



Room Temperature Columnar Liquid Crystalline Perylene Bisimide as a Novel Corrosion Resistant Surface Film for Mild Steel Surface

Paresh Kumar Behera¹ · Srilatha Rao² · Lekan Taofeek Popoola³ · Sowmyashree Ayachit Swamirayachar² · Mothana Ghazi Kadhim AlFalah^{4,5} · Fatma Kandemirli⁶ · Shwetha Kodange² · Gopala Krishna Prashanth⁷ · Ammathnadu Sudhakar Achalkumar⁸

Received: 26 August 2022 / Revised: 22 November 2022 / Accepted: 30 November 2022 / Published online: 15 December 2022
© The Author(s) 2022

Abstract

The corrosion process can be seen as a widespread phenomenon, which is both pervasive and unstoppable. This is an undesirable phenomenon that reduces the life of materials and takes away their beauty. Potentiodynamic and electrochemical impedance tests are used to explore the corrosion inhibition abilities of a room temperature columnar liquid crystalline perylene bisimide (PBIO10) on mild steel (MS) samples in 1 M HCl. The inhibitor PBIO10 was demonstrated to be an outstanding corrosion inhibitor, with a maximum inhibition efficiency of 76%. In light of potentiometric polarization results, corrosion inhibition was achieved as the inhibitor getting adsorbed on the metal, and they fit into the category of anodic inhibitors. The protective layer was examined from SEM to confirm the protective coating generated on the MS surface. The increase in contact angle confirms the formation of a uniform layer on the MS surface. Analysis of the optical textures observed in POM, the nature of the mesophase under examination to columnar rectangular (Colr) phase. From the TGA, it was found that PBIO10 exhibits higher thermal stability up to 370 °C. The density functional theory (DFT) and Monte Carlo simulation approach were used to investigate the relationship between molecular structure and inhibitory efficacy. The thermal behavior of PBIO10 was investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) studies. The phase transition from crystal to LC phase was at first examined with the help of POM observation.

✉ Lekan Taofeek Popoola
ltpopoola@abuad.edu.ng; popoolalekantaofeek@yahoo.com

✉ Ammathnadu Sudhakar Achalkumar
achalkumar@iitg.ac.in

¹ Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India

² Department of Chemistry, Nitte Meenakshi Institute of Technology, Bangalore, India

³ Chemical and Petroleum Engineering Department, Afe Babalola University, Ado-Ekiti, Ekiti State, Nigeria

⁴ Metallurgy and Materials Engineering Department, Faculty of Engineering and Architecture, Kastamonu University, 37150 Kastamonu, Turkey

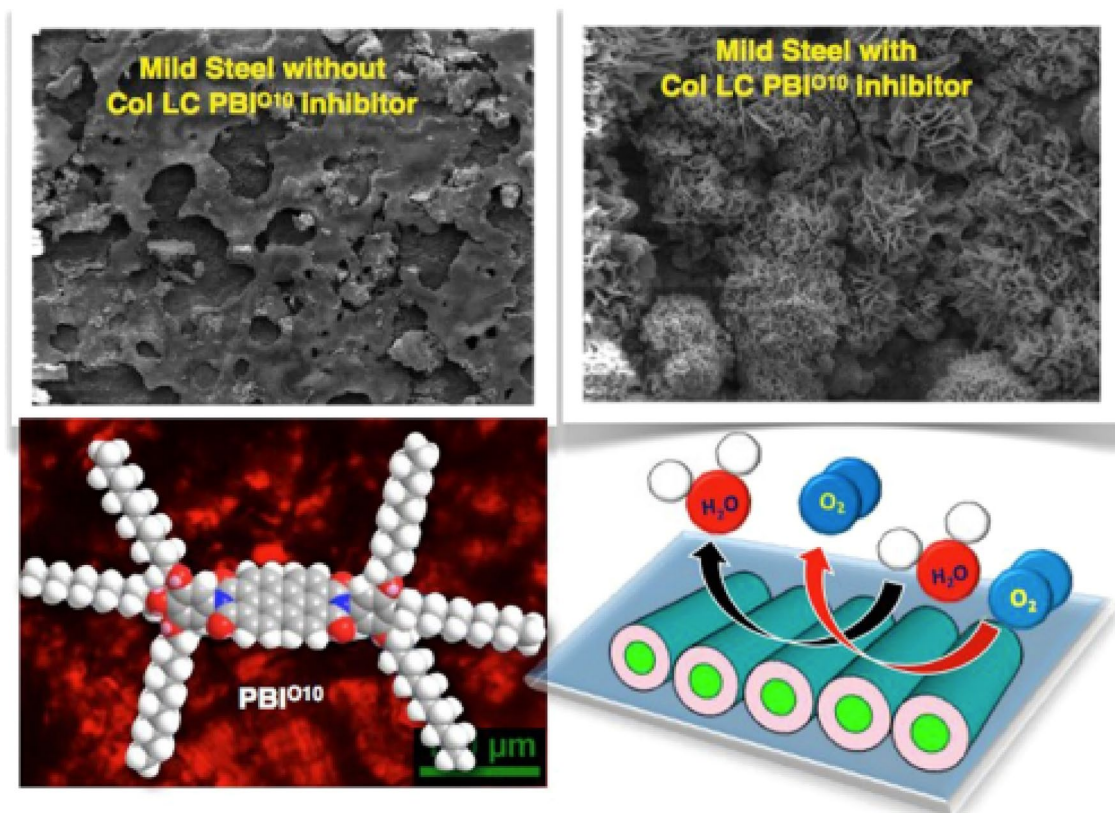
⁵ Materials of Engineering Department, College of Engineering, University of Al-Qadisiyah, 58002 Al-Qadisiyah, Iraq

⁶ Biomedical Engineering Department, Faculty of Engineering and Architecture, Kastamonu University, 37150 Kastamonu, Turkey

⁷ Department of Chemistry, Sir M. Visvesvaraya Institute of Technology (Affiliated to Visvesvaraya Technological University, Belagavi-590 018, India), Bengaluru 562157, India

⁸ Centre for Sustainable Polymers, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India

Graphical Abstract



Keywords Perylene bisimide · Mild Steel surface · Adsorption · EIS · Polarization · Molecular structure (DFT) · Columnar Liquid Crystal

1 Introduction

The corrosion process is a natural one driven by energy considerations. Usually, in pickling baths, sulphuric acid and hydrochloric acids are typically used to remove the metal oxides from the surface. In engineering and commercial processes, inhibitors are used to minimize metal failure and acid utilization [1–3]. Almost all environments are corrosive to some extent and contribute to material failure and also lead to huge economic loss to society [4]. Inhibition in a way helps to prevent corrosive attacks on metallic materials [5] extensively studied using corrosion inhibitors that offer simple solutions for protecting metals from corrosion in aqueous environments, which have been extensively studied. By adding a small concentration of an inhibitor, it can reduce the loss of metal, reduce hydrogen embrittlement, effectively prevent pitting of metals, reduce over-pickling and acid fumes, and reduce acid consumption by forming an adsorbed layer or retarding the anode, cathode, or both corrosion [6]. Under the considerations,

the mechanism of inhibition by an inhibitor is mainly due to the adsorption that is influenced by the nature of the inhibitor, surface charge, diffusion barrier, electrical double layer, electrode reactions, blocking reaction sites, and chemical structure of inhibitors. Oxygen-containing compounds such as chromates, phosphates, and tungstate inhibit corrosion by anodic inhibition, thereby reversing the corrosion potential's direction to cathodic [7]. Compounds such as sodium, barium, and sulphur are commonly used as cathodic poisons and lower corrosion rates through hydrogen reduction reactions by slowing down the rate of cell reduction to reduce corrosion [8]. By reacting with metal in neutral or alkaline solution, these inhibitors form a protective film on anodes or cathodes, where the main cathodic reaction is an oxygen reduction reaction in which the metal surface is coated with a film oxide or hydroxide or by depositing directly on the metal surface by changing surface charges and dipoles [9]. Some studies have shown that halogen ions to a certain extent can inhibit corrosion in acid solutions that follow the effectiveness order;

$I^- > Br^- > Cl^-$. Generally, the inhibition performance of different inhibitors will follow the opposite order of their electronegativities, for example among S, N, O, and P, the inhibition performance will follow: $O < N < S < P$. Moreover, heavy metal complexes of Pb^{2+} , Ti^+ , Mn^{2+} , and Cd^{2+} are capable of inhibiting corrosion in acid media because of their extreme polarizability and low electronegativities [10, 11, 11]. These inhibitors are effective on metals and non-metals alike since they cover large areas of surface and effortlessly transfer electrons to the vacant orbitals of their atoms [12]. Among lone-pair electron-containing compounds are amines, quinolines, thio compounds, aldehydes, imidazoles, and derivatives of the hydrazide act as excellent corrosion inhibitors [13–17]. The inhibition action of mild steel by benzaldehyde thiosemicarbazone derivatives in 0.5 M H_2SO_4 is also reported [18]. Nowadays, a key focus of corrosion inhibition has become human health and safety concerns. Therefore, researchers have started focusing on the use of eco-friendly compounds like plant extracts [19–21], the nontoxic organic compounds as green alternatives for toxic and harmful compounds [22, 23]. Due to the biodegradability, eco-friendliness, low cost, and easy availability of inhibitors they are used as corrosion inhibitors for several metals and metal alloys under different environmental conditions [19, 24–26].

