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RESEARCH ARTICLE

Multifunctional Fluorinated Polybenzoxazine Coatings with Durable Superhydrophobicity, Anticorrosion, and Oil–Water Separation Capability

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ABSTRACT

In this work, fluoro-core polybenzoxazine coatings were developed to overcome the limitations of conventional organic coatings towards aggressive corrosion in marine and industrial environments. Bis(benzoxazine) monomers were synthesized using a hexafluoropropane-based fluorinated diamine combined with allylphenol, phenol, 3,5-bis(trifluoromethyl)phenol and subsequently cured to form highly crosslinked polybenzoxazine networks. The monomer structures were confirmed by ATR-FTIR, HRMS, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. Curing behavior depended strongly on phenolic structure, with Ap-fa exhibited the lowest curing temperature of 234°C, indicating favorable processability. Thermal stability with degradation temperatures above 490°C and char yields reaching 45%. Pronounced superhydrophobic behavior was observed, with water contact angles exceeding 150° and a maximum value of 156° for poly(Fp-fa). When applied to cotton fabric, the poly(Fp-fa) coating imparted durable super-hydrophobicity and enabled efficient oil–water separation, achieving separation efficiencies of above 95%. The coated fabric retained superhydrophobic nature even after exposure to acidic and alkaline media, demonstrating strong chemical durability. X-ray photoelectron spectroscopy (XPS) analysis further confirmed surface fluorine enrichment and the presence of $-CF_3$ functionalities, evidencing the formation of a low-surface-energy interface. Electrochemical impedance spectroscopy, Tafel polarization and salt spray testing revealed outstanding corrosion protection on mild steel, with inhibition efficiencies up to 99.99%. In addition, all benzoxazines exhibited strong antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* up to 25 mm of inhibition zone. The monomer of Fp-fa coated cotton fabric possesses 17.5 mm, confirmed the activity against both *Staphylococcus aureus* ATCC 6538 and *Klebsiella pneumoniae* ATCC 4352 with the relatively low leaching and high retention indicate sustained functional activity. Overall, fluorinated diamine-based polybenzoxazines are high thermal stability, super-hydrophobicity, durable anticorrosive protection and fabric-level oil–water separation capability within a single coating matrix, making them well suited for demanding marine and harsh environmental applications.

1 | Introduction

Organic coatings are extensively employed to protect metallic substrates in marine, offshore, and industrial applications [1, 2]. In service, these coatings are routinely exposed to moisture, acidic and saline species, temperature changes, and microbiological activity. With persistent exposure, these elements slowly weaken the covering and stimulate corrosion of the underlying metal, often leading to early failure [3–5]. Although tremendous progress has been achieved in coating formulation and commercial development, corrosion damage to coated metals remains a chronic economic and safety challenge.

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This highlights that currently available coating systems still lack sufficient long-term barrier stability under aggressive service conditions [6, 7].

Conventional organic coating systems such as epoxies, polyurethanes, and acrylics exhibit good adhesion and mechanical strength; however, their long-term durability is often limited by water permeation, loss of barrier efficiency, and susceptibility to microbial colonization in humid and saline environments [8–10]. In contrast, fluoropolymer-based coatings are well known for their low surface energy and excellent water repellence; hitherto, their application as protective coatings is restricted by poor adhesion to metallic substrates, processing challenges, and high material cost [11, 12]. Multilayer coatings and additive-based strategies have been explored to impart multifunctionality however, such approaches frequently suffer from increased system complexity limited durability and potential leaching of functional additives during prolonged exposure. These drawbacks reduce long-term reliability and hinder practical deployment in harsh environments.

Polybenzoxazines have emerged as a promising class of thermosetting materials for advanced organic coating applications owing to their intrinsic advantages including low curing shrinkage, near-zero volatile release during polymerization, excellent chemical resistance, and strong adhesion to metallic substrates [13–16]. The highly crosslinked networks formed during benzoxazine ring-opening polymerization produce compact polymer structures that are well suited for corrosion protection [17, 18]. In addition, the structural modifications suggestively effect the properties of benzoxazine monomers [19–21]. The chemistry of benzoxazines allows considerable flexibility in molecular design as systematic variation of the phenolic and amine components enables tuning of thermal, mechanical, and surface properties [22, 23]. Benzoxazine-based functionalised porous organic polymers demonstrate potential for applications in sustainability, gas separation, and energy devices [24–26].

