Interactions of Different Redox States of Phenyl-Capped Aniline Tetrarmers with Iron Oxide Surfaces and Consequences for Corrosion Inhibition

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The phenyl capped aniline tetramer (PCAT) is known for its redox properties and is being studied for its ability to inhibit corrosion of iron and steel in addition to being of interest for sensors and molecular electronics. Here we investigate the interactions, orientation and corrosion inhibition ability of the free base form of PCAT with iron oxide surfaces. Raman spectroscopy demonstrates interconversion of these molecules to one another due to charge transfer to the surface. Polarized mid-IR spectroscopy and atomic force microscopy were used to elucidate the molecular orientations on the surface. Electrochemical impedance spectroscopy shows the corrosion resistance of fully reduced PCAT coatings on low carbon steel to be higher than that for half-oxidized and fully oxidized PCAT coatings. A weight loss test, laser line measurements and Raman spectroscopy reveal that even though half-oxidized PCAT initially shows a lower corrosion resistance due to transformation into the fully oxidized form, with time it transforms back into the half-oxidized form and protects the surface. Fully oxidized PCAT molecules show opposite behavior, causing the degradation of the surface over time. We thus attained a deeper insight into the interplay of the different oxidation states for corrosion control.

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Polyaniline (PANI) is a prominent member of the conducting polymer family because of its diverse application in biosensors, electronic devices, fuel cells, etc. One of the most studied applications of this polymer is corrosion inhibition of metals. DeBerry showed in 1985 that PANI can inhibit corrosion of iron and steel by passivating the surface via a mixed oxide. Similarity to the native oxides, the passive oxides on iron or steel maintain a layered structure of a fully oxidized outer layer, followed by an intermediate mixed iron (II) and iron (III) oxide layer transitioning to a very thin inner iron (II) oxide layer next to the bulk metal. PANI is mainly found in three different stable oxidation states (fully reduced or leucoemeraldine, half-oxidized or emeraldine, and fully oxidized or permigraniline) and several protonation states. The complete mechanism behind the corrosion inhibition ability of this polymer is still unclear due to its complex chemistry. PANI coatings can break down catastrophically, which is the reason why their commercialization has failed. Recent work demonstrated that this breakdown happens due to a high conductivity and long-range electronic interactions. Even though historically it had been assumed that conductivity is essential to the inhibition mechanism, recent work has shown that conductivity of pure PANI coatings and PANI containing coatings can be interrupted by sparse addition of small PANI particles without hurting corrosion inhibition efficiency.

Oligoanilines do not share some certain drawbacks intrinsic to PANI coatings (e.g. catastrophic failure, poor solubility). Very little work has been done on oligoanilines, which have related physical and chemical properties.

We have chosen the phenyl-capped aniline tetramer (PCAT, 4-(phenylamino)phenyl-1,4-benzenediamine) for a detailed investigation of its interactions with iron oxide surfaces because it is the simplest aniline oligomer to fully mimic the redox properties of PANI. PCAT coatings have been shown to improve the corrosion resistance of steel with the remarkable property of withstanding mechanical damage to the coating.

PCAT fully mimics the electronic behavior of PANI in that it can also exist in three different oxidation states and several protonation states (unprotonated, semiquinone and monoprotonated). The three oxidation states (Fig. 1) are the fully reduced or leucoemeraldine base (B5 = 5 benzene rings), the half oxidized or emeraldine base (B4Q1 = 4 benzene rings and 1 quinoid ring), and the fully oxidized or permigraniline base (B3Q2 = 3 benzene and 2 quinoid rings). It has been suggested that the inter-conversion between different oxidation states is at the core of corrosion inhibition by PCAT. Moreover, the self-healing properties of PCAT also make it more interesting than a simple barrier protector like a conventional coating (i.e. paint) but the nature of the interactions of these molecules with the (hydrated, native) iron oxide surface is not entirely clear. We have previously looked at the interactions of the reduced base form of PCAT with native iron oxide films, but an understanding of the interplay between the oxidation states was lacking. Recently we have demonstrated that the oxidation state of PCAT has an impact on the amount of charge transfer to underlying substrates, but the molecular orientation at the interface and the impact of interfacial structure on corrosion inhibition performance remained unclear.

Here we investigate the interactions of B5, B4Q1, and B3Q2 with iron oxide surfaces using Raman, mid-IR, and visible spectroscopy. Atomic force microscopy (AFM) and mid-IR spectroscopy are used to investigate the orientations of all these forms of PCAT on the iron oxide surface. The corrosion inhibition properties are studied using electrochemical impedance spectroscopy (EIS) and weight loss measurements. Our focus is to elucidate the nature of the interaction of the different oxygenation states of these oligomers with iron oxide surfaces and determine their capability for corrosion inhibition. The results of our work will aid in the establishment of rational design criteria for smart protective coatings.

Experimental

Low carbon steel (~0.05% Mn, ~0.07% Cr, ~0.01% Si, ~0.05% Al, balance Fe) was obtained from ArcelorMittal Dofasco. The steel sheet was cut into coupon sizes of 1 cm × 1 cm, except for 2.5 cm × 2.5 cm sample coupons for EIS. These steel coupons were mechanically polished with an automatic polisher by first using coarse grit silicon carbide emery paper then followed by 3 μm and 1 μm diamond particle emulsion combined with lubricating solution (25% propylene glycol and 75% ethanol). The final polishing step for all samples except those for the EIS test was 0.05 μm colloidal silica. All samples were then washed with water and ultrasound briefly. The steel coupons were ultrasonically-briefly immersed in acetone and methanol. Iron (III) oxide (α-Fe₂O₃) nanopowder was obtained from Sigma-Aldrich. Its particle size is below 50 nm, with a surface area of 16 mg/m².
B5 powder was synthesized according to a literature procedure.\textsuperscript{17} The fully oxidized form of PCAT (B3Q2) powder was prepared by first mixing reduced B5 powder with ammonium persulfate (reagent grade 98\%, Sigma-Aldrich) (B5: ammonium persulfate molar ratio of 1:2.1), then dissolving in methanol and stirring for 24 hours. After evaporation of the methanol, the dried product was washed with DI water several times to remove ammonium persulfate and vacuum suctioned. The wet powder is then dissolved in 0.1 M NH4OH and again stirred for 24 hours to obtain the free base of B3Q2. The residue was then washed with 0.05 M of NH4OH and dried in a desiccator. To obtain the half-oxidized form of PCAT (B4Q1), a B5: ammonium persulfate molar ratio of 1:1.04 was used, following the same procedure as for preparation of the oxidized form. To obtain the fully reduced form of the PCAT, ascorbic acid was used, with a B5: ascorbic acid molar ratio of 1:3.2, following otherwise the same procedure as for making the oxidized form. After synthesis, all oxidation states of PCAT were individually stored in a desiccator under low vacuum until use.

Raman spectroscopy was performed using a Renshaw InVia Raman microscope with a 514.5 nm green laser. All spectra were taken with the same spot size, laser power and integration time. Raman spectroscopy was used to characterize all forms of pure PCAT powder, powder mixtures of all individual three forms of PCAT with α-Fe\textsubscript{2}O\textsubscript{3}, powder and drop cast samples of all three forms from methanol onto steel coupons. Since the HPLC grade methanol evaporated without residue, none of it was present by the time the Raman spectra were taken. At least 10 Raman spectra were taken on different spots of each sample on steel coupons, while spectra of powder samples were repeated in at least 5 locations per sample.