There are several literature reports point out that effective organic inhibitors usually possess π -conjugation and polar groups. The physiochemisorption mechanism plays a major role in this inhibition activity of conjugated aromatic organic molecules. The corrosion inhibition process depends on the nucleophilicity of the polar substituents and π -conjugated aromatic cores, which enhances the inhibition response in the corrosion process. Well-ordered applications were also important for anti-corrosion application. Liquid crystals (LCs) are a special state of matter, which have got the prominence due to their unique blend of order and mobility between solids and liquids. They are exceptionally sensitive to external perturbations like temperature, pressure, electric and magnetic fields and are thus successfully employed in the fabrications of display devices and sensors. The application of LCs for the inhibition of corrosion on metal surfaces has been reported. The exceptional inhibition potential of LCs can be accredited to their hydrophobic nature and good protective coat formation on the metal surface due to their self-healing nature [27]. Discotic LCs (DLCs) are an active research area, which is presently studied from the perspective of organic semiconductors capable of 1D charge transport, and is usually composed of a central polyaromatic core and several peripheral flexible chains [28]. DLCs based on perylene bisimides (PBIs) are one such widely studied DLCs due to the presence of an electron-deficient (n-type behavior) central core. PBI-based DLCs usually stabilize columnar

(Col) phases that can act as 1D pathways for charge migration, over a wide thermal range and they are also known for high photo, thermal and chemical stability. Thus we envisaged that the Col LCs formed from PBIs may provide a well-defined highly stable hydrophobic supramolecular structure with a large homogeneous corrosion-resistant film on MS substrate over a wide temperature range.

2 Experimental

2.1 Materials

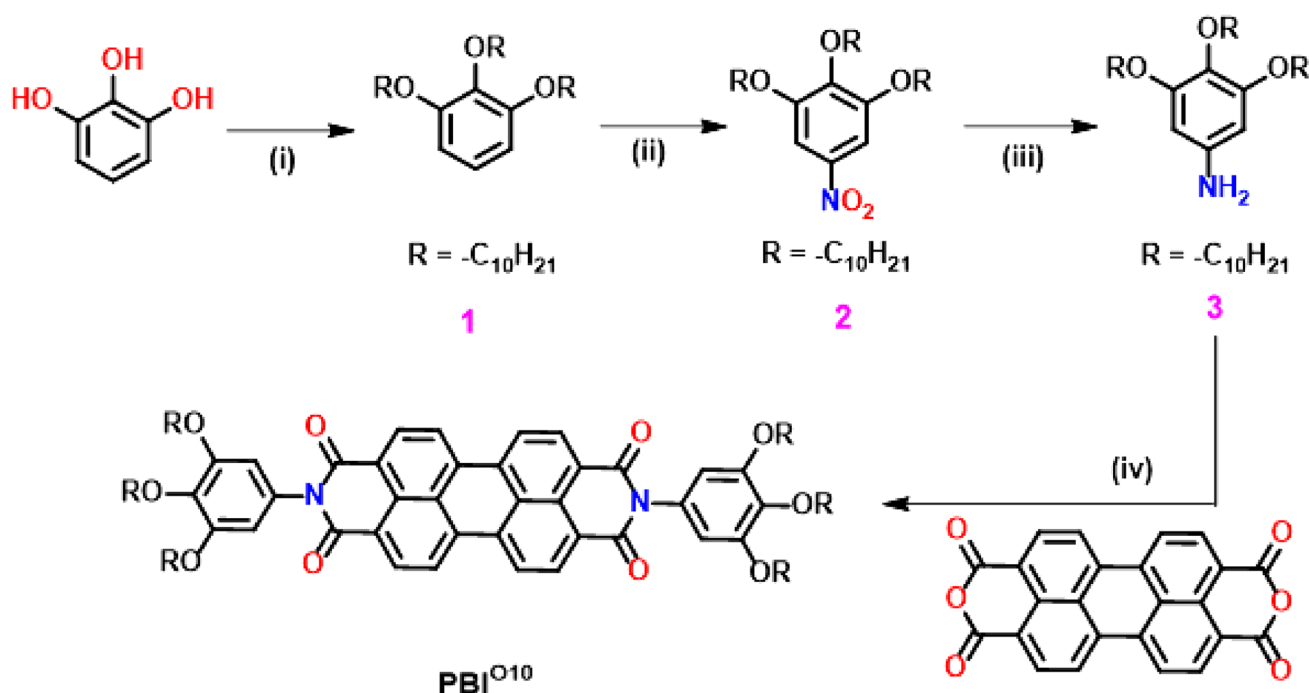
In this study, AR grades were utilized without any purification, solvents were dried following the typical standard procedures. The HCl was procured from Merck, India. MS samples of composition C (0.051 percent), Mn (0.179 percent), S (0.023 percent), P (0.0005 percent), and Fe (99.42 percent) [29, 30] were procured from the local market, and were sliced into 1 cm^2 area, washed, ultrasonicated in absolute ethyl alcohol and polished by the sandpapers of 200–1600 grids. The samples were then dried and placed in desiccators for future use.

2.2 Synthesis

The synthetic methodology utilized for the preparation of tri-alkoxy phenyl-functionalized PBI^{O10} is outlined in Scheme 1. Pyragallol was *O*-alkylated with *n*-bromodecane using Williamson ether synthesis using anhydrous K_2CO_3 as a base to get tri-*n*-decyloxybenzene (1). This was subjected to nitration to obtain 3,4,5-tridecyloxynitrobenzene (2). The nitro compound was reduced to corresponding aniline (3) by reduction using hydrazine hydrate in the presence of 10% palladium on charcoal. The aniline obtained was condensed with perylene tetracarboxylic bisanhydride in presence of imidazole and zinc acetate in a microwave reactor to give the final desired product with 82% yield. The crude compound was then subjected for repeated column purifications on neutral alumina with chloroform-hexane mixture (50%) as an eluent to obtain the final product as gummy red-colored solid. PBI^{10} was completely characterized by 1H NMR, ^{13}C NMR, IR spectroscopy and, mass spectrometry (Please see SI for details).

2.3 Preparation of Sample Medium and Mild Steel

Initially, metal samples with 1 cm^2 exposed surface area were investigated electrochemically, and the epoxy resin was used to cover the unexposed areas. MS specimens were abraded with 200–1600 grade SiC emery sheets before being cleaned in double distilled water, then with tissue paper, the samples were then dipped in ethyl alcohol



Scheme 1 Reagents and conditions. **i** anhydrous K_2CO_3 , Dry DMF, $C_{10}H_{21}Br$, 80 °C, 12 h (75%), **ii** $NaNO_2$, HNO_3 , 0 °C, 1 h (90%), **iii** N_2H_4 , H_2O , EtOH, H_2 -Pd/C, rt, overnight (67%), **iv** $Zn(OAc)_2$, imidazole, microwave irradiation, 35 W, 35 min, 165 °C (82%)

for five seconds, dried fully, and stored in desiccators [29, 30]. In this experiment, we used a commercially available AR grade 37% HCl to prepare 1 M HCl solution. An estimated amount of PBI^{O10} inhibitor was dissolved in chloroform to prepare concentrations of 100, 200, 300, and 400 parts per million. This inhibitor solution was dropped onto mild steel (MS) surfaces under rapid vibration to ensure the formation of a thin film. In order to ensure proper alignment of the LC film, the MS is heated and cooled several times, then air dried for future use.

2.4 Electrochemical Impedance Spectroscopy and Potentiodynamic Polarization Measurements (EIS and PDP)

An electrochemical workstation (CHI660E) was used for the EIS measurements. The measurements were operated using a three-electrode cell containing a platinum electrode, an Ag/AgCl electrode, and a MS plate as a working electrode with a 50 mL solution volume. Various concentrations of the PBI^{O10} were electrochemically tested at 30 °C after immersing it for 30 min in the test solution [31]. In EIS investigations, the frequency range was from 10.0 kHz to 0.1 kHz, with an amplitude of 0.005 V. The inhibition efficiency ($\eta\%$) was determined by utilizing the below Eq. (1).

$$\eta\% = \frac{\frac{1}{(R_p)_a} - \frac{1}{(R_p)_p}}{\frac{1}{(R_p)_a}} \times 100 \quad (1)$$

Here, $(R_p)_a$ and $(R_p)_p$ being polarization resistances in absence and presence of inhibitor, respectively.

The potentiodynamic polarization were computed at a scan rate of 0.4 mV/s across a potential range of -200 to +200 mV [20]. By extending Tafel plots to corrosion potentials, based on anodic and cathodic branches, we can determine the current density (i_{corr}) and corrosion potential (E_{corr}). Using the Tafel extrapolation plot and Eq. 2, we were able to determine inhibition efficiency ($\eta\%$).

$$\eta\% = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100 \quad (2)$$

Here, $i_{(corr)a}$ and $i_{(corr)p}$ are the corrosion current densities in μAcm^{-2} in absence and presence of inhibitor, respectively.

2.5 Contact Angle Measurements

A Goniometer Insc. was used to measure water contact angles (WCA) on the MS surface, using the sessile drop method [32] and FAMAS (Interface Measurement and Analysis System) software. On MS surfaces, 2 μL water droplets were placed. From this analysis, when testing with water, advancing angles

will correspond to the hydrophobic domains and receding angles will characterize the hydrophilic domains, on the surface. Thus, contact angle measurements were performed before and after adsorption process of the inhibitor, and the measurement was repeated ten times.

