

Supplementary Information for

Cationic Gemini surfactants with a bipyridyl spacer as corrosion inhibitors for carbon steel

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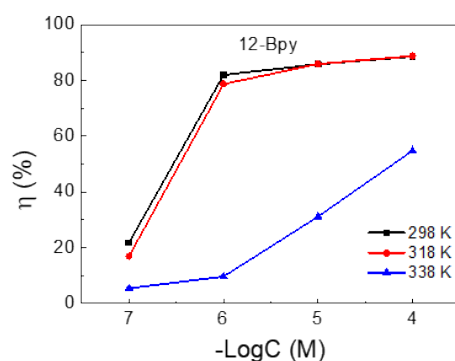


Figure S1. The effect of temperature on the corrosion inhibition efficiency of 12-Bpy.

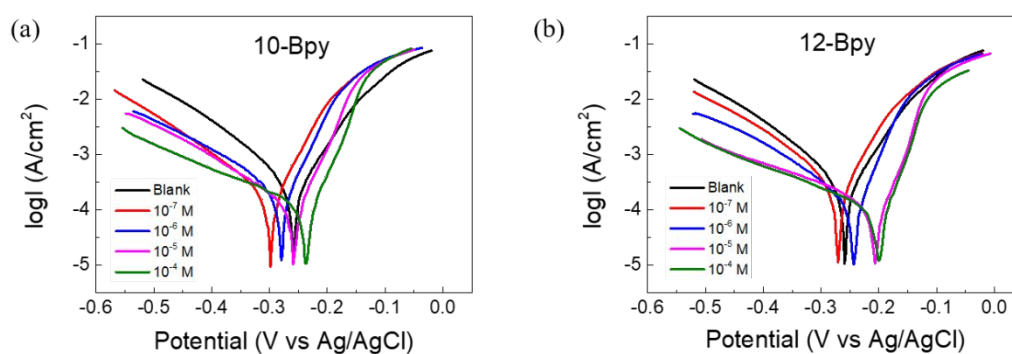


Figure S2. Potentiodynamic polarization curves for carbon steel in 1 M HCl without and with different concentrations of (a) 10-Bpy and (b) 12-Bpy.

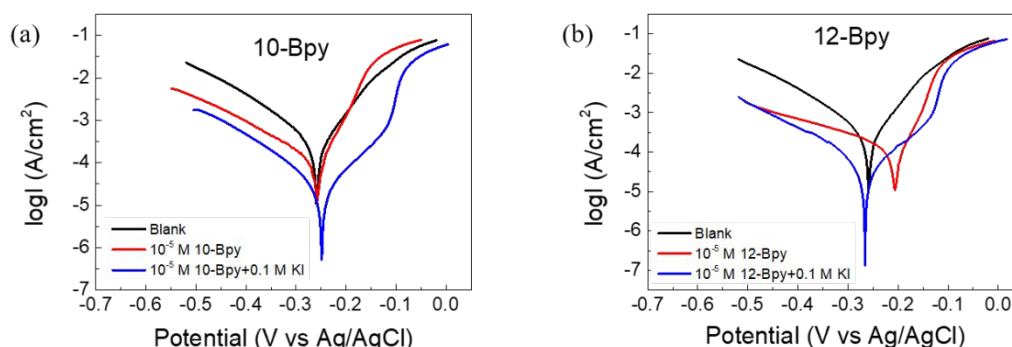


Figure S3. Potentiodynamic polarization curves for carbon steel in 1 M HCl + 10^{-5} M (a) 10-Bpy and (b) 12-Bpy in the absence and presence of 0.1 M KI.

