8	41.8

[a] n.a. means not available.

Table S2. EIS parameters fitted for copper in 1 M HCl in the absence (blank) and presence of inhibitor with different concentrations at 25 °C

Compd.	Conc. (M)	OCP (V)	R_s (Ω cm^2)	Q_{sam} (μF cm^{-2})	n_1	R_{sam} (Ω cm^2)	W (mΩ^{-1} cm^{-2} s$^{1/2}$)	Q_{dl} (μF cm^{-2})	n_2	R_t (Ω cm^2)	η (%)
BTI1 (in 1 M HCl)	0	-0.203	1.7	n.a.[a]	0.7	n.a.	52.7	2522	n.a.	174.8	n.a.
	1.0×10^{-3}	-0.263	2.9	55.50	0.8	11.40	0.50	13.60	0.9	13090	98.7
	3.2×10^{-4}	-0.251	1.4	62.30	0.8	2049	1.80	137.5	0.7	8673.0	98.4
	1.0×10^{-4}	-0.235	1.7	28.30	0.8	3809	3.00	162.5	0.8	3361.0	97.6
	3.2×10^{-5}	-0.220	1.8	15.80	0.8	807.3	2.40	111.4	0.8	2458.0	94.7
	1.0×10^{-5}	-0.206	2.3	20.30	0.8	532.8	5.70	132.3	0.8	1539.0	91.6
BTA (in 1 M HCl)	0	0.015	1.8	n.a.	0.8	n.a.	14.8	348.0	n.a.	62.7	n.a.
	1.0×10^{-3}	-0.212	2.3	778.1	0.7	29.80	18.7	1428	0.7	304.0	42.5
	3.0×10^{-4}	-0.265	1.9	679.8	0.8	2145	0.70	1567	0.8	277.9	36.4
	1.0×10^{-4}	-0.178	2.0	657.7	0.9	1120	1.30	1879	0.9	263	33.5
	3.0×10^{-5}	-0.198	1.8	698.4	0.7	908.5	1.80	2012	0.7	247	29.3
	1.0×10^{-5}	-0.217	1.7	701.4	0.8	1345	3.40	2133	0.8	234	25.6
BTI2 (in 1 M HCl)	0	-0.203	1.7	n.a.[a]	0.7	n.a.	52.7	2522	n.a.	174.8	n.a.
	1.0×10^{-3}	-0.217	3.6	62.7	0.9	743.7	2.60	143.1	0.7	8226	98.1
BTI3 (in 1 M HCl)	0	-0.203	1.7	n.a.[a]	0.7	n.a.	52.7	2522	n.a.	174.8	n.a.
	1.0×10^{-3}	-0.234	2.3	29.6	0.9	277.5	18.3	225.6	0.8	1306	86.2

[a] n.a. means not available.

Table S3. EIS parameters fitted for copper in HCl in the absence (blank) and presence of inhibitor with different conditions

Compd.	Conc. (M)	OCP (V)	R_s (Ω cm^2)	Q_{sam} (μF cm^{-2})	n_1	R_{sam} (Ω cm^2)	W (mΩ^{-1} cm^{-2} s$^{1/2}$)	Q_{dl} (μF cm^{-2})	n_2	R_t (Ω cm^2)	η (%)
BTI1 (in 1 M HCl)	0	-0.203	1.7	n.a.[a]	0.7	n.a.	52.7	2522	n.a.	174.8	n.a.
	3.2 × 10^{-4}	-0.251	1.4	62.30	0.8	2049	1.80	137.5	0.7	8673.0	98.4
BTI1 (in 2 M HCl)	0	-0.246	1.1	n.a.[a]	0.8	n.a.	58.5	2255	n.a.	68.1	n.a.
	3.2 × 10^{-4}	-0.176	0.8	408.3	0.6	47.3	2.10	2061	0.6	1364	95.2
BTI1 (in 4 M HCl)	0	-0.333	0.9	n.a.	0.8	n.a.	79.9	2097	n.a.	61.0	n.a.
	3.2 × 10^{-4}	-0.217	1.2	981.5	0.6	2.9	1.30	1277	0.7	857.1	92.9
BTA (in 1 M HCl)	0	0.015	1.8	n.a.	0.8	n.a.	14.8	348.0	n.a.	62.7	n.a.
	3.2 × 10^{-4}	-0.265	2.1	567.1	0.7	28.9	18.7	1428	0.7	265.1	40.6
BTA (in 2 M HCl)	0	-0.215	1.8	n.a.	0.7	n.a.	17.8	332.0	n.a.	112.0	n.a.
	3.2 × 10^{-4}	-0.214	1.3	465.6	0.9	36.8	34.7	363.0	0.8	230.4	36.9.
BTA (in 4 M HCl)	0	-0.241	1.4	n.a.	0.8	n.a.	71.6	2258	n.a.	130.2	n.a.
	3.2 × 10^{-4}	-0.202	1.3	423.6	0.9	32.4	34.7	363.0	0.8	244.0	32.7.
BTI1 (in 1 M HCl for 2 h)	0	-0.203	1.7	n.a.[a]	0.7	n.a.	52.7	2522	n.a.	174.8	n.a.
	3.2 × 10^{-4}	-0.251	1.4	62.30	0.8	2049	1.80	137.5	0.7	8673.0	98.4
BTI1 (in 1 M HCl for 6 h)	0	-0.194	1.2	n.a.	0.8	n.a.	30.1	2240	n.a.	128.4	n.a.
	3.2 × 10^{-4}	-0.126	1.8	85.10	0.8	548.3	5.50	35.1	0.8	1429	93.5
BTI1 (in 1 M HCl for 12 h)	0	-0.175	2.3	n.a.	0.8	n.a.	78.4	2273	n.a.	65.80	n.a.
	3.2 × 10^{-4}	-0.101	1.5	35.90	0.8	335.6	3.10	44.3	0.7	1434	96.3
BTI1 (in 1 M HCl for 24 h)	0	-0.131	2.1	n.a.	0.8	n.a.	111.3	2213	n.a.	32.70	n.a.
	3.2 × 10^{-4}	-0.086	2.5	27.50	0.9	471.1	1.90	118.1	0.8	1077	97.8
BTI1 (in 1 M HCl for 48 h)	0	-0.072	3.6	n.a.	0.8	n.a.	407.1	1987	n.a.	23.10	n.a.
	3.2 × 10^{-4}	-0.043	1.9	46.70	0.9	28.9	1.30	80.1	0.7	700.9	96.8
BTI1 (in 1 M HCl at 298 K)	0	-0.203	1.7	n.a.[a]	0.7	n.a.	52.7	2522	n.a.	174.8	n.a.
	3.2 × 10^{-4}	-0.251	1.4	62.30	0.8	2049	1.80	137.5	0.7	8673.0	98.4
BTI1 (in 1 M HCl at 308 K)	0	-0.201	1.7	n.a.	0.8	n.a.	21.4	2538	n.a.	157.4	n.a.