The interactions with the surface, as well as the orientations of these different forms of PCAT molecules, were mapped by mid-IR spectroscopy at the Canadian Light Source in Saskatoon. At least two full maps across the film boundary were acquired per sample. The endstation used for this purpose was a Bruker Vertex 70/S spectrometer with a Hyperion 3000 microscope (online system), equipped with a 100 micron size single element MCT detector and a 64 × 64 pixel focal plane (with beamline) and detector. A grazing incidence of reflection (GIR) objective was used to observe thin films of these molecules on steel surfaces. 90° and 0° polarizers were used with the GIR objective to study molecular orientations. The error bars given in Tables II, III and IV were calculated individually for each spectrum by averaging 50 continuous data points of a peak-free baseline stretch in the region between 950 cm\textsuperscript{-1} and 1200 cm\textsuperscript{-1} to give a standard deviation.

For mapping, the molecules were deposited from glass crucibles inside a home-built stainless steel vacuum chamber onto one-half of the steel coupon and the other half was kept clean using a tantalum shadow mask. The chamber was pumped oil-free to a base pressure of 6 Torr. The substrate temperatures for deposition of B5 (25 nm film), B4Q1 (10.5 nm film) and B3Q2 (16.2 nm film) were measured using a quartz crystal microbalance.

AFM was performed using a Veeco Enviroscope with a Nanoscope IIIa controller and Veeco RTESPA phosphorus (n) Si tips with nominal radii of 10 nm or less. The AFM images were analyzed using Gwyddion data analysis software.\textsuperscript{18} The height resolution of the AFM data is 0.06 nm. Three different organic film thicknesses were vacuum deposited for step height analysis: B5 (~2.5 nm at 20 °C in 320 sec), B4Q1 (~1 nm at 20 °C in 66 sec) and B3Q2 (~1.5 nm at 24 °C in 90 sec).

Electrochemical measurements were carried out using a 1287 Solartron potentialstat coupled to a 1252 Solartron frequency response analyzer for electrochemical impedance spectroscopy (EIS) measurements. A Para cell for flat specimen was used for this experiment which is designed for mounting flat and large samples on either end of the cell for experiments. Steel coupons with coatings of different forms of PCAT were used as a working electrode with a platinum counter electrode and a calomel (SCE) reference electrode. EIS spectra were recorded after the working electrode was conditioned at the corrosion potential for 2 h. The EIS experiments were carried out in the frequency range from 0.01 Hz to 100 kHz with an AC excitation potential of 10 mV in a 3.5% NaCl solution. The experimental time varied from 5 hrs (2 cycles, 1 cycle = 2 hrs) to 48 hrs (24 cycles) for fresh and week old coated samples. The exposed area of each sample was 2.85 cm\textsuperscript{2}. Data were recorded and analyzed using Corrware and Zplot software (Scribner Associates). For each oxidation state, at least 5 sets of EIS data were acquired. An optical surface profiler (model M470-OSP) with a 30 μm laser spot size was used to measure the surface roughness of the corroded samples in the EIS experiment. The line scan was taken across the center of the circle in each sample.

**Results and Discussion**

**Characterization of different forms of PCAT.**—Raman spectra of different oxidation states of PCAT were recorded for comparison with the species that will arise from the interactions with iron (III) oxide surfaces. Raman spectra of B5, B4Q1, and B3Q2 powders are shown in Figure 2. All the related bands of these three molecules (B5, B4Q1, and B3Q2) are shown in Table I. The intense Raman bands at 1623 cm\textsuperscript{-1} (Figure 2a) of B5 and at 1617 cm\textsuperscript{-1} (Figure 2b) of B4Q1 were attributed to C-C stretching of the benzene rings while the band of B3Q2 at around 1585 cm\textsuperscript{-1} is a shoulder of another band at 1585 cm\textsuperscript{-1}.\textsuperscript{19} The three oxidation states can further be distinguished by the different relative intensities of these three bands. The bands at 1519 cm\textsuperscript{-1} and 1496 cm\textsuperscript{-1} of B3Q2 and B4Q1, respectively are due to a combination band of C-C and C-H bending.\textsuperscript{20} The band of B3Q2 at around 1585 cm\textsuperscript{-1} is due to C=C stretching of the quinoid ring.\textsuperscript{19} The bands around 1515 cm\textsuperscript{-1} and 1585 cm\textsuperscript{-1} only arise in B3Q2. Similar kind of band as 1585 cm\textsuperscript{-1} can arise in B4Q1 only at higher wavenumbers (such as 1588 cm\textsuperscript{-1}). The three bands at 1164, 1163 and 1181 cm\textsuperscript{-1} of B3Q2, B4Q1, and B5, respectively are assigned to C-H bending at the quinoid ring (first two) and a benzene ring (last band).\textsuperscript{19} Three other bands at 1215 (B3Q2), 1223 (B5) and 1206 cm\textsuperscript{-1} (shifted, B4Q1) arise due to C-N stretching.\textsuperscript{20} The two bands at 996 and 1030 cm\textsuperscript{-1} that only arise in B5 are attributed to ring deformation of benzene.\textsuperscript{19}

The identity and purity of the synthesized B5 powder were verified by high-resolution electrospray ionization mass spectrometry (Fig. 2d) and NMR (Fig. 2e). The expected molecular weight of B5 is 442.22 g/mol, as confirmed by the dominant peak in the high-resolution mass spectrum (Fig. 2d). The NMR spectrum also confirms to the expected peak pattern\textsuperscript{17} and demonstrates the absence of impurities.

**Interactions of B5, B4Q1, and B3Q2 with α-Fe\textsubscript{2}O\textsubscript{3} surfaces.**—The species that arise from the interactions of different forms of PCAT with iron oxide surfaces and with methanol were investigated. Figure 3a shows a Raman spectrum of B5 drop cast from methanol onto a glass substrate. When compared to the Raman spectrum of pure powder B5 in Figure 2a, even though almost all the bands are slightly red-shifted all spectroscopic features of the molecules are preserved,
with a new band of B4Q1 arising at 1481 cm$^{-1}$. This means that the B5 molecules remain mostly in the same oxidation states with some tendency to transform into B4Q1 upon interaction with methanol. The Raman features of a methanolic solution of B5 drop cast onto a steel substrate (native oxide) in Figure 3b are different from B5 in MeOH (Figure 3a) or pure powder B5 (Figure 2a). The Raman bands at 1002 cm$^{-1}$, 1335 cm$^{-1}$ and 1407 cm$^{-1}$ in this spectrum (Figure 3b) are assigned to semiquinone species.$^{21-24}$ The band at 1636 cm$^{-1}$ can be assigned to a radical cation species that formed.$^{21,24}$ The other bands arising in this spectrum are 1603 cm$^{-1}$, 1567 cm$^{-1}$ and 1496 cm$^{-1}$ (very weak).$^{19}$ The first band corresponds to B5, the second and third one are indications of B5 tending to transform into B3Q2 and also