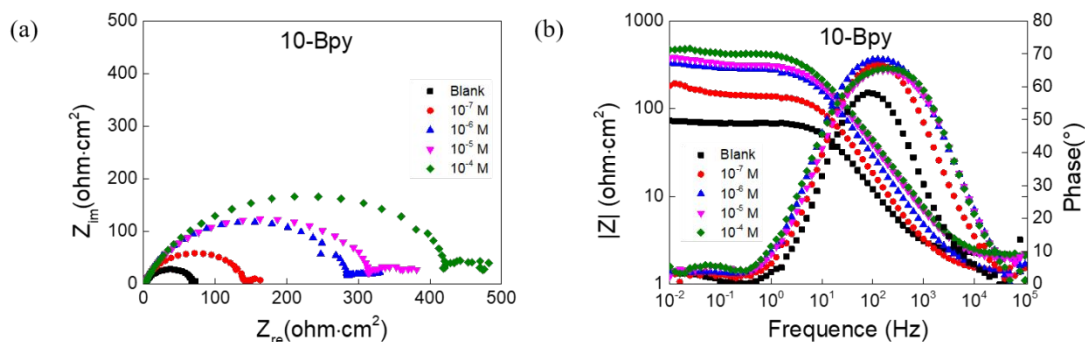


Figure S4. (a) Nyquist plots and (b) Bode plots for carbon steel in 1 M HCl containing different concentrations of 10-Bpy.

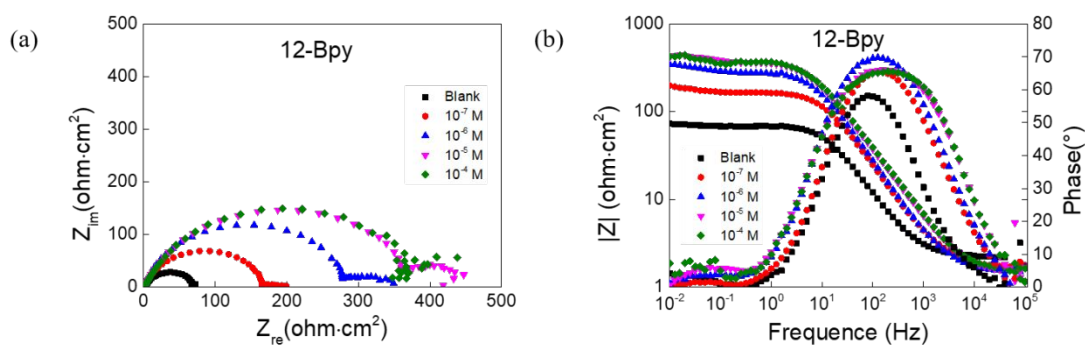


Figure S5. (a) Nyquist plots and (b) Bode plots for carbon steel in 1 M HCl containing different concentrations of 12-Bpy.

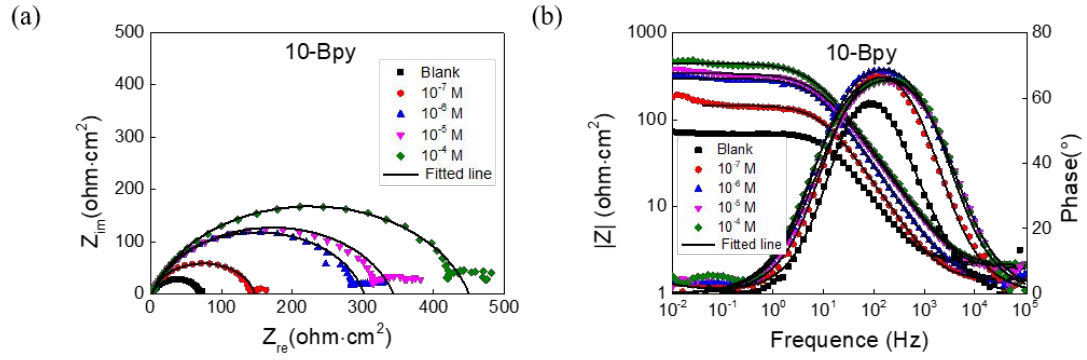


Figure S6. (a) Nyquist plots and (b) Bode plots of 10-Bpy fitted by the used equivalent circuits.