2.6 Surface Morphology Studies

The scanning electron microscopy experiment was aimed at observing the morphology of MS metal surfaces before and after the addition of the PBI⁰¹⁰ corrosion inhibitor. Fresh MS samples were air-dried after being immersed in a 1 M HCl solution for 22–24 h. A Tescan Vega 3 scanning electron microscope was used to evaluate inhibitor-treated specimens. To learn about the effects of the inhibitor at 400 ppm concentrations, the sample was soaked in a 1 M HCl solution and then dried in the air.

2.7 Density Functional Theory Calculation (DFT)

DFT experiments utilizing the DMol3 module in Material Studio 2017 (Method: GGA/BLYP; Basis set: DNP 3.5; Solvation model: COSMO) supported the electrochemical findings [33]. These equations were utilized to generate the various DFT indices mentioned in Table 1 [33–36] based on the energy of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) Eq. 3 and 4.

$$I = -E_{HOMO} \quad (3)$$

$$A = -E_{LUMO} \quad (4)$$

$$X = \frac{I + A}{2} \quad (5)$$

$$\eta = \frac{I - A}{2} \quad (6)$$

$$\mu = -X \quad (7)$$

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (8)$$

$$\Delta N = \frac{(X_{Fe} - X_{inh})}{2(\eta_{Fe} + \eta_{inh})} \quad (9)$$

The energy of the highest-occupied molecular orbital is denoted by E_{HOMO} , whereas the energy of the lowest-unoccupied molecular orbital is denoted by E_{LUMO} . I and A , respectively, stand for the electron affinities and ionization potentials. The symbols X , η , μ , ΔE , and ΔN , respectively, stand for electronegativity, chemical potential, hardness, energy band, and electron transfer percentage. The work function provided by Fe $X_{Fe} = 7$ eV and $\eta_{Fe} (\eta_{Fe} = 0)$ was utilized to get the value of ΔN .

2.8 Monte Carlo Calculations

Monte Carlo simulations were utilized to show how the adsorbate and substrate chemicals interacted using Material Studio (2017)'s adsorption locator module. The Adsorption Locator module was created by BIOVIA Company based on the Monte Carlo (MC) simulation methodology [37]. We may get more knowledge using Monte Carlo simulations to examine the interfacial interactions between inhibitor molecules and the steel surface. The pre-geometrized conformers were administered at 298 K using Berendsen's thermostat Displacement, force, and energy convergence criteria, which were established at 0.015 Å, 0.5 kcal.mol⁻¹. Å, and 10⁻³ kcal.mol⁻¹, respectively. The simulation box was 37.23 × 37.23 × 74.19 Å³ (8 layers of Fe (110), 60 Å as a vacuum zone, and super cell: 15 × 15), and the system included 500 H₂O + 5H₃O⁺ + 5Cl⁻ + 1 inhibitor. We have chosen to replicate the adsorption process on the packed surface of Fe (110) because of its high density and high degree of stability throughout simulation. The bulk atoms on the Fe (110) plane were kept frozen throughout the simulations procedure. The van der Waals potential energy was estimated using the atom-based approach, and the electrostatic potential energy was determined using the Ewald summation method. Every structure in the system under consideration was optimized using the COMPASSII force field [38]. The Forcite module has handled geometry optimization. The studied PBI⁰¹⁰'s adsorption energy on the Fe substrate was calculated using Eq. 8 and documented in Table 1 [39, 40]

$$E_{ads} = E_{total} - E_{Metalsurface} - E_{inhibitor} \quad (10)$$

Here, E_{total} , $E_{Metalsurface}$, $E_{inhibitor}$ denote to the total energy of a system, energy of a metal surface, and energy of an inhibitor respectively.

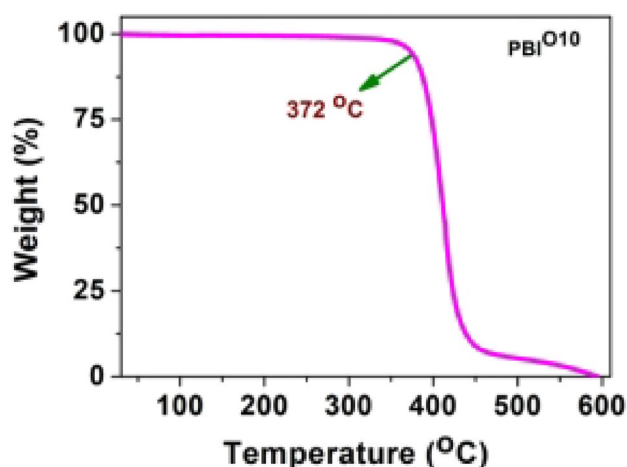
Table 1 DFT parameters and Adsorption energies for PBI⁰¹⁰

Molecule	$E_{HOMO}(eV)$	$E_{LUMO}(eV)$	$\Delta E(eV)$	$\eta(eV)$	$X(eV)$	$\Delta N(eV)$	$E_{ads}(kcal.mol^{-1})$
PBI ⁰¹⁰	-4.806	-3.830	0.976	0.488	4.318	2.748	-122.49

Table 2 Phase transition temperatures ($^{\circ}\text{C}$), corresponding enthalpies (kJmol^{-1}) obtained from DSC and decomposition temperature obtained by TGA

Phase sequence (kJ/mol)		Temperature at which 5 wt% decomposition occurred ($^{\circ}\text{C}$)
Second heating	First cooling	
Col_r 359.23 (2.87) I	I 354.92 (2.10) Col_r	372

Peak temperatures in the DSC thermo grams obtained during the second heating and first cooling cycles at $5\text{ }^{\circ}\text{C min}^{-1}$. *Col_r* Columnar rectangular phase, *I* Isotropic phase. Heating rate of $10\text{ }^{\circ}\text{C/min}$, Nitrogen atmosphere

**Fig. 1** TGA plots of compound **PBI^{O10}** (heating rate of $10\text{ }^{\circ}\text{C/min}$, Nitrogen atmosphere)

3 Results and Discussion

3.1 Thermal Behavior

The thermal behavior of **PBI^{O10}** was investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) studies. The phase transition from crystal to LC phase was first examined with the help of POM observation, which showed the appearance of strong birefringence in conjunction with an increase in the fluidity of the compounds on heating. The phase transition temperatures and the corresponding changes in enthalpy were confirmed by DSC thermograms. These values were in agreement with peak temperatures noted in POM studies (Table 2). An analysis of the optical textures observed in POM and the information obtained from XRD studies shown the nature of the mesophase under examination. From the TGA, it was found that **PBI^{O10}** exhibits higher thermal stability up to $370\text{ }^{\circ}\text{C}$ (Fig. 1). Under

POM observation, **PBI^{O10}** exhibits textures corresponding to the columnar rectangular (Col_r) phase. DSC thermograms showed that the mesophase was stable over a broad thermal range, including ambient temperature. The high clearing temperature confirms the strong core-core interactions between the aromatic cores. The assignment of the Col phase was confirmed from the powder XRD studies carried out at different temperatures (Table 3, Fig. 2).

The compound **PBI^{O10}**, which was a sticky mass, placed between a glass slide and coverslip, on slow heating in a programmable hotstage placed under a POM, showed an increase in fluidity and birefringence. The viscous mass was shearable on the application of mechanical stress and transformed into an isotropic liquid at $\approx 359\text{ }^{\circ}\text{C}$. Slow cooling of the isotropic melt at a rate of $5\text{ }^{\circ}\text{C/min}$, showed the mosaic texture emerging from large homeotropic domains, which is a characteristic feature of Col_r phases (Fig. 2a,b). The texture remains unaltered even at room temperature, while the DSC shows no signature of crystallization, confirming that the Col phase is stable even at room temperature (Fig. 2b). Powder XRD studies were carried out at different thermal intervals to analyze the mesophase structure. The XRD patterns obtained at $100\text{ }^{\circ}\text{C}$ is comparatively simpler than the ones obtained at room temperature which exhibited many peaks in the low-angle region (Table 3, Fig. 3). The plot of intensity vs 2θ obtained for compound **PBI^{O10}** at $28\text{ }^{\circ}\text{C}$ (Fig. 2c) showed a strong peak corresponding to a d spacing of $27.3\text{ }\text{\AA}$, followed by weaker peaks centered at smaller d spacings ($24.1\text{ }\text{\AA}$, $14.1\text{ }\text{\AA}$, 12.76 , $9.16\text{ }\text{\AA}$, $6.94\text{ }\text{\AA}$ and $5.69\text{ }\text{\AA}$) along with two diffused peaks with d -spacings of $4.36\text{ }\text{\AA}$ and $3.37\text{ }\text{\AA}$ in the wide angle region (Fig. 2c inset). These values could be indexed to the (10), (11), (12), (21), (30), (33) and (45) reflections of the Col_r phase (Fig. 2c). The first diffuse peak in the wide angle region arises from the packing of aliphatic tails, while the second peak corresponds to the stacking of discs within the columns. The second peak is usually seen when there is superior interaction between the discs in the column, and here it is driven by attractive π - π interactions of the PBI cores. The rectangular lattice parameters calculated were found to be $a = 27.30\text{ }\text{\AA}$, $b = 33.0\text{ }\text{\AA}$ with $c = 3.37\text{ }\text{\AA}$ shown in a schematic diagram (Fig. 2d).

From the lattice parameters, the lattice area (S) and molecular volume (V) were calculated. From the values of S and V the number of molecules forming the unit rectangular cell, *i.e.* Z was found to be 1. The XRD pattern obtained at higher temperature (*i.e.* $T = 100\text{ }^{\circ}\text{C}$, Fig.S5b) also showed a similar pattern but a lesser number of peaks at small angle, confirming the Col_r phase. Notably, the core-core peak was not observed here, which is understandable due to the reduced core-core interactions at higher temperatures.