| B5               | B4Q1             | B3Q2             | Semiquinoid species               |
|------------------|------------------|------------------|-----------------------------------|
| Exp. (cm$^{-1}$) | Ref# (cm$^{-1}$) | Exp. (cm$^{-1}$) | Ref# (cm$^{-1}$)                  |
| 1623, 1622       | 1617             | 1619             | C-C stretching of the benzene rings |
| 1603             | 1607             | 1609             | C-C stretch ring                  |
|                  | 1590, 1593       | 1588, 1586       | C=C stretching of the quinoid ring |
|                  | 1481, 1496,      | 1470, 1490,      | C=N stretching and C-H bending (benzene) |
|                  | 1494, 1497,      | 1498, 1502,      |                                |
|                  | 1500, 1508       | 1421 [19]        |                                |
|                  | 1415             | 1416, 1415       | C-C stretch ring (quinoid)        |
|                  |                  | 1407             | C-N** stretching                 |
|                  |                  | 1398             | 1401 [21]                       |
|                  |                  | 1335             | C-N** stretching                 |
|                  |                  | 1352             | 1312-1322                       |
|                  |                  | 1252             | 1220-1253                       |
| 1223, 1217       | 1206             | 1215             | C-N stretching                   |
|                  | 1163, 1142       | 1214, 1222       | C-H bending (quinoid ring)        |
|                  |                  | 1164             |                                |
| 1181, 1179       | 1180, 1174,      | 1176             | C-H bending (benzene ring)        |
|                  | 1170 [19]        | 1171, 1180       |                                |
| 1030             | 1028 [19]        |                  |                                |
|                  | 996, 993, 989    |                  |                                |
B4Q1 by contact with the native oxide of steel in methanolic solution. A significant amount of charge transfer is hence taking place during the interaction of B5 with iron oxide, which can be expected to result in the partial reduction of the iron oxide substrate. The native oxide film on steel is too thin (5 nm) to directly observe this effect. Furthermore, it is desirable to eliminate the possible interference of methanol in this interaction. Therefore, we also prepared solvent-free high surface area powder mixtures of PCAT with iron oxide nanoparticles.

Figure 3c shows the Raman spectrum of a B5 and α-Fe2O3 powder mixture, which had no contact with methanol. This spectrum has Raman bands at 1622, 1179, 1217, and 1314 cm\(^{-1}\) which are almost the same features as in Figure 3a, corresponding to B5.\(^{19}\) On the other hand, the two bands at 1494 cm\(^{-1}\) (very intense) and 1588 cm\(^{-1}\) are attributable to a mixture of the oxidized forms of PCAT, B4Q1 and B3Q2 (Table I).\(^{19}\) This same spectrum also has bands at 218, 286 and 408 cm\(^{-1}\), which can be assigned to hematite (α-Fe2O3) but are a little bit shifted.\(^{25,26}\) These results suggest that B5 does not change its oxidation state in any significant way in methanol itself but there is interaction as a result of drop casting B5 in methanol on the steel surface. This interaction is between B5 and native oxide of iron (α-Fe2O3) which converts most of the B5 molecules into the semiquinone form, and a very small portion also into the B3Q2 (fully oxidized) and B4Q1 (half oxidized) forms. These results suggest that hydroxyl groups on the iron oxide surface and from methanol are playing a role in the hydrogen bonding of B5 with iron oxide surfaces to produce semiquinone, B3Q2 and B4Q1 species. In the absence of methanol, the B5 molecules tend to transform into B4Q1 (half oxidized).

In order to systematically understand the interactions of different oxidation states of the phenyl-capped aniline tetramer, we next looked at B4Q1 (half oxidized). Figure 4a shows a Raman spectrum of B4Q1 drop cast from methanol onto a glass substrate, while Figure 4b shows a Raman spectrum of B4Q1 drop-cast from methanol onto a steel substrate (native oxide) and Figure 4c shows a Raman spectrum of B4Q1 in the α-Fe2O3 powder mixture. There are substantial differences between the Raman spectrum of B4Q1 cast from methanol onto a glass substrate (Figure 4a) and the Raman spectrum of pure powder B4Q1 (Figure 2b). The intensity of the bands at 1617, 1496, and 1163 cm\(^{-1}\) (Figure 2b) decreased and shifted to 1635, 1498 and 1180 cm\(^{-1}\), respectively (Figure 4a). New bands arise at 1335 and 1568 cm\(^{-1}\). The Raman bands at 1335 and 1635 cm\(^{-1}\) are assigned to the semiquinone species.\(^{21-24}\) The band at 1498 cm\(^{-1}\) still belongs to B4Q1 but the bands at 1568 and 1180 cm\(^{-1}\) are an indication that B4Q1 tends to transform into the fully oxidized form (B3Q2) upon exposure to methanol. It means that B4Q1 molecules change their oxidation states in part to semiquinone and in part to B3Q2 through interaction with methanol.

The Raman spectrum of B4Q1 drop cast from methanol onto a native oxide covered steel substrate (Figure 4b), looks similar to the Raman spectrum of B4Q1 in MeOH (Figure 4a), indicating that B4Q1 molecules interact in a similar way with iron oxide surfaces as with methanol, or are prevented from interacting with iron oxide surfaces in the presence of methanol. Figure 4c shows the Raman spectrum of a powder mixture of B4Q1 and α-Fe2O3 which did not have contact with methanol. The Raman bands at 1162 cm\(^{-1}\) and 1497 cm\(^{-1}\) correspond to B4Q1 and the bands at 1415 cm\(^{-1}\) and 1597 cm\(^{-1}\) correspond to B3Q2 and B5, respectively.\(^{19}\) The band at 1319 cm\(^{-1}\) corresponds to semiquinone species (Table I).\(^{21-24}\) This same spectrum has bands at lower wavelengths 223, 293, 410 and 611 cm\(^{-1}\), all these bands are assigned to hematite (α-Fe2O3).\(^{25,26}\) These results suggest that B4Q1 molecules at α-Fe2O3 surfaces tend to transform into a mixture of semiquinone, B5 and B3Q2 forms in the absence of methanol. On the other hand, methanol itself transforms B4Q1 mostly into the semiquinone form and partially into the B3Q2 form. As a result, when drop-casting B4Q1 in MeOH on a steel substrate, B4Q1 does not significantly interact with the native iron oxide of steel and does not form any detectable films via dip coating.

The interaction of the fully oxidized form of the phenyl-capped aniline tetramer (B3Q2) with iron oxide surfaces was also observed in the same fashion as the other two oxidation states. Figure 5a shows a Raman spectrum of B3Q2 drop cast from methanol onto a glass substrate, Figure 5b shows a Raman spectrum of B3Q2 drop-cast from methanol onto a steel substrate (native oxide), and Figure 5c shows a Raman spectrum of B3Q2 in a dry powder mixture with α-Fe2O3. The Raman spectrum of B3Q2 drop cast from methanol onto a glass substrate (Figure 5a) differs from the Raman spectrum of pure powder B3Q2 (Figure 2c). The bands at 1585, 1416, 1215 and 1164 cm\(^{-1}\) (Figure 2c) are shifted to higher wavenumbers at 1591, 1419, 1218 and 1167 cm\(^{-1}\), respectively (Figure 5a). All these bands still belong to B3Q2. New bands arise at 1142, 1407 and 1500 cm\(^{-1}\). The band at 1407 cm\(^{-1}\) is assigned to the semiquinone species.\(^{21}\) The bands at 1142 cm\(^{-1}\) and 1500 cm\(^{-1}\) belong to B4Q1.\(^{19,22}\) This means that in methanol a portion of fully oxidized (B3Q2) molecules

![Figure 3. Raman spectra of powder of (a) B5 in methanol, (b) B5 on a native oxide covered steel substrate, and (c) B5 in Fe2O3 powder mixture.](image1)

![Figure 4. Raman spectra of B4Q1 (a) in methanol, (b) on steel substrate (native oxide Fe2O3) and (c) in the α-Fe2O3 powder mixture.](image2)
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change their oxidation states to the half-oxidized form (B4Q1) and to a smaller extent into the semiquinone form.

The bands in the Raman spectrum in Figure 5b of B3Q2 drop cast onto a steel substrate (native oxide) are shifted but show the same interaction as B3Q2 in MeOH (Figure 5a). The bands at 1139 cm\(^{-1}\) (C-H bending of Q), 1497 cm\(^{-1}\), and 1608 cm\(^{-1}\) correspond to B4Q1.\(^{19,21}\) The band at 1398 cm\(^{-1}\) is assigned to the semiquinone species.\(^{24}\) B3Q2 molecules tend to convert into B4Q1 and partially into the semiquinone form by interacting either with iron oxide or with methanol.