	3.2×10^{-4}	-0.236	1.7	26.10	0.8	3831	3.10	217.7	0.8	3146	97.7
BTI1 (in 1 M HCl at 318 K)	0	-0.209	1.6	n.a.	0.8	n.a.	19.3	1938	n.a.	136.7	n.a.
	3.2×10^{-4}	-0.202	1.4	24.30	0.8	361.6	2.60	103	0.8	1541	92.8
BTI1 (in 1 M HCl at 328 K)	0	-0.195	1.5	n.a.	0.8	n.a.	26.8	2064	n.a.	125.7	n.a.
	3.2×10^{-4}	-0.198	2.6	27.50	0.9	421.1	9.10	198.1	0.8	1077	91.6
BTA (in 1 M HCl at 298 K)	0	-0.241	8.2	180.5	0.8	219.1	2.3	813.2	0.7	1168	n.a.
	3.2×10^{-4}	-0.265	2.1	567.1	0.7	28.9	18.7	1428	0.7	265.1	40.6
BTA (in 1 M HCl at 308 K)	0	-0.117	5.6	230.9	0.8	223.8	1.9	765.9	0.8	1787	n.a.
	3.2×10^{-4}	-0.211	1.6	234.7	0.8	31.6	19.2	2134	0.7	259.4	39.8
BTA (in 1 M HCl at 318 K)	0	-0.154	6.7	189.5	0.7	312.7	1.9	778.4	0.8	1567	n.a.
	3.2×10^{-4}	-0.116	1.9	209.8	0.8	34.6	24.7	2371	0.7	246.4	37.75
BTA (in 1 M HCl at 328 K)	0	-0.181	3.9	210.7	0.8	267.4	2.6	788.5	0.7	1765	n.a.
	3.2×10^{-4}	-0.132	2.0	231.6	0.7	34.5	22.3	2431	0.8	233.5	35.15
BTA (in 1 M HCl for 2 h)	0	-0.015	1.8	n.a.	0.8	n.a.	14.8	348.0	n.a.	62.7	n.a.
	3.2×10^{-4}	-0.265	2.1	567.1	0.7	28.9	18.7	1428	0.7	275.1	42.1
BTA (in 1 M HCl for 6 h)	0	-0.165	2.3	n.a.	0.7	n.a.	15.6	278.0	n.a.	43.6	n.a.
	3.2×10^{-4}	-0.211	1.8	358.7	0.7	23.4	23.4	2016	0.8	260.6	37.2
BTA (in 1 M HCl for 12 h)	0	-0.115	3.4	n.a.	0.9	n.a.	20.9	245.7	n.a.	76.8	n.a.
	3.2×10^{-4}	-0.243	2.3	647.3	0.8	33.8	23.6	2351	0.6	228.2	33.5
BTA (in 1 M HCl for 24 h)	0	-1.135	2.1	n.a.	0.7	n.a.	21.2	231.5	n.a.	56.3	n.a.
	3.2×10^{-4}	-0.245	1.1	465.1	0.8	34.6	19.8	1567	0.7	213.4	29.1
BTA (in 1 M HCl for 48 h)	0	-0.075	1.6	n.a.	0.7	n.a.	15.6	432.1	n.a.	56.9	n.a.
	3.2×10^{-4}	-0.118	1.7	546.7	0.7	21.7	19.8	1546	0.8	216.3	25.5

[a] n.a. means not available.