Recent fluorinated polybenzoxazines, such as fluorine–silicon main-chain systems [27] and Schiff base–derived monomers [28], have demonstrated excellent dielectric and thermal properties; however, these systems generally rely on passive fouling resistance and do not integrate active antibacterial functionality. In contrast, the present work introduces fluoro-core bis(benzoxazine) monomers synthesized from a hexafluoropropane-based fluorinated diamine and tailored phenolic precursors, designed to surpass these quantitatively, including high water contact angles, enhanced corrosion resistance, and antibacterial inhibition. Mechanistically, these improvements arise from the synergistic interplay of hierarchical surface morphology, dense crosslinking, and incorporation of antimicrobial functionalities, which together deliver multifunctionality beyond conventional fluorinated systems. This study highlights a novel design strategy that integrates fluorine-based hydrophobicity with sustainable, application-oriented enhancements.

Despite these advantages, most polybenzoxazine coatings exhibited only moderate surface hydrophobicity and limited antimicrobial activity [29, 30]. This indicates that high crosslink density alone is insufficient to prevent moisture ingress and biofouling under prolonged exposure conditions. Incorporation of fluorinated structural units into polybenzoxazine networks has been widely explored as a practical way to reduce surface energy, limit water uptake, and improve chemical stability [31, 32]. Several studies have reported fluorinated benzoxazine systems derived from mono-amine precursors primarily aiming to improve surface hydrophobicity. For example, Aikifa Raza et al. [33] demonstrated that fluorinated mono-amine benzoxazines exhibit reduced surface energy and enhanced water repellence due to the presence of $-CF_3$ groups; however, the resulting polymers form comparatively less crosslinked networks, which limits their long-term barrier performance when applied as protective coatings. Similarly, Mohammed Mydeen et al. [34] reported favorable initial corrosion resistance for monoamine-based fluorinated benzoxazines, but continued exposure to strong chemical environments, like strong base and strong acid nature situations, led to gradual performance degradation attributed to insufficient network density and the formation of micro defects.

Further investigations by Priyanka et al. [35] revealed that although fluorinated monoamine benzoxazine coatings display enhanced hydrophobic behavior, their mechanical strength and resistance to electrolyte permeation remain inferior to more highly crosslinked benzoxazine systems. This limitation is directly associated with the reduced number of reactive sites available for network formation in mono-amine structure. In addition, recent studies pointed out that mono-amine fluorinated benzoxazines often show a functional trade-off where improved surface wettability does not lead to sustained anticorrosion or antimicrobial performance during long-term exposure [36–38]. This trade-off clearly indicates that surface energy reduction alone is insufficient without simultaneous enhancement of network density and structural robustness. Taken together, these studies suggest that although fluorinated mono-amine benzoxazines can enhance surface hydrophobicity, their low crosslink density, mechanical weakness, and poor long-term durability limit their suitability for multifunctional coating applications.

In the present work, a series of fluoro-core bis(benzoxazine) monomers was synthesized using a hexafluoropropane-based fluorinated diamine and different phenolic precursors followed by controlled thermal curing to obtain the corresponding polybenzoxazine coatings. Unlike mono-amine systems, the use of a diamine-based fluorinated core increases the number of reactive sites, enabling the formation of a highly crosslinked and structurally robust network while retaining low surface energy characteristics. The influence of molecular structure on curing behavior, thermal stability, surface wettability, antimicrobial activity, and corrosion resistance were systematically evaluated. The results demonstrate that rational integration of a fluorinated diamine core within a bis-benzoxazine framework coupled with phenolic structural tuning enables the development of multifunctional organic coatings that combine pronounced superhydrophobic behavior, exceptional anticorrosion performance, and mechanical property. This design strategy directly addresses the previously reported limitation of low crosslink density in fluorinated benzoxazines and establishes a clear structure–property relationship between molecular architecture and coating performance. Such multifunctional behavior within a single

organic coating matrix reduces the need for multilayer architectures and additive-based formulations, offering a simplified and durable approach for long-term surface protection. These findings highlight the potential of fluoro-core polybenzoxazines as durable protective coatings for marine and other harsh service environments.

2 | Materials

2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (98%) and 3,5-bis(trifluoromethyl)phenol (99%) were obtained from BLD Pharm, India.

2-Allylphenol (99%) and paraformaldehyde (98%) were supplied by Sigma-Aldrich, India.

Phenol (99%) was sourced from Sisco Research Laboratories (Mumbai, India), and ethyl acetate (97%) was procured from Nice Chemicals, India. Commercially available plain-woven cotton fabric with an estimated pore size of 50–200 μm was used as the substrate and cut into 2 × 2 cm [2] pieces purchased from Arun Tex, Tamilnadu.

3 | Experimental

3.1 | Instrumentation and Measurements

Detailed measurement procedure and instrumental parameters are explained in Section S1.