Figure 5c shows the Raman spectrum of a B3Q2 and \(\alpha\)-Fe\(_2\)O\(_3\) dry powder mixture, which has had no contact with methanol. This spectrum has a very weak semiquinone band at 1405 cm\(^{-1}\) and intense bands belonging to B4Q1 at 1498 cm\(^{-1}\) and 1508 cm\(^{-1}\) (C = N stretching).\(^{19,21}\) The rest of the bands belongs to B3Q2.\(^{19}\) We conclude that in the absence of methanol, a portion of the B3Q2 molecules tends to transform into B4Q1 and into the semiquinone form upon interaction with iron oxide. On the other hand, methanol itself transforms a portion of B3Q2 molecules into the semiquinone form and into the B4Q1 form. When drop-casting methanolic B3Q2 solution onto a steel substrate, B3Q2 is not significantly changed any further through interaction with the native iron oxide of steel.

In summary, we have looked at the interactions of the B5, B4Q1, and B3Q2 forms of PCAT with iron oxide surfaces as a first step toward understanding the corrosion inhibition mechanism of these molecules. Methanol is found to be a suitable solvent for B5 molecules because it for the most part does not change their oxidation state. As a result, B5 molecules can strongly interact with the native oxide and adhere to the surface, which is beneficial for corrosion inhibition. After drop casting the molecules transform mostly into the semiquinone form and B4Q1, and to a smaller extent into B3Q2. On the other hand, the powder mixture of B5 and \(\alpha\)-Fe\(_2\)O\(_3\) shows very little interactions and this converts only a very small amount of B5 into B4Q1 but the rest remains as B5. We have also found that methanol not only changes the oxidation states of B4Q1 and B3Q2 but also hinders the interactions between the native oxides of steel surface and these two molecules. B4Q1 turns into the semiquinone form and B3Q2 after dissolving in methanol. Drop-casting that solution onto steel surfaces results in interactions comparable to those with methanol. The lower intensity of the molecular bands of this sample is also an indication of less interaction with the surface. In the dry powder mixture of B4Q1 and \(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles, however, B4Q1 transforms mostly into B5 by interacting with \(\alpha\)-Fe\(_2\)O\(_3\). B3Q2 exhibited similar interactions with both methanol and native oxides of steel surfaces (\(\alpha\)-Fe\(_2\)O\(_3\)). In both cases, B3Q2 transforms into the semiquinone and B4Q1 forms. Drop-cast B3Q2 also showed fewer Raman bands which are an indication of weak bonding interaction with the surface. B3Q2 in a powder mixture with \(\alpha\)-Fe\(_2\)O\(_3\) transformed into both the semiquinone and the B4Q1 forms as a result of the interactions. Powder mixtures showed indications of stronger bonding than drop cast samples.

**Orientation of B5 on native iron oxide surfaces.**—After elucidating the interactions of different oxidation states of PCAT with iron oxide surfaces, we can now turn our attention toward the orientation of these molecules at these surfaces. We start by investigating B5 using synchrotron-based mid-IR spectromicroscopy. For this experiment, B5 was vacuum deposited on one-half of a steel coupon and the other half was kept clean using a tantalum shadow mask. Figure 6a (A-D, left image) shows the IR mapping spectra of B5 from the deposited film toward the clean part at \(\theta_E = 0^\circ\) and the right image, Figure 6b (A-D, right image) shows the spectra on the same spots (A-D) at \(\theta_E = 90^\circ\). The spectra in Figures 6a and 6b correspond to the points (A-D) shown on the bottom optical image of the sample in Figure 6c. The black T-shaped line represents a mechanical scratch made on the sample to visually separate the deposited area and the clean part as shown in Figure 6c. The 3 points on the left side of the black line (Figure 6c (A - C)) are points on the B5 molecular film and one point on the right side of the black line (Figure 6c (D)) is on the clean side. A grazing incidence (\(\theta = 80^\circ\) to the surface normal) objective in reflection geometry was used to take the spectra. Two polarizer orientations, \(\theta_E = 0^\circ\) and \(\theta_E = 90^\circ\) were used to study the orientation of the molecules. With the polarizer orientation \(\theta_E = 0^\circ\), the electric field of the polarized light was parallel to the substrate surface and with the polarizer orientation, \(\theta_E = 90^\circ\) it was perpendicular to the substrate surface. IR bands can be divided into two regions: Out-of-plane ring vibrations mostly below 1000 cm\(^{-1}\) and in-plane ring vibrations in the range of 1000 – 1700 cm\(^{-1}\).\(^{27}\) The intensity ratio between these two regions of vibrations can be used to determine the orientation of the molecules on the surface.\(^{27}\) In case of B5 molecules, the two bands that were taken into account for orientation calculations are 1529 cm\(^{-1}\) and 836 cm\(^{-1}\). The band at 1529 cm\(^{-1}\) is assigned to the C-H in-plane bending vibration and the band at 836 cm\(^{-1}\) is the C-H out of plane wag of the mono-substituted benzene ring.\(^{19,28}\)

All the intensity ratios for \(\theta_E = 90^\circ\) and \(\theta_E = 0^\circ\) for the bands at 836 cm\(^{-1}\) and 1529 cm\(^{-1}\) are gathered in Table II. On the molecular film region (left side of the line) the band at 1529 cm\(^{-1}\) is very prominent for \(\theta_E = 90^\circ\) but the band 836 cm\(^{-1}\) is just a shoulder of another band in Figure 6b, whereas for \(\theta_E = 0^\circ\) both bands are prominent. Three spectra are shown on these points of the molecular side and one on the clean side. The presence of the molecules on the clean side at point (D) in Figures 6a, 6b, and 6c is a result of migration of some molecules during or after deposition. The intensity ratios (836 cm\(^{-1}\)/1529 cm\(^{-1}\)) in Table II show that the ratio for \(\theta_E = 90^\circ\) is very low in comparison to the ratio for \(\theta_E = 0^\circ\) on the organic film (points A - C). It can also be seen that the overall ratio (836 cm\(^{-1}\)/1529 cm\(^{-1}\)) individually for \(\theta_E = 90^\circ\) and \(\theta_E = 0^\circ\) increases as the film is getting thinner. A lower ratio means that the molecules are standing on their edge or standing up on the surface as opposed to lying down.\(^{27}\) Due to the high coverage of molecules in this region, the dominant interactions are between molecules rather than with the surface. On the other hand, on the clean region the point (D) for \(\theta_E = 90^\circ\) the intensity of the band at 1529 cm\(^{-1}\) became too low to meaningfully calculate the ratio but the intensity of the band at 836 cm\(^{-1}\) still remains almost the same on that point. On the other hand, on the same point for \(\theta_E = 0^\circ\) the intensity of the band 836 cm\(^{-1}\) became lower and is still present but the band at 1529 cm\(^{-1}\) disappeared. This is an indication that the orientation of the molecules changes in the clean region. Due to the very low coverage of migrated molecules in the clean region, these molecules have close interactions with the iron oxide surface. We conclude that these B5 molecules are lying down on the surface.\(^{27}\) B5 molecules very close to the surface may also partially be standing on their edges.
but a twisted backbone of the molecule still leads to its identification as lying down in the IR spectra.