Table 3 Results of (hkl) indexation of XRD profiles of the compounds at a given temperature (T) of mesophases

Compounds (<i>D</i> /Å)	Phase (T/°C)	<i>d</i> _{obs} (Å)	<i>d</i> _{cal} (Å)	Miller indices <i>hk</i>	Lattice parameters (Å), Lattice area <i>S</i> (Å ²), Molecular volume (Å ³)
PBI⁰¹⁰ (47.34)	Col _r (100)	27.21	27.21	10	<i>a</i> = 27.21
		15.03	15.03	11	<i>b</i> = 18.03
		13.62	13.60	20	<i>S</i> = 490.6
		8.33	8.56	12	<i>V</i> = 2261.65
		6.03	6.39	32	<i>Z</i> = 0.9
	Col _r (28)	4.61 (<i>h_a</i>)			
		27.30	27.30	10	<i>a</i> = 27.30
		24.10	21.03	11	<i>b</i> = 33.00
		14.12	14.12	12	<i>S</i> = 900.9
		12.76	12.61	21	<i>V</i> = 3036.03
		9.16	9.10	30	<i>Z</i> = 1.2
		6.94	7.01	33	
		5.69	5.80	45	
		4.36 (<i>h_a</i>)			
		3.37 (<i>h_c</i>)			

The diameter (*D*) of the disk (estimated from Chem 3D Pro 8.0 molecular model software from Cambridge Soft)

*d*_{obs} spacing observed, *d*_{cal} spacing calculated (deduced from the lattice parameters; *a*, *b* for Col_r phase, *c* is height of the unit cell). The spacings marked *h_a* and *h_c* correspond to diffuse reflections in the wide angle region arising from correlations between the alkyl chains and core regions, respectively. *Z* indicates the number of molecules per columnar slice of thickness *h_c* estimated from the lattice area *S* and the volume *V*. In the absence of *h_c*, *h_a* is used for the calculation of *Z*.

3.2 Electrochemical Impedance Spectroscopy Measurements

The inhibitory effect of **PBI⁰¹⁰** in 1 M HCl medium was studied over a frequency range of 100 kHz to 0.1 Hz using electrochemical impedance spectroscopy. Figure 3a shows the Nyquist plots for MS in the presence of **PBI⁰¹⁰** at concentrations ranging from 100 to 400 ppm in a 1 M HCl acid medium. The semicircular nature of the Nyquist plot suggests that charge transfer is taking place with non-ideal plots with depressed semicircles. The semicircle deviates slightly from a perfect circle due to the inhomogeneity and impurities of the metal surface. Furthermore, the diameter of the graph increases as **PBI⁰¹⁰** inhibitor concentration increases, indicating that it is more difficult to transfer charge from MS to the electrolyte (HCl) as inhibitor concentration increases. The following Table 4, shows the polarization parameters such as polarization resistance (*R_p*), double layer capacitance (*C_{dl}*), and inhibition efficiency (*η*%), respectively. The charge transfer resistance values gradually increased from 19.19 (blank) to 79.96 (400 ppm), and a gradual decrease in *C_{dl}* values suggested that an inhibitory protective film had been created on the surface of MS through adsorption. The value of the double layer capacitance (*C_{dl}*) decreases as a result of the decrease in local dielectric constant and increase in electrical double layer thickness that results in

the formation of layer of inhibitor at metal-solution interfaces. At 400 ppm concentration, 76% efficiency of the inhibitor was resulted. The inhibitor upon adsorption on the MS surface, leads to the formation of a double layer, which serves as a barrier between the MS surface and corrosive medium as evidenced by the double layer capacitance. The Bode plots (log *Z* vs. log Frequency) and Bode phase plots (phase angle vs. log Frequency) are given in Fig. 3b, where it can be seen that the slopes are not equal to -1 due to the nonhomogeneity of the solid surface. Additionally, the observed one-time constant behavior for blank as well as various inhibitor concentrations, displays the charge transfer process as the only relaxation process. An improved corrosion inhibition property is primarily the result of the adsorption of more and more inhibitor molecules to the surface, at higher concentrations on the surface of MS. Using the ZSimpWin software, the EIS spectrum obtained for mild steel was best fitted with the equivalent circuit, as shown in Fig. 3c, where *R_s* is the solution resistance, *R_p* is the polarization resistance, and *C_{dl}* is the double layer capacitance.

3.3 Studies on Potentiodynamic Polarization

The polarization curves for MS in 1 M HCl for a blank and for various concentrations of **PBI⁰¹⁰** in 1 M hydrochloric acid are shown in Fig. 4. The corrosion current density *i*_{corr}

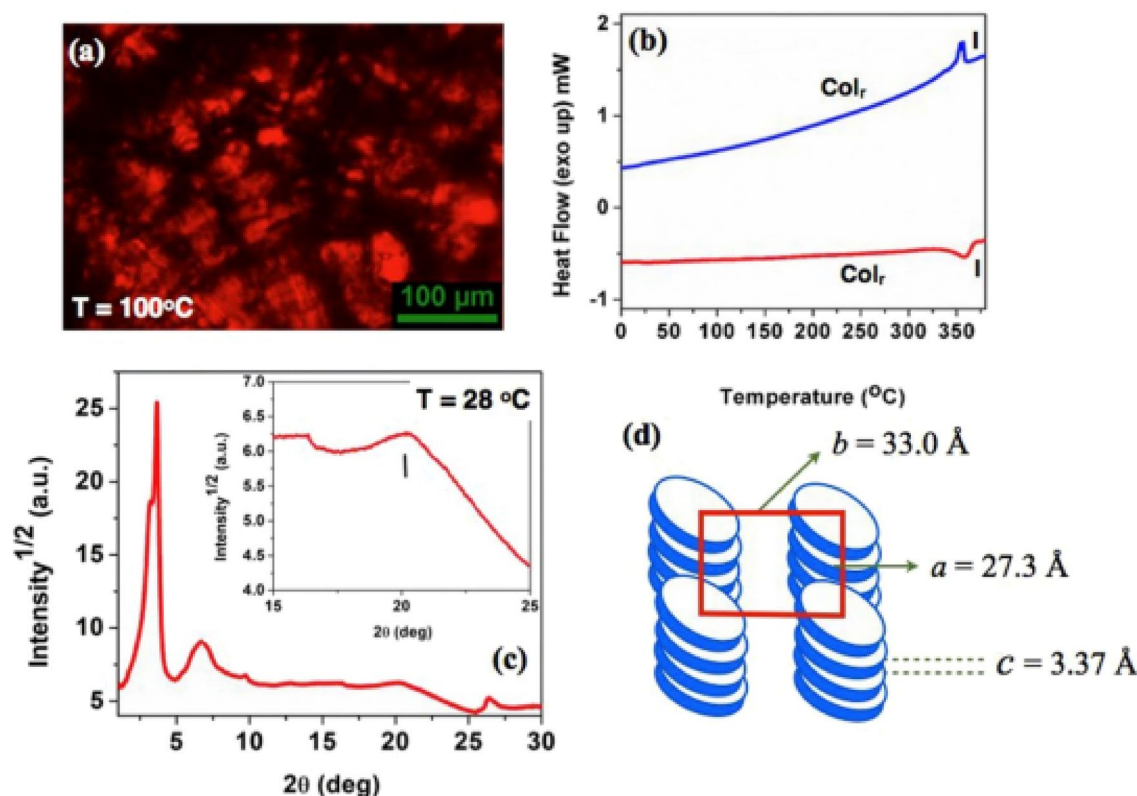


Fig. 2 POM image of $\text{PBI}^{\text{O}10}$ showing Col_r phase obtained on slow cooling (1°Cmin^{-1}) from the isotropic phase at 100°C (a) DSC thermograms obtained for the first cooling (blue curve) and second heating (red curve) at a rate of 5°C/min (b); Powder XRD pattern show-

ing the intensity against 2θ for the Col_r phase at 28°C (c); Schematic diagram of $\text{PBI}^{\text{O}10}$ showing the Col_r phase (considered the XRD pattern obtained at 28°C) (d)

(mA cm^{-2}) can be calculated from the graph exploration of polarization curves so that the corrosion rate (C_R) can be calculated. Following, the polarization parameters, including corrosion current (i_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope ($-\beta_c$), anodic Tafel slope (β_a), and inhibition efficiency (η) have been clearly given in Table 5. The addition of an inhibitor affects both the anodic and cathodic branches, as revealed by the polarization curves. As a result of the presence of some active sites in the molecules, such as aromatic rings, heteroatoms. [26], the inhibitor concentration slows down cathodic reduction and anodic metal dissolution. Therefore, both anodic and cathodic curves shifted towards lower current densities, with deflection values not exceeding ± 85 mV relative to the blank. Anodic corrosion inhibition occurs when the E_{corr} value moves toward positive with regard to a blank, and cathodic corrosion inhibition occurs when the E_{corr} value is negative with respect to a blank. In this case, the values are moving toward the positive, which indicates that predominantly anodic corrosion is occurring. During the adsorption process, inhibitors functional groups and structural characteristics are crucial. Potentiodynamic polarization curves and EIS measurements show good agreement when determining $\eta\%$.