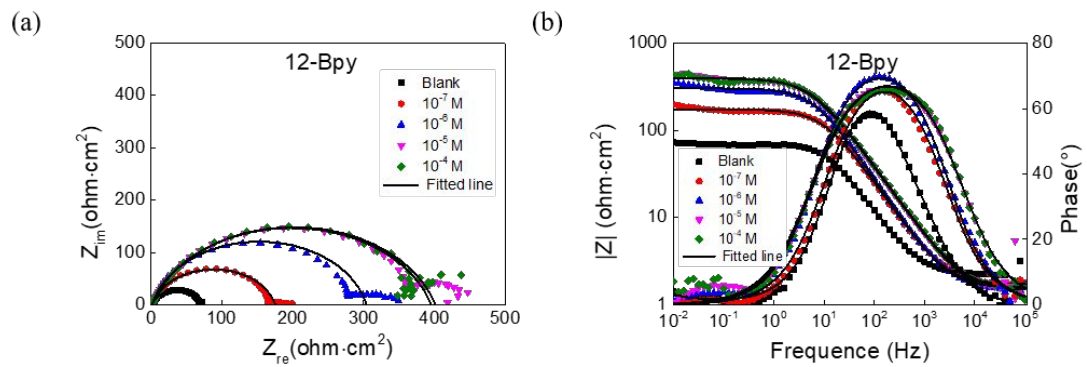


Figure S7. (a) Nyquist plots and (b) Bode plots of 12-Bpy fitted by the used equivalent circuits.

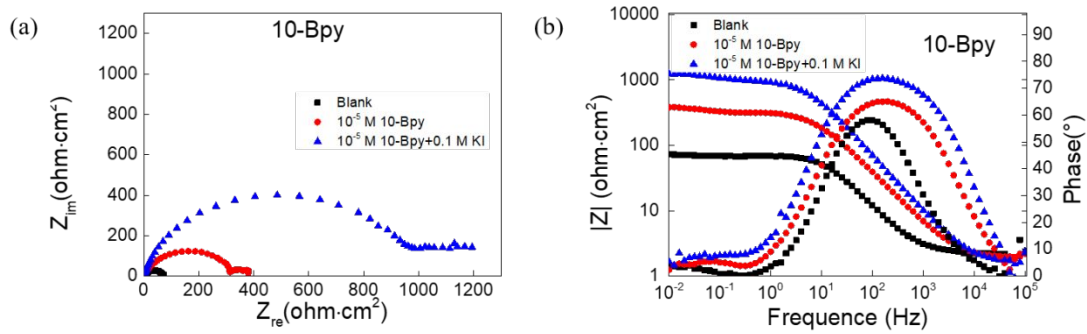


Figure S8. (a) Nyquist plots and (b) Bode plots for carbon steel in 1M HCl of blank, blank + 10^{-5} M 10-Bpy and blank + 10^{-5} M 10-Bpy + 0.1M KI.

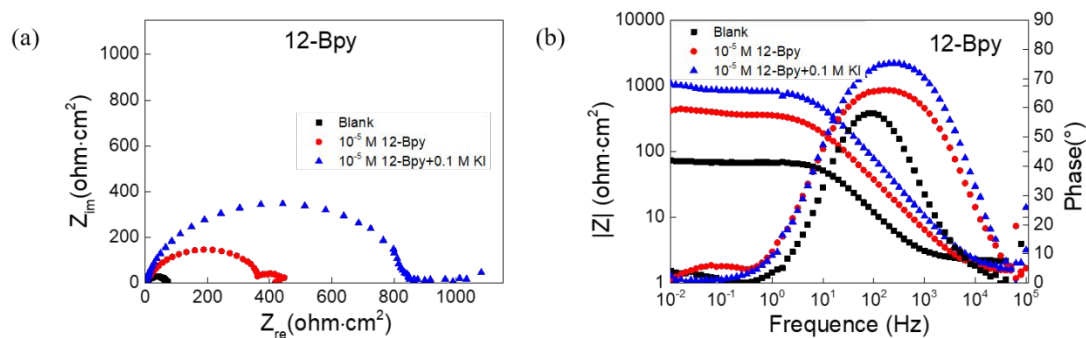


Figure S9. (a) Nyquist plots and (b) Bode plots for carbon steel in 1M HCl of blank, blank + 10^{-5} M 12-Bpy and blank + 10^{-5} M 12-Bpy + 0.1M KI.