**Orientation of B4Q1 on native iron oxide surfaces.**—For B4Q1 molecules on an iron oxide surface, the intensity ratio was obtained for the two bands at 1531 cm\(^{-1}\) (shifted) and 817 cm\(^{-1}\). Figure 7a (A-E, left image) shows the IR mapping spectra of B3Q2 from the deposited film toward the clean part at \(\theta_E = 0^\circ\) and Figure 7b (A-E, right image) shows the spectra on the same spots (A-E) at \(\theta_E = 90^\circ\). The intensity ratios between the bands at 817 cm\(^{-1}\) and 1531 cm\(^{-1}\) for \(\theta_E = 90^\circ\) and \(\theta_E = 0^\circ\) are shown in Table III. Three IR spectra are shown in Figures 7a and 7b (spectra, A-C) that are belonging to three points ((A-C) in Figure 7c) on the molecular side (left side of the vertical line) and two spectra are shown in Figures 7a and 7b (spectra, A-D) belonging to two points (D-E) on the clean side (right side of the vertical line).

Table III shows that the overall intensity ratios for \(\theta_E = 90^\circ\) are very low in comparison to the intensity ratios for \(\theta_E = 0^\circ\) in the molecular region (points A-C). This lower intensity ratio means that the molecules are more aligned with the electric field for \(\theta_E = 90^\circ\) than \(\theta_E = 0^\circ\). This is an indication of B4Q1 molecules standing on their edge or standing up, interacting in the same way as B5 molecules. On the clean region, the first point (D) shows the presence of molecules and shows a trend in the ratio similar to the organic film side (low ratio for \(\theta_E = 90^\circ\) and higher for \(\theta_E = 0^\circ\)). It means that B4Q1 molecules form multilayers until this point (D), and they are also standing on their edge or standing up to this point. However, the last existence of B4Q1 molecules observed at point (E) shows the intensity ratio for \(\theta_E = 0^\circ\) as before but the ratio for \(\theta_E = 90^\circ\) on the same point became unquantifiable due to too low intensity of the band at 1529 cm\(^{-1}\) of in-plane vibration. This is again the indication of these molecules being oriented in lying down or standing on their edge similar to B5 molecules during interaction with the iron oxide surfaces.

**Orientation of B3Q2 on native iron oxide surfaces.**—For investigating the orientation of B3Q2 molecules on iron oxide surfaces, the two bands that were considered are 1529 cm\(^{-1}\) and 852 cm\(^{-1}\). Figure 8a (A-G, left image) shows the IR mapping spectra of B3Q2 from the deposited film toward the clean part at \(\theta_E = 0^\circ\) and Figure 8b (A-G, right image) shows the spectra on the same spots (A-G) at \(\theta_E = 90^\circ\). These spectra in Figures 8a and 8b correspond to the points (A-G) shown on the bottom optical image of the sample in Figure 8c. The

### Table II. Intensity ratio of the selected IR absorption bands for \(\theta_E = 0^\circ\) and \(\theta_E = 90^\circ\) of B5.

| Point          | 836 cm\(^{-1}\) peak intensity for \(\theta_E = 0^\circ\) | 1529 cm\(^{-1}\) peak intensity for \(\theta_E = 0^\circ\) | 836 cm\(^{-1}\) peak intensity for \(\theta_E = 90^\circ\) | 1529 cm\(^{-1}\) peak intensity for \(\theta_E = 90^\circ\) | 836 cm\(^{-1}\) peak intensity for \(\theta_E = 90^\circ\) | 1529 cm\(^{-1}\) peak intensity for \(\theta_E = 90^\circ\) |
|----------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| 1st point (A) of the mapping image | 0.0055±0.0001 | 0.0070±0.0001 | 0.79 | 0.0104±0.0004 | 0.077±0.0004 | 0.13 |
| 3rd point (B) | 0.0055±0.0002 | 0.0068±0.0002 | 0.81 | 0.011±0.0004 | 0.079±0.0005 | 0.14 |
| 4th point (C) | 0.0076±0.0004 | 0.0077±0.0004 | 0.99 | 0.012±0.0005 | 0.077±0.0005 | 0.16 |
| 10th point (D) after the molecular edge | 0.0055±0.0001 | - | - | 0.0093±0.0004 | 0.0016±0.0004 | - |
band at 1529 cm\(^{-1}\) is assigned to C=N stretching and C-H in-plane bending vibration and the band at 852 cm\(^{-1}\) is the C-H out of plane wag of the para-substituted benzene ring.\(^{19,28}\)

The intensity ratios between the bands at 852 cm\(^{-1}\) and 1529 cm\(^{-1}\) for \(\theta_E = 90^\circ\) and \(\theta_E = 0^\circ\) are shown in Table IV. Four spectra are shown of four points on the organic film side (left side of the vertical line) (points (A-D) in Figures 8a and 8b) and three spectra of three points (E-G) on the clean side (right side of the vertical line). The presence of a spectral signature of the molecules on the clean side is an indication of molecules migration during or after deposition (points (E-G) in Figures 8a–8c).

Table IV shows that the intensity for band 1529 cm\(^{-1}\) for \(\theta_E = 90^\circ\) is high in comparison to the intensity of that same band for \(\theta_E = 0^\circ\) on the molecular films (points A - D). This means that the molecules are more aligned with the electric field for \(\theta_E = 90^\circ\) than \(\theta_E = 0^\circ\). This is an indication of B3Q2 molecules are lying on their edge or standing up when they are interacting with each other because the side of the molecular film has a higher coverage of molecules. On the molecular film there is a variation in ratios for \(\theta_E = 90^\circ\) in different points from (A-D), likely due to inhomogeneities in the film thickness. The Table III also shows that for one of those four points (A-D) and as well as other three points (E-G) on clean side the intensity ratio is unquantifiable due to the very low intensity of the band 1529 cm\(^{-1}\) for \(\theta_E = 0^\circ\). On the clean region, the first point (E), almost on the vertical line shows a intensity drop for both bands at 852 cm\(^{-1}\) and 1529 cm\(^{-1}\) for \(\theta_E = 0^\circ\) but higher for \(\theta_E = 90^\circ\). This drop is probably due to defects created by the scratch (vertical line) or molecules are fully aligned with the electric field for \(\theta_E = 90^\circ\). The point (F) on the clean side also shows the presence of molecules and the same intensity trend for both bands as on the molecular film for \(\theta_E = 0^\circ\) but intensity drop for the band at 1529 cm\(^{-1}\) for \(\theta_E = 90^\circ\). It means that the B3Q2 molecules are changing their orientation from this point on. On the other hand, point (G) marks the furthest distance from the deposited film at which evidence of B3Q2 molecules is observed. Here we also see further intensity drop of the band at 1529 cm\(^{-1}\) for \(\theta_E = 90^\circ\) and maintaining almost same intensity for the both bands (852 cm\(^{-1}\) and 1529 cm\(^{-1}\)) for \(\theta_E = 0^\circ\). This suggests that during interaction with the iron oxide surface the B3Q2 molecules are oriented either lying down or standing on their edge with a twisted chain. IR spectroscopy makes it possible to differentiate between standing up and lying down orientations, but not necessarily between molecules that are lying down or are twisted while standing on their edge. While there is a significant difference between the standing up film layer thickness (2.2 nm) and the other two orientations (lying down at 0.44 nm or standing on their edge at 0.57 nm), the lying down and standing on their edge orientations are very close to each other in