3.2 | Synthesis of Fluoro-Core Bis(Benzoxazines)

5.0 g (0.01 mol) of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (Fa) and 1.15 g (0.04 mol) of paraformaldehyde were dissolved in 1,4-dioxane (5 mL) in a 100 mL two-necked round-bottomed flask fitted with a reflux condenser and magnetic stirrer. The mixture was stirred at 60°C for 1 h to promote pre-activation, followed by the addition of 2-allylphenol (Ap) 2.55 mL (0.02 mol). The reaction was subsequently heated to 110°C and maintained under continuous stirring for 24 h. Reaction completion was ascertained via thin-layer chromatography (hexane/ethyl acetate). The crude adduct was dissolved in ethyl acetate (20 mL) and sequentially washed with 2 N NaOH to remove unreacted phenolic residues, followed by two washes with distilled water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed using a rotary evaporator. The residue was dried at 60°C to furnish the fluoro-core bis(benzoxazine) Ap-fa as a purified solid. Employing the same methodology, Ph-fa and Fp-fa were synthesized using phenol (Ph) and 3,5-bis(trifluoromethyl)phenol (Fp), respectively, as depicted in Scheme 1. The isolated yield of the monomers was around 80%.

3.2.1 | HR-Mass Spectra (m/z)

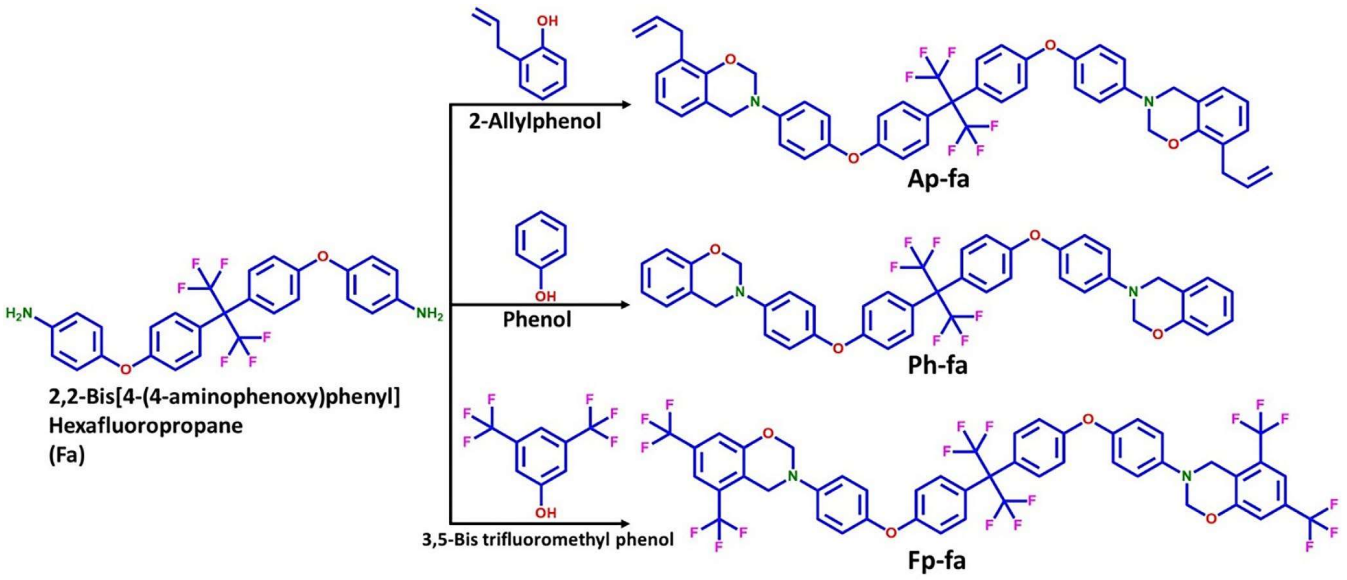
Ap-fa: Calculated value = 834.29 Da; Experimental value = 836.62 Da. **Ph-fa:** Calculated value = 754.23 Da; Experimental value = 754.23 Da. **Fp-fa:** Calculated value = 1026.18 Da; Experimental value = 1026.75 Da.

3.2.2 | ATR-FTIR (ν cm^{-1})

Ap-fa: 984 (Ar–O–C), 1150 and 1383 (C–O–C), 1360 (C–N), 2850 and 2924 (–CH–). **Ph-fa:** 986 (Ar–O–C), 1152 and 1380 (C–O–C), 1362 (C–N), 2850 and 2924 (–CH–). **Fp-fa:** 984 (Ar–O–C), 1150 and 1383 (C–O–C), 1362 (C–N), 2850 and 2924 (–CH–).