Experimental

π -A isotherm of an analogue of n-Bpys, 18-Bpy

The surface pressure measurements were performed on a Model 612D computer-controlled Langmuir film balance (Nima Technology, Coventry, UK). The rectangular polytetrafluoroethylene (PTFE) trough (20×30 cm) with two movable barriers moving with the same compression rates was used. It was filled with water purified by means of a Milli-Q Plus water purification system with an electrical resistance of 18.2 M Ω . The subphase temperature was controlled at 25 $^{\circ}$ C by flowing water from a thermostat (Phoenix P1 Circulator, Thermo Haake, Germany) circulated through the base plate of the trough during the experiment. To eliminate the influence of the contaminant, a PTFE nozzle with an aspirator pump connected was applied to suck the surface of the subphase before experiments. The surface was deemed to be clean when the fluctuation in surface pressures was found to be less than 0.2 mN/m during complete compression of the surface without the Gemini surfactant. The surface pressure was measured by the Wilhelmy method using a low-ash filter paper plate (10 mm \times 23.5 mm) with the aid of a template and a razor knife.

A chloroform solution of 18-Bpy was used as the spreading solution for the formation of Gemini surfactant monolayer and spread the solution on the subphase with a micrometer syringe. After waiting for 10 min to let the solvent evaporate entirely, the compression curves were recorded. All of the compression rates adopted were 15

cm²/min.

Surface pressure-molecular area isotherms

The structure and orientation of n-Bpys adsorbed on steel surface were considered to be similar to those of 18-Bpy derived from its surface pressure-molecular area isotherm. The pure water and 0.01 M FeCl₃ solution was selected as subphase of LB trough. The π -A isotherm of 18-Bpy on pure water and FeCl₃ solution is shown in Figure S10. The curve was measured at least three times to confirm reproducibility. The liftoff area (A_L , the molecular occupation area where the isotherm rising just emerges related to the baseline), the limiting area (A_∞ , an empirical parameter approximating the area occupied by the molecules at zero pressure) and the molecular area at collapse are ~ 276 , 174 and 86 Å²/molecule, respectively, based on Figure S10a. Correspondingly, the area values on FeCl₃ solution are ~ 200 , 133 and 83 Å²/molecule, respectively, based on Figure S10b.

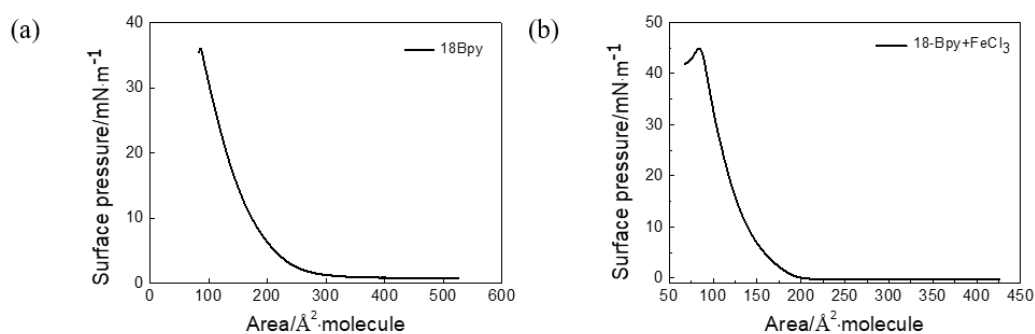


Figure S10. The π -A isotherm of 18-Bpy on (a) pure water and (b) FeCl₃ solution.