| Point | 817 cm\(^{-1}\) peak intensity for \(\theta_E = 0^\circ\) | 1531 cm\(^{-1}\) peak intensity for \(\theta_E = 0^\circ\) | 817 cm\(^{-1}\)/1531 cm\(^{-1}\) for \(\theta_E = 0^\circ\) | 817 cm\(^{-1}\) peak intensity for \(\theta_E = 90^\circ\) | 1531 cm\(^{-1}\) peak intensity for \(\theta_E = 90^\circ\) | 817 cm\(^{-1}\)/1531 cm\(^{-1}\) for \(\theta_E = 90^\circ\) |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1\textsuperscript{st} point (A) of the mapping image | 0.0046±0.0005 | 0.0038±0.0005 | 1.21 | 0.0092±0.0003 | 0.038±0.0003 | 0.24 |
| 3\textsuperscript{rd} point (B) | 0.0083±0.0005 | 0.0024±0.0005 | 3.46 | 0.0024±0.0002 | 0.035±0.0002 | 0.069 |
| 4\textsuperscript{th} point (C) | 0.011±0.0004 | 0.0045±0.0004 | 2.44 | 0.0086±0.0006 | 0.036±0.0006 | 0.24 |
| 6\textsuperscript{th} point (D) after the molecular edge | 0.0104±0.0002 | 0.0072±0.0002 | 1.44 | 0.0083±0.0002 | 0.033±0.0002 | 0.25 |
| 8\textsuperscript{th} point (E) | 0.0081±0.0002 | 0.0052±0.0002 | 1.55 | 0.0039±0.0003 | 0.0009±0.0003 | - |
Figure 8. Mid-IR mapping spectra of B3Q2 on steel substrate, (a) at \( \theta_E = 0^\circ \) (upper left) and (b) \( \theta_E = 90^\circ \) (upper right). (c) The IR spectrum (A-G) represents the point from molecules side to clean side. These points are shown in the optical image map at the bottom. The spacing between sample points (black marks) is 100 \( \mu \text{m} \), for a total cross-section length of about 2 mm.

Layer thickness. Furthermore, the transition between lying face-on and standing on edge is fluent, given the possibility of twisted molecular geometries and tilted orientations. The orientation of the fully oxidized form (B2Q1) of the phenyl-capped aniline dimer is shown in previous work by us, to be lying down on iron oxide surfaces.29 On the other hand, the fully reduced dimer (B3) is standing on its edge on iron oxide surfaces.26 IR spectroscopy shows all three oxidation states of the tetramer to have either lying down or standing on their edge orientations during interaction with the surface. In the work of Poncet et al., it is shown that non-planar B5 is lying down flat on the surface.27

Step height analysis of B5, B4Q1 and B3Q2 films on iron oxide surfaces.—Step heights in the molecular layer were also measured using atomic force microscopy, giving information about the thickness of the different layers formed on the surface. The different step heights were measured by taking vertical cross-sections of the molecular islands. All three forms of PCAT were vacuum deposited for the AFM experiments. Both B5 (2.5 nm film) and B4Q1 (1 nm film) molecules were deposited at 20°C, while the B3Q2 film (1.5 nm thick) was deposited at 24°C substrate temperature on steel substrates. A detailed analysis of the surface roughness of the bare samples is available in Figure S8 (Supporting Information) of reference 26.

The step height analysis of the B5 molecules is shown in Figures 9a, 9b. In the histogram (Figure 9b) the most frequent first layer thicknesses of B5 molecules are found to be \( \sim 0.5 \) nm and \( \sim 0.4 \) nm followed by 0.3 nm. Since the resolution of the AFM used is \( \sim 0.06 \) nm, the histogram bins used were in 0.1 nm steps. According to Evain et al.,30 tetramer molecules lying on their edge have a thickness of \( \sim 0.57 \) nm and when these molecules are lying down they will form a \( \sim 0.44 \) nm thick layer. On the other hand, if these molecules are standing up they will form a \( \sim 2.2 \) nm thick monolayer. These results mean that B5 molecules largely prefer the face-on lying down orientation. There is also a considerable occurrence of 0.8 nm steps, indicative of bilayer formation,26 but no indication whatsoever of standing up molecular domains (around 2.2 nm).

Figure 10a shows the homogeneous islands of B4Q1 molecules on native oxide covered steel on which a nominally 1 nm thick film of molecules was deposited. Figure 10b shows the histogram of measured

| Table IV. Intensity ratio of the selected IR absorption bands for \( \theta_E = 0^\circ \) and \( \theta_E = 90^\circ \) of B3Q2. |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                  | 852 cm\(^{-1}\) peak intensity for \( \theta_E = 0^\circ \) | 1529 cm\(^{-1}\) peak intensity for \( \theta_E = 0^\circ \) | 852 cm\(^{-1}\)/1529 cm\(^{-1}\) for \( \theta_E = 0^\circ \) | 852 cm\(^{-1}\) peak intensity for \( \theta_E = 90^\circ \) | 1529 cm\(^{-1}\) peak intensity for \( \theta_E = 90^\circ \) | 852 cm\(^{-1}\)/1529 cm\(^{-1}\) for \( \theta_E = 90^\circ \) |
| 1\(^{st}\) point (A) of the mapping image. | 0.0039±.0003 | 0.0018±.0003 | - | 0.023±.0003 | 0.042±.0003 | 0.55 |
| 2\(^{nd}\) point (B) | 0.0052±.0004 | 0.0016±.0004 | - | 0.015±.0004 | 0.039±.0004 | 0.38 |
| 3\(^{rd}\) point (C) | 0.0067±.0004 | 0.0016±.0004 | - | 0.015±.0003 | 0.047±.0003 | 0.32 |
| 4\(^{th}\) point (D) | 0.0072±.0004 | 0.0018±.0004 | - | 0.023±.0002 | 0.046±.0002 | 0.50 |
| 5\(^{th}\) point (E) after the molecular edge | 0.0011±.0004 | 0.0018±.0004 | - | 0.021±.0003 | 0.045±.0003 | 0.47 |
| 8\(^{th}\) point (F) | 0.0051±.0002 | 0.0020±.0002 | - | 0.0050±.0006 | 0.015±.0006 | 0.33 |
| 9\(^{th}\) point (G) | 0.0039±.0002 | 0.0019±.0002 | - | 0.015±.0002 | 0.0037±.0002 | - |
step heights and Figures 10c, 10d show examples of how the step height was obtained from the line profile. The histogram shows the most frequent first layer thickness of B4Q1 molecules to be \( \sim 0.5 \) nm, followed by 0.4 nm. The AFM step height of most of the first layer is \( \sim 0.5 \) nm for B4Q1 molecules, somewhere between the edge-on and face-on orientations, which is either a result of the molecules being twisted along their axis or possibly suggesting a tilt angle of \( \sim 60^\circ \). The twisted configuration is the more likely explanation, also in line with mid-IR results.

In the histogram (Figure 11b) for B3Q2 molecules, the most frequent first layer thickness is observed to be \( \sim 0.5 \) nm, indicating that these molecules are preferentially standing on edge compared...
to the other two molecules (B5 & B4Q1). Some islands are less than \( \sim 0.5 \text{ nm} \) thick, indicative of face-on orientation. The two next most common island thicknesses for these molecules that were observed are \( \sim 0.8 \text{ nm} \) and \( \sim 1.0 \text{ nm} \), an indication of multilayer formation on the surface. B3Q2 molecules prefer to form multilayers (\( \sim 0.8 \text{ nm} \) and \( \sim 1.0 \text{ nm} \)) due to strong interactions with each other. Unlike for B5, there is a small but distinct population of 2.2 nm steps, consistent with either multilayer formation or molecules standing on end.\(^{29}\) This is consistent with the diminished surface interactions of B3Q2 molecules.

**Electrochemical impedance spectroscopy (EIS) measurements of B5, B4Q1 and B3Q2 coated steel surfaces.**—The corrosion performance of B5, B4Q1 and B3Q2 coated steel was monitored using EIS measurements. Two kinds of samples (coated for 24 hours or one week before EIS) were prepared by coating (drop casting) steel coupons with each of the molecules.

