## **Supporting Information:**

## Novel and facile strategy to inhibit corrosion: thiol-click synthesis of polythiols and their skinning on metal surface to form super thick protective films

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Figure S1. <sup>1</sup>H NMR spectrum of VMS.



Figure S2. <sup>1</sup>H NMR spectrum of the intermediate prepared by thiol-ene click reaction between VMS and AcSH.



Figure S3. <sup>13</sup>C NMR spectrum of the intermediate prepared by thiol-ene click reaction between VMS and AcSH.



Figure S4. <sup>1</sup>H NMR spectrum of SPT.



Figure S5. <sup>1</sup>H NMR spectrum of propargyl thioacetate.



Figure S6. <sup>1</sup>H NMR spectrum of the intermediate prepared by thiol-yne click polymerization between propargyl thioacetate and dithioglycol.



Figure S7. <sup>13</sup>C NMR spectrum of the intermediate prepared by thiol-yne click polymerization between propargyl thioacetate and dithioglycol.



Figure S8. <sup>1</sup>H NMR spectrum of **TPT**.



Figure S9. <sup>1</sup>H NMR spectrum of the intermediate obtained from the reaction between glycidyl propargyl ether and AcSH.



Figure S10. <sup>1</sup>H NMR spectrum of LTPT.



Figure S11. <sup>1</sup>H NMR spectrum of the polythiol generated by SOAM of LTPT.



Figure S12. Evolution of surface morphologies of the crosslinked SPT films on copper as immersion time increased from 5 to 60 min.



Figure S13. Phase angle plot (left) and Nyquist plot (right) of the copper samples covered with the crosslinked SPT films.



Figure S14. Polarization curves (left) and Bode plot (right) of the copper electrodes covered with the crosslinked TPT films in 3.5 wt% NaCl aqueous solution.

Table S1.	Electrochemical	data of the	copper san	ples covered	l with the	e crosslinked	TPT films.
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Electrode	E <sub>corr</sub> /mV(SCE)	I <sub>corr</sub> /A cm <sup>-2</sup>	η (%)
Bare	-211	1.387 ×10 <sup>-6</sup>	-
5 min	-406	3.870 ×10 <sup>-8</sup>	97.2
10 min	-409	$2.646 \times 10^{-8}$	98.1
20 min	-419	$1.401 \times 10^{-8}$	99.0
30 min	-429	$1.159 \times 10^{-8}$	99.2
60 min	-417	$6.048 \times 10^{-10}$	99.9



Figure S15. Polarization curves (left) and electrochemical impedance spectroscopy plots (right) of the copper electrodes covered with various films formed by immersion in the solutions for 60 min.