The chain orientation of 18-Bpy on air/water interface have two extreme forms, i.e., perpendicular (Figure S11a) or horizontal (Figure S11b) arranging modes on the water surface. According to the bond length and bond angle, the molecular area of 18-Bpy in such two modes was found to be ~ 70 (perpendicular, Figure S11a) and 270 (horizontal, Figure S11b) Å², respectively. In general, A_L provides very useful information about molecular orientation at the onset of intermolecular contact and a

gas-liquid two phase region exists at large molecular areas until all the gas is compressed to liquid, and then the liftoff occurs. Herein, the A_L is in a great agreement with the molecular area calculated from the fully extended configuration of 18-Bpy, suggesting that prior to A_L , 18-Bpy adopts a fully extended configuration, entirely lying flat on the water surface. More interestingly, the A_∞ of 18-Bpy is less than A_L , but larger than the molecular area calculated from the perpendicular mode, meaning that when the molecular density increases, the chains would start to detach themselves completely from the water surface, but the chain orientation of 18-Bpy is not completely vertical, as discussed in our previous work¹⁻³. Consequently, from the molecular area of the experimented area and the calculated area, we may conclude that the chain orientation of 18-Bpy is not likely completely vertical but is partially tilting or with some inhomogeneous structure.

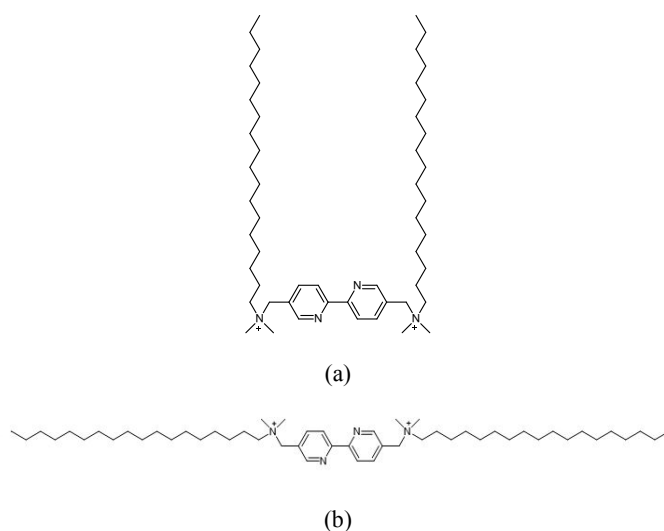


Figure S11. Two molecular configurations (a) perpendicular and (b) horizontal of 18-Bpy on the water surface.

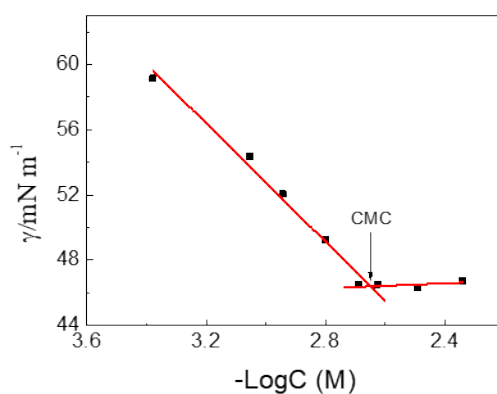


Figure S12. The surface tension of 8-Bpy at different concentration at 298K.

References

- (1) Chen, Q. B.; Yao, J. Y.; Hu, X.; Shen, J. C.; Sheng, Y. J.; Liu, H. L. Monolayer effect of a gemini surfactant with a rigid biphenyl spacer on its self-crystallization at the air/liquid interface. *J. Appl. Cryst.* **2015**, 48, 728-735.
- (2) Chen, Q. B.; Liang X. D.; Wang S. L.; Xu S. H.; Liu H. L.; Hu, Y. Cationic Gemini surfactant at the air/water interface. *J. Colloid Interf. Sci.* **2007**, 314, 651-658.
- (3) Chen, Q. B.; Zhang, D. Z.; Li, R.; Liu, H. L.; Hu, Y., Effect of the spacer group on the behavior of the cationic Gemini surfactant monolayer at the air/water interface. *Thin Solid Films* **2008**, 516, 8782-8787.