3.4 Contact Angle Measurements

The hydrophobic and hydrophilic characteristics of the MS surface in the presence and absence of an inhibitor were estimated using the liquid sessile drop method and the Goniometer device from Tech Inc. An intermolecular interaction between water and the MS surface was observed using a drop of water placed on the MS surface. Figure 5a illustrates the contact angle of MS in the absence of the inhibitor 75.868° , confirming its partially hydrophilic nature. Figure 5b shows a more hydrophobic nature with 90.948° , in the presence of an inhibitor. The development of a protective layer on MS surfaces helps to improve corrosion resistance.

3.5 Surface Examination

The SEM images revealed extensive corrosion of MS surfaces in acidic environments. Figure 6a and b illustrate the surface morphology when MS is not exposed to the $\text{PBI}^{\text{O}10}$ inhibitor and when it is exposed to the $\text{PBI}^{\text{O}10}$ inhibitor, respectively. A SEM image of a fresh MS sample exposed to 1 M HCl at room temperature is shown in Fig. 6a. There were pits, cracks, and cavities on the

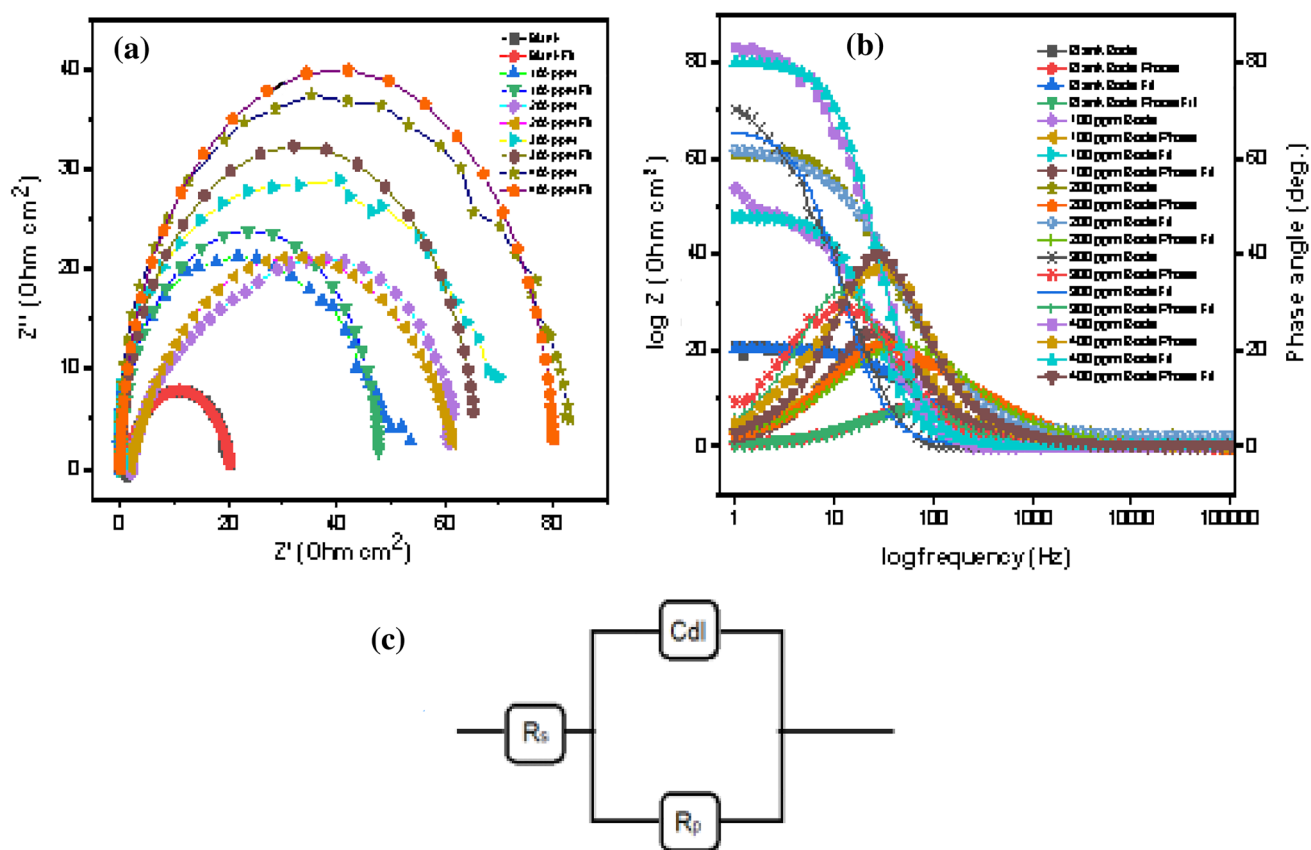


Fig. 3 **a** Nyquist plots **b** Bode and Bode Phase plots for MS obtained with the absence and presence of 100–400 ppm of **PBI⁰¹⁰** in 1 M HCl **c** Equivalent circuit for EIS

Table 4 Electrochemical impedance characteristics and inhibition efficiencies for MS in 1 M HCl solution in the absence and presence of various inhibitor concentrations

Sample (ppm)	R_s	Y_0	η	Cdl	R_p	η %
Blank	1.318 ± 0.05	2.639×10^{-4}	0.8718	$1.213 \times 10^{-4} \pm 0.08$	19.19 ± 1.13	–
100	0.1438 ± 0.06	1.293×10^{-4}	1.0000	$1.293 \times 10^{-4} \pm 0.07$	47.74 ± 1.97	59.80
200	1.957 ± 0.04	1.900×10^{-4}	0.7759	$5.239 \times 10^{-4} \pm 0.04$	60.81 ± 2.13	68.44
300	0.0993 ± 0.02	2.167×10^{-4}	0.9879	$2.057 \times 10^{-4} \pm 0.02$	65.90 ± 2.94	70.88
400	0.1546 ± 0.02	7.258×10^{-4}	1.0000	$7.258 \times 10^{-4} \pm 0.03$	79.96 ± 1.61	76.00

exposed surface. Also in Fig. 6b, the **PBI⁰¹⁰** modified surface exhibits no pits or cracks, which indicates that **PBI⁰¹⁰** molecules have been evenly coated on the MS surface, inhibiting corrosion. Figures 7a and b show the energy dispersive X-ray spectroscopy (EDX) surface composition of the metal in the absence and presence of **PBI⁰¹⁰** using EDX images from the composition table (insets), confirming the deposition of.

PBI⁰¹⁰ on the surface. The elements present in Fig. 7a are O-24.31%, P-0.04%, S-0.27%, Cl-7.95%, Fe-67.43% clearly shows metal undergoing corrosion dipped in HCl. In contrast, Fig. 7b showing the elemental composition of N- 5.11%, C-73.57% clearly shows that inhibitor molecules are deposited on the metal surface.

3.6 DFT Calculations

Figure 8a-d displays the **PBI⁰¹⁰** optimized structure, molecular electrostatic potential (ESP), HOMO, and LUMO. As shown in Fig. 8c, the HOMO energy is demonstrated to be localized on the heteroatoms (O=C-N group, aromatic group). The LUMO energy is present on the bulk of heteroatoms and the phenyl ring, as seen in Fig. 8d. Additionally, **PBI⁰¹⁰** has a HOMO value of -4.806 eV and a LUMO energy of -3.830 eV. They are the ideal places for interacting with the metal surface as a consequence. The ESP example lends further evidence to this. In Fig. 8b (ESP), the yellow region denotes electrophilicity, whereas the blue area denotes nucleophilicity. The yellow regions are dominated

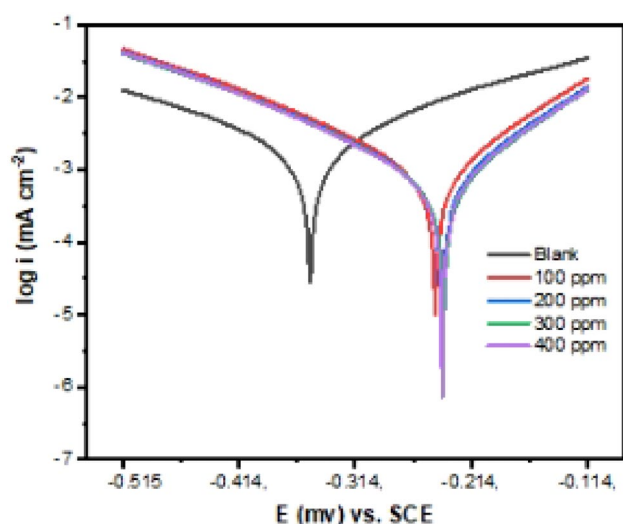


Fig. 4 Potentiodynamic polarization plots for MS in 1 M HCl solution in the absence and presence of various inhibitor concentrations

by N and O atoms, which are more likely to form covalent bonds with Fe-d orbitals [41, 42]. In general, a smaller gap E (Table 1) promotes higher inhibitor efficacy, increased surface adsorption, and easier molecule polarization. In other words, the experimental data strongly confirm the energy gap for $\text{PBI}^{\text{O}10}$ being 0.976 eV [31, 32]. Additionally, it displays the proportion of transmitted electrons (ΔN), a crucial statistic for assessing the effectiveness of the inhibition.

