

Electronic supplementary information (ESI)

Spontaneous formation of mono-n-butyl phosphate and mono-n-hexyl phosphate thin films on the iron surface in aqueous solution and their corrosion protection property

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S1. Synthesis and purification of BP and HP

Herein the synthesis and purification of BP were taken as an example. 1-Butanol (0.135 mol) was heated at 40 ~ 50 °C, and then P₂O₅ powders (0.045 mol) were added in three portions and the reaction was maintained at 70°C for 3 h. Afterwards deionized water (0.045 mol) was added to the reaction mixture and kept under stirring at 80°C for another 2 h. After the esterification reaction finished, the desired product BP was obtained from the mixture through the following three steps: At first, an excessive amount of NaOH solution was added and stirred for at least 30 min. The resulting aqueous phase was separated out and collected by adding diethyl ether. Next, an excessive amount of HCl solution was added to the collected aqueous phase and fully stirred, followed by the extraction of organic phase with diethyl ether. Finally, BP was obtained by the distillation of the collected organic solution. The synthesis and purification of HP followed the similar procedure.

Table S1

Surface tension values of pure water and the aqueous solutions with different BP and HP concentrations.

Solutions	Surface tension (γ) (mN m ⁻¹)
Pure H ₂ O	72.90
BP solution (0.001 wt%)	72.70
BP solution (0.01 wt%)	66.87
BP solution (0.1 wt%)	51.35
HP solution (0.001 wt%)	69.41
HP solution (0.01 wt%)	45.13
HP solution (0.1 wt%)	28.54

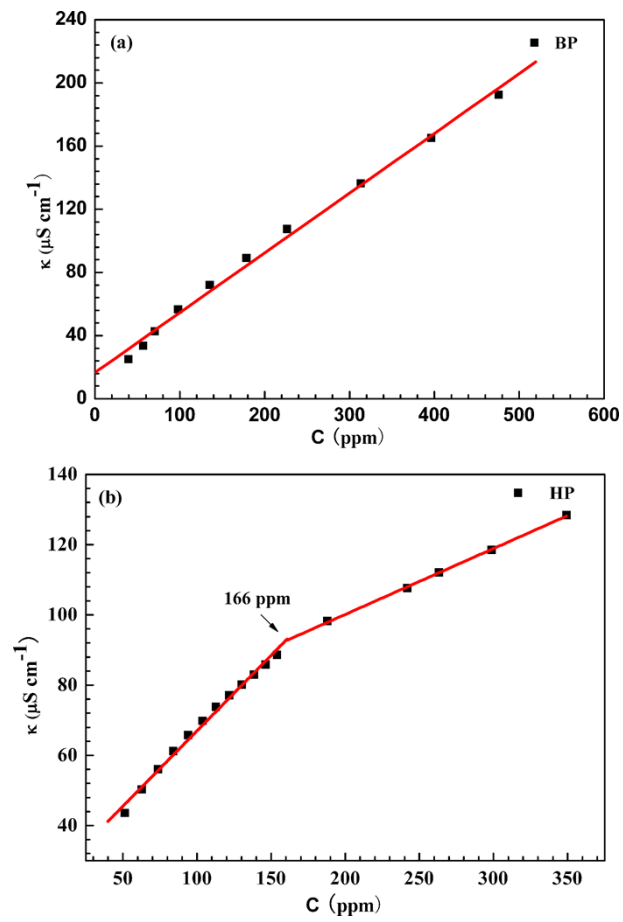


Fig. S1. Curves of electrical conductivity against the concentrations of BP and HP at 25 °C.

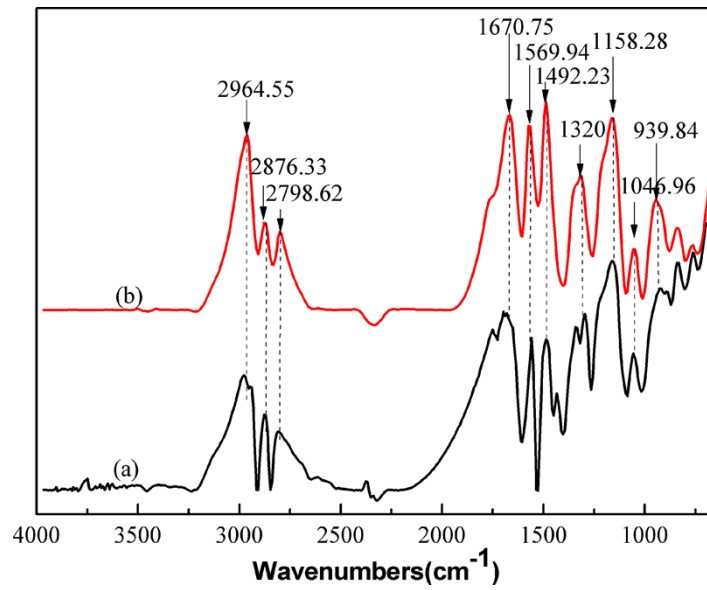


Fig. S2. FTIR spectra of the iron plate samples modified BP thin films after EIS (a) and polarization curve (b) measurements.