The 24-hour samples were denoted as fresh samples and one-week-old samples as aged samples. Figure 12a shows Nyquist plots of samples freshly coated (24 hours) with B5, B4Q1, B3Q2, as well as uncoated samples. The semicircle represents the charge transfer resistance of the interface between the coated (uncoated) samples and the solution. A larger diameter of the semicircle indicates better corrosion resistance.\(^{31}\) Figure 12a allows to qualitatively conclude that among the freshly coated samples B5 provides the highest corrosion resistance, followed by B3Q2 coated steel. B4Q1 results in less corrosion resistance than the other two molecules. When the samples were kept for one week after coating with the molecules they show better corrosion resistance and the trend stays the same, meaning that corrosion resistance increased with time (Figure 12b). However, B4Q1 coated samples stayed steady with time, neither increasing nor decreasing corrosion resistance nor being degraded. Here the EIS result is discussed qualitatively, while the complex behavior of the plot (low frequency capacitive and inductive effects) is yet to be explored.

**Weight loss measurement of the EIS samples.**—The degree to which a coating protects the underlying surface can also be ascertained through measuring weight loss. The weights of both aged and fresh EIS samples were measured before and after their EIS tests. The samples were rinsed with acetone, methanol, and DI water before weighing. The inhibition efficiency was measured using Equation 1, where \( W^0 \) is the weight loss of uncoated samples and \( W^1 \) is the weight loss of the coated samples.\(^{31}\)

\[
\% IE = \frac{W^0 - W^1}{W^0} \times 100\%
\]

Table V shows the inhibition efficiency and weight loss of the uncoated iron oxide surface and freshly (24 hours) coated samples with B5, B4Q1 and B3Q2 after 48 hours of EIS measurements. It shows that B5 and B4Q1 lose almost the same amount, and less weight than B3Q2, which makes their corrosion inhibition efficiency higher (\( \sim 66\% \)). B3Q2 would in fact seem to enhance corrosion as indicated by the negative value. Table VI shows the weight loss of the uncoated iron oxide surface and aged samples (one week) coated with B5, B4Q1 and B3Q2 after 48 hours of EIS measurements. Even though B3Q2 improved a lot in the total weight loss with time, still the B5 and the B4Q1 coatings are showing better results. It is possible to distinguish the contribution of uniform corrosion across the sample from the contribution of crevice corrosion along the rubber ring seal to the total weight loss. For this purpose, in addition to taking the weight of the EIS samples before and after the experiment, an optical surface profiler was used to measure the depth of general corrosion. Using the density of iron and volume of the inside ring area, the mass loss of the ring area due to uniform corrosion can be calculated. Subtracting the mass loss inside the ring from the total mass loss gives the mass loss underneath the O-ring area which is believed to be due to crevice corrosion.

The aged samples were further studied to observe the corrosion effect visually under an optical microscope and with an optical surface profiler. Figure 13 shows the aged samples before and after EIS test.
Table V. Inhibition efficiency after 48 hours EIS measurement using weight loss of uncoated iron oxide surface and freshly (24 hrs) coated with B5, B4Q1, and B3Q2 in 3.5% aqueous NaCl.

| Sample                  | Weight before EIS exp. (g) | Weight after EIS exp. (g) | Weight loss of Fresh samples (g) | Inhibition efficiency for fresh samples %IE |
|-------------------------|----------------------------|---------------------------|----------------------------------|--------------------------------------------|
| Uncoated steel coupon   | 3.2105                     | 3.1825                    | 0.0280                           |                                            |
| Coated with B5          | 3.7323                     | 3.7227                    | 0.0093                           | 66.78                                      |
| Coated with B4Q1        | 3.7370                     | 3.7275                    | 0.0095                           | 66.07                                      |
| Coated with B3Q2        | 4.0460                     | 3.9950                    | 0.0510                           | −82.14                                     |

Table VI. Inhibition efficiency after 48 hour EIS measurement using weight loss of uncoated iron oxide surface and aged (one week old) coated with B5, B4Q1, and B3Q2 in 3.5% aqueous NaCl.

| Sample                  | Weight before EIS exp. (g) | Weight after EIS exp. (g) | Total weight loss of aged samples (g) | Weight loss of the middle part (g) | Weight loss of the crevice corrosion (g) |
|-------------------------|----------------------------|---------------------------|--------------------------------------|-----------------------------------|----------------------------------------|
| Uncoated steel coupon   | 3.2105                     | 3.1825                    | 0.0280                               |                                   |                                        |
| Coated with B5          | 3.5244                     | 3.5132                    | 0.0112                               | 0.0065                            | 0.0047                                 |
| Coated with B4Q1        | 3.5055                     | 3.4922                    | 0.0133                               | 0.0061                            | 0.0072                                 |
| Coated with B3Q2        | 4.0702                     | 4.0351                    | 0.0351                               | 0.0172                            | 0.0173                                 |

Figure 13. Optical image of (a & b) B5 coated steel before and after EIS test and laser line scan, (c & d) B4Q1 coated steel before and after EIS test and laser line scan, (e & f) B3Q2 coated steel before and after EIS test and laser line scan, (g & h) uncoated steel before and after EIS test and laser line scan. The size of the coupons displayed in the optical images is 25 mm × 25 mm.
and the related laser line scans. The circle shown on those samples is the area exposed to 3.5% aqueous NaCl for 48 hours during the EIS test. The edge of the circle is about 2 mm wide. The optical line scan was taken approximately across the center of the circle from edge to edge. The B5 coated sample (Figures 13a, 13b) shows less crevice corrosion compared to the other two coated samples. The depth of corrosion inside the ring of this sample is \(\sim 1.99\) \(\mu\)m. It can be seen from Figures 13c, 13d for the B4Q1 sample and Figures 13e, 13f for the B3Q2 sample and their laser line scans that mostly crevice corrosion takes place at the edge of the circle as well as small subsequent corrosion progress across the surface on both samples. The crevice corrosion could be due to tightening of the ring creating large defects on the coatings at the edge of the ring which initiate localized corrosion. The average depth of the corrosion inside the ring of B4Q1 and B3Q2 coated samples are \(\sim 1.86\) \(\mu\)m and \(\sim 5.26\) \(\mu\)m, respectively. Comparing these three samples with the uncoated sample (Figs. 13g, 13h), it is easy to evaluate the relative benefits of the different coatings. The uncoated sample is corroded all over the exposed area as well as at the circle edge to the same extent. The average depth of corrosion in the middle is \(\sim 7.06\) \(\mu\)m. Out of the total weight loss, the contribution due to corrosion inside the ring of B5 and B4Q1 is 0.0065 g and 0.0061 g respectively, with the rest being attributable to crevice corrosion at the ring. This result also indicates that B5 is less likely to enhance crevice corrosion than B4Q1, whereas, B3Q2 coated samples show equal proportions of weight loss due to crevice corrosion and also corrosion inside the ring. Among the three coatings, B5 shows overall better corrosion inhibition than B4Q1 and B3Q2. Even though B3Q2 shows better corrosion resistance at the beginning of the EIS test (Figures 13c, 13d), the weight loss data shows that the situation changed with time. On the other hand, B4Q1 showed low impedance at the beginning of the EIS test but from weight loss data it is as good as B5 at creating protection for the sample.