Table 5 Potentiodynamic polarization characteristics [$\pm$ Standard Deviation (SD)] and inhibition efficiencies for MS in 1 M HCl solution in the absence and presence of various inhibitor concentrations

Sample	E_{corr}	I_{corr}	$-\beta_c$	β_a	$\eta \%$
Blank	-0.3531	$2.037 \times 10^{-3} \pm 1.005$	5.789 ± 1.30	6.774 ± 1.78	—
100	-0.1811	$8.933 \times 10^{-4} \pm 0.85$	7.409 ± 1.25	10.410 ± 1.65	56.14
200	-0.1757	$6.736 \times 10^{-4} \pm 0.69$	7.373 ± 1.32	10.535 ± 1.39	66.93
300	-0.1744	$6.443 \times 10^{-4} \pm 0.58$	7.502 ± 1.51	10.897 ± 1.18	68.37
400	-0.1757	$6.041 \times 10^{-4} \pm 0.55$	7.766 ± 1.63	10.670 ± 1.29	70.34

The literature indicates that the capacity to transfer electrons to the metal surface is enhanced by raising the inhibition efficacy to a value of ΔN (2.748) < 3.6 [43–45]

3.7 Monte Carlo Simulations (MCS)

Using Monte Carlo simulations, the inhibitors' adsorption behavior on the surface of Fe (110) was examined while also taking into consideration the testing circumstances (the continuance of the tested compounds in an HCl solution). Figure 9 shows how inhibitors have significantly steadier low-energy adsorption characteristics on the $500 \text{ H}_2\text{O} + 5 \text{ H}_3\text{O}^+ + 5 \text{ Cl}^-/\text{Fe}$ (110) molecule system. The adsorption energy of the inhibitor evaluated on the Fe (110)/inhibitor system is listed in Table 1. The investigated inhibitor molecules produced an umbrella-like cover on the Fe surface, as illustrated in Fig. 9, with a preference for vertical orientation, optimizing contact and enhancing surface defence. This adsorption paradigm results from the strong interaction between the phenyl rings of inhibitor compounds and the metal surface. The N and O atoms exhibit strong interactions with one another, many electrons, and the metal surface, which may allow vacant orbital electrons of iron coordinate bonds to form, according to these data. Consequently, MCS was able to confirm the inhibitor adsorption and the development of a stable barrier layer on the mild steel surface as a result. This sequence is also supported by the results of surface characterization and electrochemistry [45]

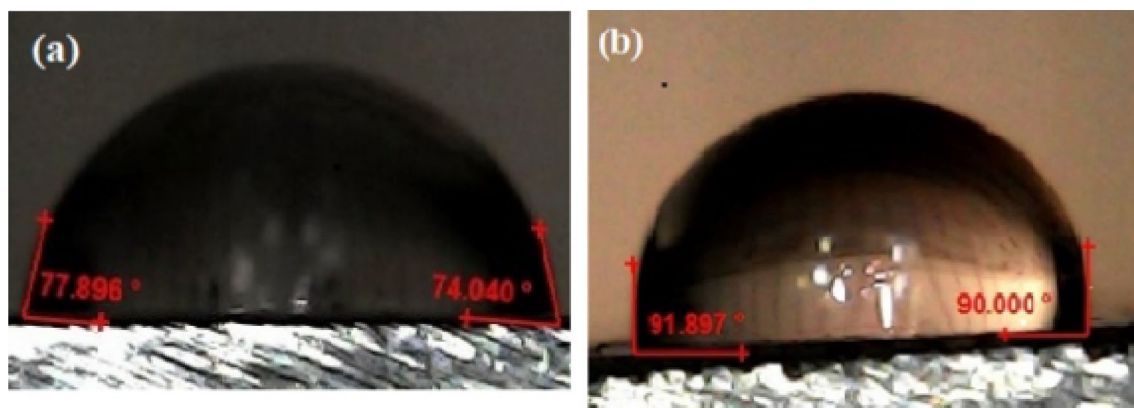


Fig. 5 Contact angle images **a** absence **b** presence of $\text{PBI}^{\text{O}10}$ inhibitor

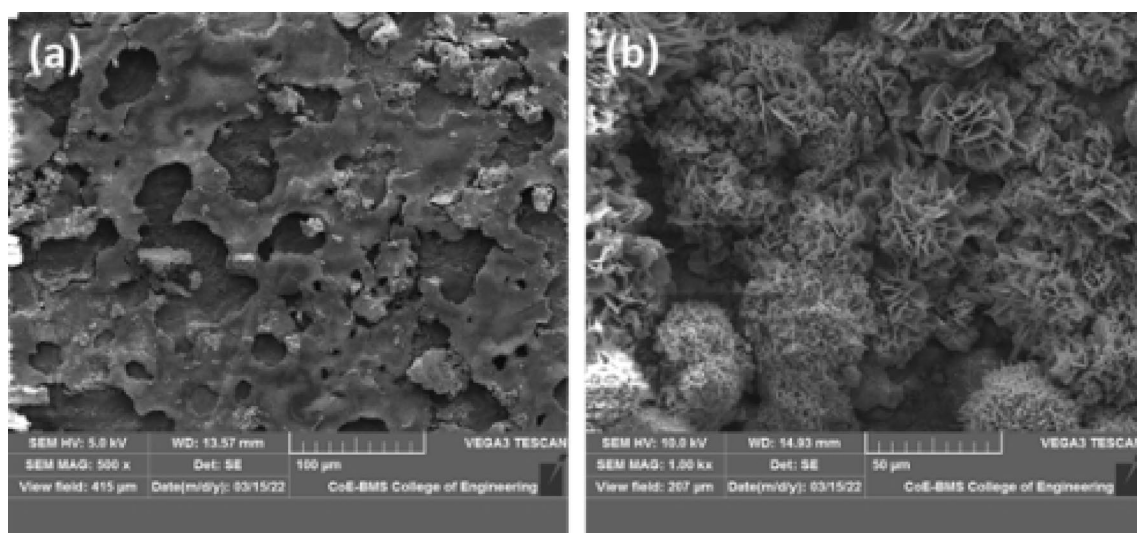


Fig. 6 SEM images of MS in 1 M HCl (a) without inhibitor (b) with PBI^{O10} inhibitor

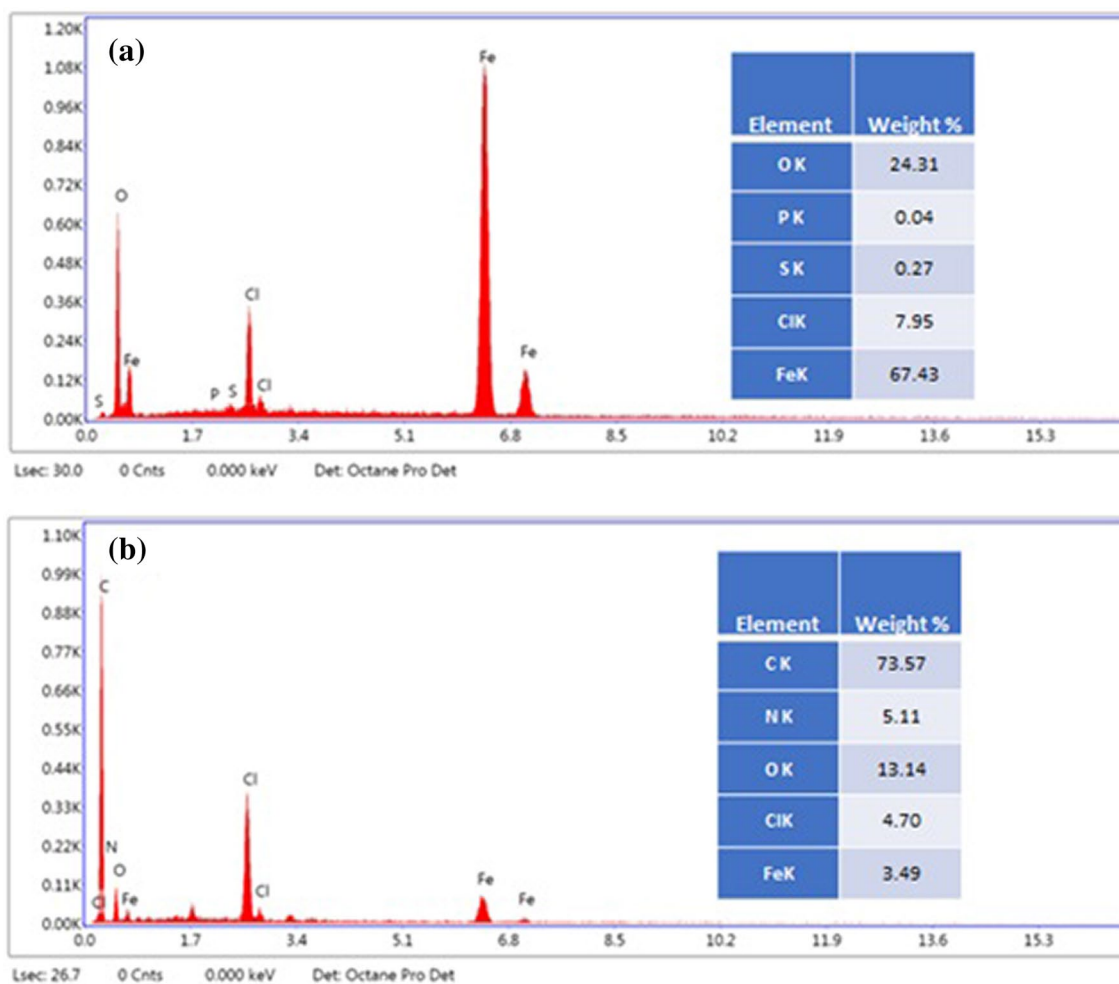


Fig. 7 EDX spectra of MS a absence b presence of inhibitor

Fig. 8 Optimized structure (a), molecular electrostatic potential (ESP) (b) HOMO (c) and LUMO (d) for quantum chemical results of **PBI⁰¹⁰** molecules