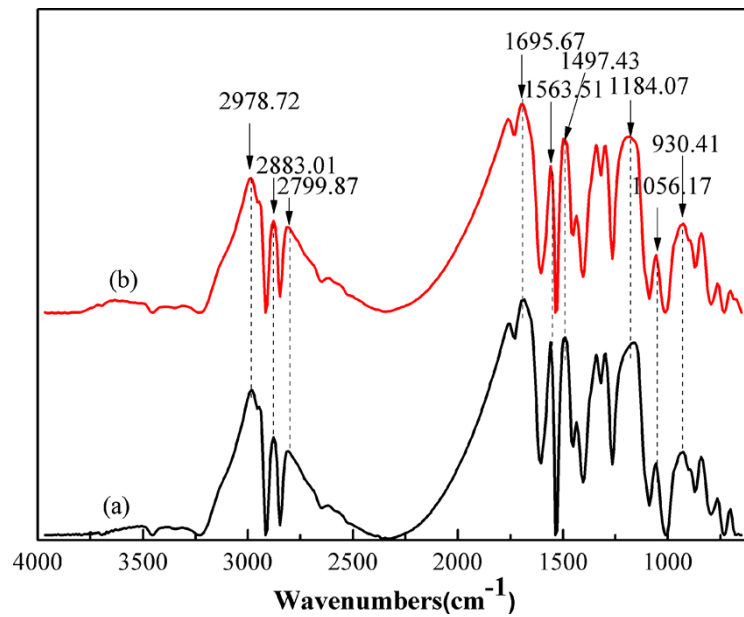


Fig. S3. FTIR spectra of the iron plate samples modified HP thin films after EIS (a) and polarization curve (b) measurements.

S2. Variation of OCPs with time

Fig. S4 describes the changing trends of open circuit potential (OCP) values of bare and modified iron electrodes with immersion time after different electrodes were immersed in 3.5 wt% NaCl aqueous solutions. For the bare iron electrode, the OCP values varied between -582.3 and -621.4 mV in 1 h. The curve was somewhat undulating, but overall the value of OCP decreased with time and tended to be stable about 3000 s later. For the BP thin film modified iron electrodes, the OCP values dropped sharply in the first 800 s and then continued to decrease slowly, approaching relatively stable values about 2600 s later. By contrast, for the HP thin film modified electrodes, the OCP values firstly increased and then decreased, or repeated several times, and gradually became stable 1 h later. It is also worth mentioning that, the modified iron electrodes showed the higher OCP values than the bare electrode, and the extent of the increase was dependent on the self-assembled molecules and the immersion time. On the basis of variation of OCPs with immersion time, the EIS test for each working electrode was conducted after the electrode was exposed to the corrosive electrolyte for 1 h in order to ensure that the electrode was in steady state during the EIS measurement. And moreover, after an EIS test finished, the variation of the OCP values with time was measured again. The obtained data demonstrated that the working electrode did not deviate from the previous steady state after the EIS test, as indicated in Fig. S2.

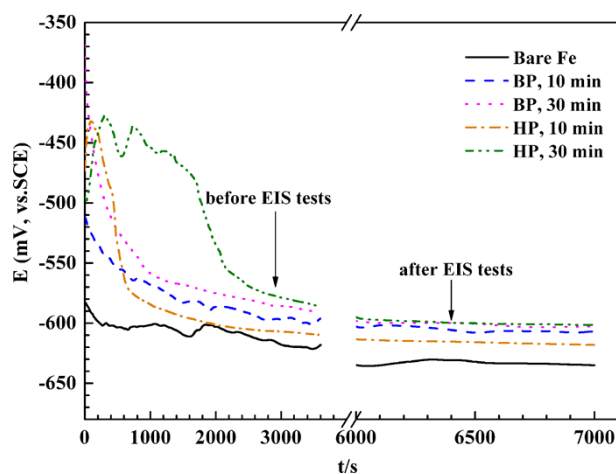


Fig. S4. Variation of the OCPs of different electrodes (bare iron and modified iron electrodes) with immersion time in 3.5 wt% NaCl solution. The modified electrodes

were prepared by immersing an iron electrode in 0.1 wt % BP or HP solutions for 10 min and 30 min respectively.