**Interactions of B5, B4Q1 and B3Q2 with iron oxide surfaces after completion of EIS tests.**—The effectiveness of these molecules for corrosion inhibition depends on their interactions with the native iron oxide layer. Figure 14a shows a Raman spectrum of B5 drop cast from methanol onto a steel substrate before the EIS test. It is comparable to the spectrum in Figure 3b of a similar sample. B5 tends to transform in small part into the semiquinone form (bands at 1639 and 1337 \(\text{cm}^{-1}\)), a very small portion into B3Q2 (1571 \(\text{cm}^{-1}\)) and B4Q1 (1496 and 1606 \(\text{cm}^{-1}\)) by interacting with the native oxide of steel while it is dissolved in methanol. On the other hand, after the EIS test is complete (Figure 14b) Raman bands at 1488, 1565 and 1415 \(\text{cm}^{-1}\) emerge corresponding to B3Q2. The band at 1352 \(\text{cm}^{-1}\) belongs to the semiquinone species and the others belong to B5.

This means that the fully reduced B5 molecules tend to convert mostly into the fully oxidized B3Q2 form during the EIS test. Figures 15a, 15b show the Raman bands of B4Q1 drop cast from methanol onto native oxide before and after the EIS test. We have already discussed the impact that methanol has on B4Q1. Methanol changes the oxidation state of the molecules in part to semiquinone and the rest to B3Q2. The Raman bands before the EIS test show semiquinone bands at 1407 and 1635 \(\text{cm}^{-1}\). The bands at 1568 and 1176 \(\text{cm}^{-1}\) are an indication of B4Q1 tending to transform into fully oxidized B3Q2 upon interaction with the iron oxide surface in the presence of methanol. On the other hand, the Raman spectrum after EIS shows that these molecules mostly convert back to their original B4Q1 state (Figure 15b) with just small portion of semiquinone (1400 \(\text{cm}^{-1}\)) and B3Q2 (1568 \(\text{cm}^{-1}\)) left.

The Raman spectrum of B3Q2 on a steel substrate after drop casting from methanolic solution is shown after the EIS test in Figures 16a and 16b, which corresponds to a thin and thick layer of molecules, respectively. Thin and thick are differentiated by visual inspection under an optical microscope. The Raman spectrum shows that when B3Q2 is very close to the iron oxide surface (Figure 16a, thin film), some portion turns into the semiquinone species due to interactions with the surface (1408 and 1252 \(\text{cm}^{-1}\)) and the rest turns into B4Q1 (1497, 1593 and 1606 \(\text{cm}^{-1}\)). For the thick film, the interactions are mostly between molecules. The Raman spectrum of a thick film of B3Q2 after the EIS test shows in Figure 16b that these molecules partially turn into B4Q1 (1497 and 1590 \(\text{cm}^{-1}\)), with the rest remaining as B3Q2.

**Figure 14.** Raman spectra of B5 molecules on steel surface (a) before EIS test (b) after EIS test.

**Figure 15.** Raman spectra of B4Q1 molecules (a) before EIS test (b) after EIS test.

**Figure 16.** Raman spectra of B3Q2 after EIS test, (a) thin films of molecules (b) thick films of molecules.
Comparing the EIS test with weight loss data and with the optical line scan results, it can be concluded that B5 is much more effective at inhibiting corrosion than the other two molecules. B5 molecules have 4 amine groups in their chain which allow them to bond more strongly with the surface than B4Q1 which has only two. A combination of amine and imine groups is also beneficial to improving the interactions within the molecular film. Above it was shown that drop cast B5 molecules bond strongly to iron oxide surfaces. After 48 hours of EIS testing there are still B5 molecules left on the surface, some turning into the semiquinone form and B3Q2. These leftover B5 and semiquinone species continue to protect the surface making a physical barrier. In contrast, B3Q2 has no amine groups resulting in only weak bonding to the surface. Even though the EIS test shows B3Q2 to be second best in corrosion resistance, the weight loss data does not bear out this story. This is because when interacting with the native oxide surface before the EIS test, B3Q2 transforms into B4Q1 and the semiquinone form which allows the molecules that are very close to the surface to stick to the surface strongly and protect. But with time (during EIS test) these molecules transform mostly into B4Q1 and the semiquinone form (Figure 15b). This allowed these B4Q1 molecules to stick to the surface more strongly over time and at last protect the surface which is visible in the weight loss test and the laser line scan data. This also explains why the B5 and B4Q1 molecules showed less weight loss due to crevice corrosion in the junction of the O-ring. The reason for this is that the B5 molecules stick to the surface and form a better physical barrier than B4Q1, and B4Q1 molecules are better than B3Q2. Their redox activity is also an important factor.

Conclusions

We have investigated the interactions of B5, B4Q1 and B3Q2 molecules with iron oxide surfaces using Raman spectroscopy. We found that methanol has very little impact on B5 molecules, but it does impact B4Q1 and B3Q2, even changing their oxidation states. As a result, B4Q1 and B3Q2 interact less with iron oxide surfaces in the presence of methanol. B5 molecules transform mostly into their semiquinone and B4Q1 forms when interacting with the iron oxide surface. Interacting with the same surface, B4Q1 transforms mostly into the semiquinone and B3Q2 forms and some of the B3Q2 transforms into the semiquinone and B4Q1 forms. Mid-IR revealed that the orientation of all three molecules closer to the surface is either lying down or standing on edge but molecules in the multilayer are either lying on edge or standing up. AFM was used to identify the specific orientations and compliment IR results during interaction with iron oxide surfaces. While the AFM results are indicative of all three molecules mostly preferring to stand on their edges, twisting of the molecular backbone and the possibility of tilted orientations make it challenging to clearly pinpoint the molecular orientation at the interface. AFM also revealed that B3Q2 molecules prefer to form multilayers due to strong interactions with each other rather than with the substrate surface. The EIS test, weight loss test and laser line measurements of the EIS samples all show that the corrosion resistance of B5 and B4Q1 coatings on steel is higher than that of B3Q2 coatings. These coatings were applied without any modification just using methanol as a solvent. Before the EIS test, the B4Q1 molecules closer to the surface transform into their semiquinone and B3Q2 forms due to interactions with the iron oxide surface. Since B3Q2 is weakly bonded to the surface, the transformed B4Q1 coating showed less corrosion resistance (EIS test) at the beginning but with time (during EIS test) these molecules transform back mostly into the B4Q1 and semiquinone forms. This allows these B4Q1 molecules, at last, to protect the surface. In contrast, B3Q2 caused degradation of the surface although EIS test shows it is the second best. This is because before the EIS test B3Q2 transforms into mostly B4Q1 and semiquinone by interacting with the native oxide surface which allows the molecules that are very close to the surface to stick to the surface strongly. But the bulk of the B3Q2 molecules that remains in the B3Q2 form detaches from the surface over time, causing degradation of the surface. These results elucidate the role of the different oxidation states of oligoanilines and polyaniline in the corrosion protection of iron and steel, and lay the foundation for the rational design of smart corrosion inhibiting coatings. We confirm that PCAT resembles PANI in its corrosion inhibition mechanism based on charge transfer leading to the repair of defects in the iron oxide layer, as previously reported in the literature. While there are benefits to the use of small molecules over polymeric inhibitors, such as ease of processing, disruption of long-range conductivity in the films, and ability to self-heal by molecular migration, challenges arise from the difference in mechanical (adhesion) properties. The oxidized form of PCAT only weakly adheres to the surface and does not form a reliable coating. The half oxidized form of PCAT, which is considered crucial for its function as a corrosion inhibitor, moderately adheres to the surface. Starting with the reduced form is essential to attaining a coating with coexisting multiple oxidation states, which is ultimately the best case for corrosion inhibition. In practice, likely a composite coating with tetra-amine fragments bound to an inert backbone would be the most feasible approach, although in that case the mobility of the oligoanilines would be compromised, preventing self-healing of these coatings in the case of mechanical damage.

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