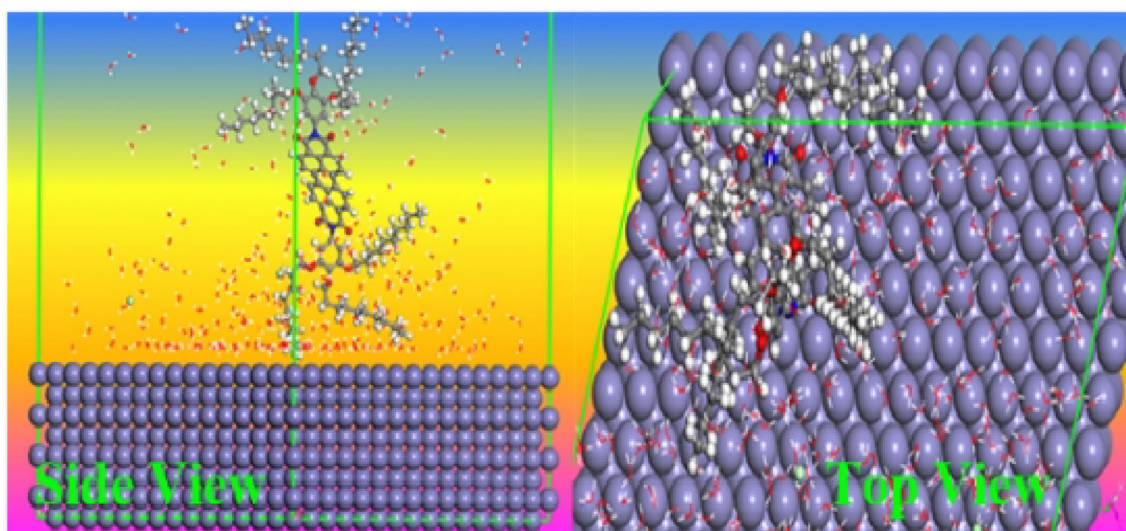
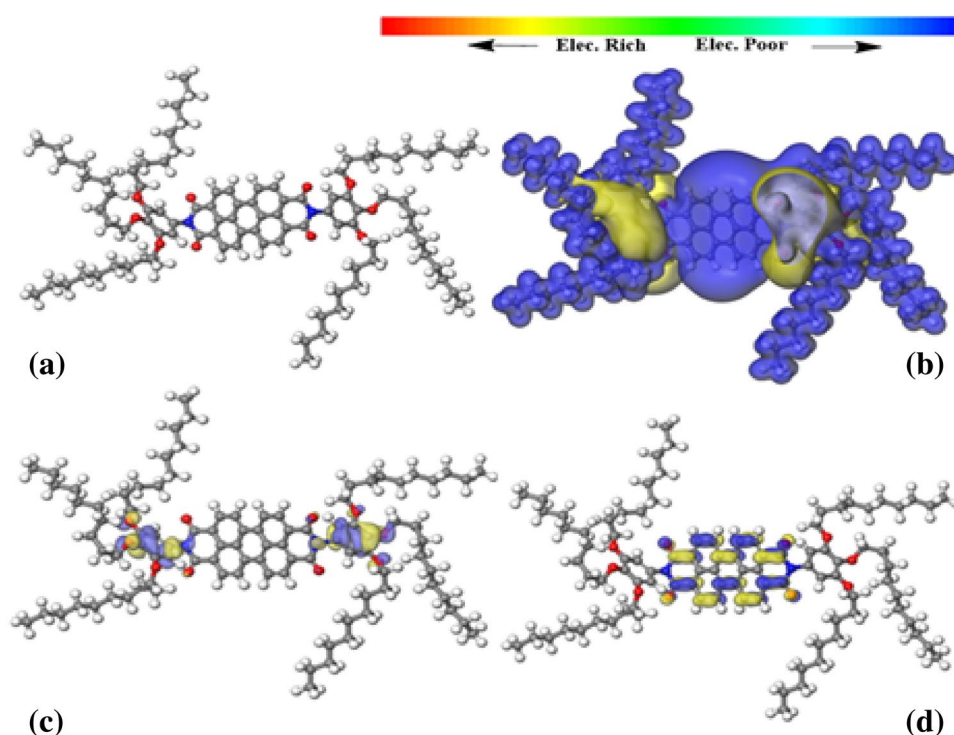


Fig. 9 Top and side views of the equilibrium configuration for **PBI⁰¹⁰** adsorbed on Fe (110)

4 Conclusions

- Perylene bisimide **PBI⁰¹⁰** stabilizing room temperature columnar liquid crystalline phase has been synthesized and characterized.
- Electrochemical studies and computational studies involving the density functional theory as well as Monte Carlo calculations were utilized to study the

effect of **PBI⁰¹⁰** on corrosion inhibition of MS in an acidic medium (1 M HCl).

- **PBI⁰¹⁰** was found to be a highly effective corrosion inhibitor for MS in 1 M HCl solution with a high inhibition efficiency of 76% at 400 ppm.
- Potentiodynamic polarization and electrochemical impedance spectroscopy of **PBI⁰¹⁰** suggest that it functions as an anodic inhibitor and indicate that corrosion

inhibition occurs through a one-way charge transfer process.

- SEM and EDX analyses demonstrate that **PBI⁰¹⁰** forms a protective film on MS.
- An analysis of DFT and Monte Carlo calculations further confirms the inhibitory effectiveness exhibited by **PBI⁰¹⁰** on MS surfaces.
- In this study, polarizing optical microscopy (POM), was first used to examine the transition from crystal to LC phase.

Author Contributions ASA and PKB conceptualized and formulated the samples. ASA supported SR, LTP, SAS, SK, and GKP in carrying out the experiments and writing the paper. Data analysis, model design, and computations were carried out by MGKA and FK. In the final draft of the manuscript, all authors contributed to the discussion of the results.

Funding Authors would like grateful thanks to the AICTE, New Delhi for financial support through RPS(8–22) and Principal, NMIT, Bangalore-560064, for providing the infrastructure facilities. The ASA would like to thank the Science and Engineering Board (SERB), DST, Government of India and BRNS-DAE funded this project through CRG/2018/000362 and No. 2012/34/31/BRNS/1039, respectively. We thank the Ministry of Human Resources and Development for the Center of Excellence in FAST (F. No. 5–7/2014-TS-VII) and the Center of Excellence in FAST at IIT Guwahati for the analytical facilities.

Data Availability Currently, datasets generated and/or analyzed during the current study are not publicly available, but they can be obtained from the corresponding authors upon request.

Declarations

Conflicts of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. Finšgar M, Jackson J (2014) Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review. *Corros Sci* 86:17–41. <https://doi.org/10.1016/j.corsci.2014.04.044>
2. Hou Y, Lei D, Li S et al (2016) Experimental investigation on corrosion effect on mechanical properties of buried metal pipes. *Int J Corrosion* 2016:1–13. <https://doi.org/10.1155/2016/5808372>
3. Verma C, Ebenso EE, Quraishi MA, Hussain CM (2021) Recent developments in sustainable corrosion inhibitors: design, performance and industrial scale applications. *Mater Adv* 2:3806–3850. <https://doi.org/10.1039/D0MA00681E>
4. Hansson CM (2011) The impact of corrosion on society. *Metal and Mat Trans A* 42:2952–2962. <https://doi.org/10.1007/s11661-011-0703-2>
5. Chen L, Lu D, Zhang Y (2022) Organic compounds as corrosion inhibitors for carbon steel in HCl solution: a comprehensive review. *Materials* 15:2023. <https://doi.org/10.3390/ma15062023>
6. Abd El Rehim SS, Sayyah SM, El-Deeb MM et al (2016) Adsorption and corrosion inhibitive properties of P(2-aminobenzothiazole) on mild steel in hydrochloric acid media. *Int J Ind Chem* 7:39–52. <https://doi.org/10.1007/s40090-015-0065-5>
7. Palanisamy G (2019) Corrosion Inhibitors. In: Singh A (ed) *Corrosion Inhibitors*. IntechOpen, London
8. Verma C, Verma DK, Ebenso EE, Quraishi MA (2018) Sulfur and phosphorus heteroatom-containing compounds as corrosion inhibitors: an overview. *Heteroatom Chem* 29:e21437. <https://doi.org/10.1002/hc.21437>
9. Verma C, Quraishi MA (2021) Recent progresses in schiff bases as aqueous phase corrosion inhibitors: design and applications. *Coord Chem Rev* 446:214105. <https://doi.org/10.1016/j.ccr.2021.214105>
10. Abdel-Karim AM, El-Shamy AM (2022) A review on green corrosion inhibitors for protection of archeological metal artifacts. *J Bio Tribo Corros* 8:35. <https://doi.org/10.1007/s40735-022-00636-6>
11. Umoren SA, Solomon MM (2015) Effect of halide ions on the corrosion inhibition efficiency of different organic species – a review. *J Ind Eng Chem* 21:81–100. <https://doi.org/10.1016/j.jiec.2014.09.033>
12. Sathiyarayanan S, Jeyaprabha C, Muralidharan S, Venkatachari G (2006) Inhibition of iron corrosion in 0.5M sulphuric acid by metal cations. *Appl Surf Sci* 252:8107–8112. <https://doi.org/10.1016/j.apsusc.2005.10.028>
13. Elayyachy M, El Idrissi A, Hammouti B (2006) New thio-compounds as corrosion inhibitor for steel in 1M HCl. *Corros Sci* 48:2470–2479. <https://doi.org/10.1016/j.corsci.2005.09.016>
14. Fouda AE-AS, El-Askalany AH, Molouk AFS et al (2021) Experimental and computational chemical studies on the corrosion inhibitive properties of carbonitrile compounds for carbon steel in aqueous solutions. *Sci Rep* 11:21672. <https://doi.org/10.1038/s41598-021-00701-z>
15. Preethi Kumari P, Shetty P, Rao SA (2017) Electrochemical measurements for the corrosion inhibition of mild steel in 1 M hydrochloric acid by using an aromatic hydrazide derivative. *Arab J Chem* 10:653–663. <https://doi.org/10.1016/j.arabjc.2014.09.005>
16. Marinescu M (2019) Recent advances in the use of benzimidazoles as corrosion inhibitors. *BMC Chemistry* 13:136. <https://doi.org/10.1186/s13065-019-0655-y>
17. Mishra A, Aslam J, Verma C et al (2020) Imidazoles as highly effective heterocyclic corrosion inhibitors for metals and alloys in aqueous electrolytes: a review. *J Taiwan Inst Chem Eng* 114:341–358. <https://doi.org/10.1016/j.jtice.2020.08.034>
18. Zhang HH, Qin CK, Chen Y, Zhang Z (2019) Inhibition behaviour of mild steel by three new benzaldehyde thiosemicarbazone derivatives in 0.5 M H₂SO₄: experimental and computational study. *R Soc Open Sci* 6:190192. <https://doi.org/10.1098/rsos.190192>
19. Anadebe VC, Nnaji PC, Okafor NA et al (2021) Evaluation of bitter kola leaf extract as an anticorrosion additive for mild steel in 1.2 M H₂SO₄ electrolyte. *SAfr J Chem*. <https://doi.org/10.17159/0379-4350/2021/v75a2>

20. Miralrio A, Espinoza Vázquez A (2020) Plant extracts as green corrosion inhibitors for different metal surfaces and corrosive media: a review. *Processes* 8:942. <https://doi.org/10.3390/pr8080942>
21. Zakeri A, Bahmani E, Aghdam ASR (2022) Plant extracts as sustainable and green corrosion inhibitors for protection of ferrous metals in corrosive media: a mini review. *Corrosion Commun* 5:25–38. <https://doi.org/10.1016/j.corcom.2022.03.002>
22. Sanni O, Sunday Isaac Fayomi O, Patricia IdowuPopoola A (2019) Eco-friendly inhibitors for corrosion protection of stainless steel: an overview. *J Phys: Conf Ser* 1378:042047. <https://doi.org/10.1088/1742-6596/1378/4/042047>
23. Yang H-M (2021) Role of organic and eco-friendly inhibitors on the corrosion mitigation of steel in acidic environments—a state-of-art review. *Molecules* 26:3473. <https://doi.org/10.3390/molecules26113473>
24. Udensi SC, Ekpe OE, Nnanna LA (2021) Corrosion inhibition performance of low cost and eco-friendly *Treculiaafricana* leaves extract on aluminium alloy AA7075-T7351 in 2.86% NaCl solutions. *Sci African* 12:e00791. <https://doi.org/10.1016/j.sciaf.2021.e00791>
25. Fazal BR, Becker T, Kinsella B, Lepkova K (2022) A review of plant extracts as green corrosion inhibitors for CO₂ corrosion of carbon steel. *npj Mater Degrad*. <https://doi.org/10.1038/s41529-021-00201-5>
26. Verma C, Rhee KY, Quraishi MA, Ebenso EE (2020) Pyridine based N-heterocyclic compounds as aqueous phase corrosion inhibitors: a review. *J Taiwan Inst Chem Eng* 117:265–277. <https://doi.org/10.1016/j.jtice.2020.12.011>
27. Verma C, Quraishi MA, Rhee KY (2022) Hydrophilicity and hydrophobicity consideration of organic surfactant compounds: effect of alkyl chain length on corrosion protection. *Adv Coll Interface Sci* 306:102723. <https://doi.org/10.1016/j.cis.2022.102723>
28. Sowmyashree AS, Somya A, Kumar S, Rao S, Jayaprakash GK (2022) Discotic anthraquinones as novel corrosion inhibitor for mild steel surface. *J Mole Liq* 347:118194. <https://doi.org/10.1016/j.molliq.2021.118194>
29. Rao S, Suhas R, Mahadevaswamy M et al (2021) Experimental and DFT explorations of tert-butyl(1-(2-(4-nitrobenzylidene)-hydrazinyl)-1-oxopropan-2yl)-carbamate on CRCA metal in 1M HCl solution. *Results Surf Interfaces* 5:100023. <https://doi.org/10.1016/j.rsurfi.2021.100023>
30. Sowmyashree AS, Somya A, Kumar CBP, Rao S (2021) Novel nano corrosion inhibitor, integrated zinc titanate nano particles: synthesis, characterization, thermodynamic and electrochemical studies. *Surf Interfaces* 22:100812. <https://doi.org/10.1016/j.surf.2020.100812>
31. Mahadevaswamy M, Paniyadi SR, Lakshmikanthan A et al (2022) Plant-mediated synthesis of NiO(II) from *Lantana camara* flowers: a study of photo-catalytic, electrochemical, and biological activities. *J Mark Res* 19:4543–4556. <https://doi.org/10.1016/j.jmrt.2022.06.166>
32. Zhang W, Wahlgren M, Sivik B (1989) Membrane characterization by the contact angle technique. *Desalination* 72:263–273. [https://doi.org/10.1016/0011-9164\(89\)80011-6](https://doi.org/10.1016/0011-9164(89)80011-6)
33. Verma C, Quraishi MA, Rhee KY (2022) Corrosion inhibition relevance of semicarbazides: electronic structure, reactivity and coordination chemistry. *Rev Chem Eng*. <https://doi.org/10.1515/revce-2022-0009>
34. Guo L, Tan J, Kaya S et al (2020) Multidimensional insights into the corrosion inhibition of 3,3-dithiodipropionic acid on Q235 steel in H₂SO₄ medium: a combined experimental and in silico investigation. *J Coll Interface Sci* 570:116–124. <https://doi.org/10.1016/j.jcis.2020.03.001>
35. Valadbeigi Y (2016) Proton affinities of hydrated molecules. *Chem Phys Lett* 660:301–306. <https://doi.org/10.1016/j.cplett.2016.08.035>
36. Obot IB, Macdonald DD, Gasem ZM (2015) Density functional theory (DFT) as a powerful tool for designing new organic corrosion inhibitors. Part I: an overview. *Corros Sci* 99:1–30. <https://doi.org/10.1016/j.corsci.2015.01.037>
37. Quadri TW, Olasunkanmi LO, Fayemi OE et al (2021) Quantitative structure activity relationship and artificial neural network as vital tools in predicting coordination capabilities of organic compounds with metal surface: a review. *Coord Chem Rev* 446:214101. <https://doi.org/10.1016/j.ccr.2021.214101>
38. El Ibrahim B (2020) Atomic-scale investigation onto the inhibition process of three 1,5-benzodiazepin-2-one derivatives against iron corrosion in acidic environment. *Coll Interface Sci Commun* 37:100279. <https://doi.org/10.1016/j.colcom.2020.100279>
39. Ibrahim EL, B, Bazzi L, EL Issami S, (2020) The role of pH in corrosion inhibition of tin using the proline amino acid: theoretical and experimental investigations. *RSC Adv* 10:29696–29704. <https://doi.org/10.1039/D0RA04333H>
40. Ferigita KSM, AlFalah MGK, Saracoglu M et al (2022) Corrosion behaviour of new oxo-pyrimidine derivatives on mild steel in acidic media: experimental, surface characterization, theoretical, and monte carlo studies. *Appl Surf Sci Adv* 7:100200. <https://doi.org/10.1016/j.apsadv.2021.100200>
41. Tan J, Guo L, Yang H et al (2020) Synergistic effect of potassium iodide and sodium dodecyl sulfonate on the corrosion inhibition of carbon steel in HCl medium: a combined experimental and theoretical investigation. *RSC Adv* 10:15163–15170. <https://doi.org/10.1039/D0RA02011G>
42. Aaad HE, Galai M, Ouakki M et al (2021) Improvement of the corrosion resistance of mild steel in sulfuric acid by new organic-inorganic hybrids of benzimidazole-pyrophosphate: facile synthesis, characterization, experimental and theoretical calculations (DFT and MC). *Surf Interfaces* 24:101084. <https://doi.org/10.1016/j.surf.2021.101084>
43. Paul PK, Yadav M, Obot IB (2020) Investigation on corrosion protection behavior and adsorption of carbohydrazide-pyrazole compounds on mild steel in 15% HCl solution: electrochemical and computational approach. *J Mol Liq* 314:113513. <https://doi.org/10.1016/j.molliq.2020.113513>
44. Sarkar TK, Saraswat V, Mitra RK et al (2021) Mitigation of corrosion in petroleum oil well/tubing steel using pyrimidines as efficient corrosion inhibitor: experimental and theoretical investigation. *Mater Today Commun* 26:101862. <https://doi.org/10.1016/j.mtcomm.2020.101862>
45. Hajjaji FE, Salim R, Taleb M et al (2021) Pyridinium-based ionic liquids as novel eco-friendly corrosion inhibitors for mild steel in molar hydrochloric acid: experimental & computational approach. *Surf Interfaces* 22:100881. <https://doi.org/10.1016/j.surf.2020.100881>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.