3.2.3 | ^{1}H-NMR ($CDCl_3$, δ Ppm)

Ap-fa: 4.5 (a, Ar–CH_2–N), 5.5 (b, O–CH_2–N), 6.8–7.8 (Ar–H). **Ph-fa:** 4.5 (a, Ar–CH_2–N), 5.5 (b, O–CH_2–N), 6.8–7.8 (Ar–H). **Fp-fa:** 4.5 (a, Ar–CH_2–N), 5.5 (b, O–CH_2–N), 6.8–7.8 (Ar–H).



SCHEME 1 | Synthesis of fluoro-core bis(benzoxazines).

TABLE 10 | Leaching behavior study results of Fp-fa coated fabric.

Time	Absorbance at 343 nm	Released concentration (mg/mL)	Amount leached in 5 mL (mg)	Remaining on fabric (mg)	Bound (%)
30 min	0.014	0.4497	2.2487	97.751	97.75%
1 h	0.017	0.5490	2.7299	97.270	97.27%
12 h	0.077	2.4733	12.366	87.633	87.63%
24 h	0.095	3.0514	15.2570	84.743	84.74%

4.22 | Antimicrobial Activity of Fluoro-Core Bis(Benzoxazine) Monomers

The antibacterial performance of the synthesized benzoxazine systems (Ap-fa, Ph-fa and Fp-fa) was evaluated against *Escherichia coli (E.coli)* and *Staphylococcus aureus (S. aureus)* using the zone-of-inhibition method (Figure 15) [29]. Ap-fa showed moderate antibacterial activity with inhibition zones of 16 mm against *E. coli* and 8 mm against *S. aureus* indicating that Gram-negative strain was more susceptible. Ph-fa showed comparatively weaker antibacterial behavior with inhibition zones of 12 mm *(E. coli)* and 6 mm *(S. aureus)* suggesting limited interaction between the polymer surface and bacterial cell envelopes. In contrast, Fp-fa showed strong antibacterial activity exhibiting identical inhibition zones of 25 mm against both bacterial strains. This behavior is attributed to the presence of trifluoromethyl-functionalized phenolic units which increase surface electronegativity and hydrophobicity turn to promote stronger interaction with bacterium surface leading to membrane disruption. The antibacterial performance followed the order Fp-fa > Ap-fa > Ph-fa underscoring the key role of fluorinated phenolic moieties in determining antibacterial behavior. Overall these results indicate that Fp-fa as the most effective antibacterial benzoxazine among the studied samples.

4.23 | Comparison With Controls

The antibacterial evaluation clearly highlights the effectiveness of the FP-fa coated fabric compared to the neat cotton fabric as control. The consistent inhibition against both *Staphylococcus aureus* ATCC 6538 (Gram-positive) and *Klebsiella pneumoniae* ATCC 4352 (Gram-negative) and the results are presented in Figure S8 summarized in Table 9.

The uncoated neat fabric exhibited no inhibition zones (0 mm) against both bacterial strains, confirming the absence of inherent bacteriostatic activity in the substrate. For both bacterial strains, the FP-fa coated fabric created clear inhibition zones of 17.5 mm, indicating a significant suppression of microbial growth. This comparison with the control test establishes that the observed antibacterial effect originates from the FP-fa coating rather than the neat fabric. The coating's broad range bacteriostatic activity is further demonstrated by the consistent inhibition against both Gram-positive and Gram-negative bacteria. This is probably due to the coating's surface chemistry and capacity to prevent bacterial growth upon contact. By integrating the control data, the results provide compelling evidence that FP-fa coated fabric transforms an inert textile into an active antimicrobial material.

4.24 | Leaching Behavior Study

The leaching study was performed to assess the stability of the active compound bound to the coated FP-fa fabric and its tendency to release into the surrounding medium over time. Absorbance measurements at 343 nm were used to quantify the released concentration, which was then converted into the total amount leached in 5 mL solution. The absorbance values recorded during the release study were very low, indicating limited release of the coated compound into the PBS medium. Based on Beer–Lambert calculations, the amount of compound released was 2.249 mg after 30 min, 2.730 mg after 1 h, 12.367 mg after 12 h, and 15.257 mg after 24 h. Approximately 84.743 mg of the compound remained attached to the fabric after 24 h, corresponding to a retention efficiency of 84.74%. The results are given in Table 10.

The amount of compound released at each time point was calculated using the Beer–Lambert relationship:

$$C_{released} / C_{Stock} = A_{released} / A_{Stock} \quad (6)$$

where $A_{stock} = 6.22$ and $C_{stock} = 1000\,mg/5\,mL = 200\,mg/mL$. These results demonstrate that the coated fabric retained the majority of the compound throughout the 24 h immersion period, with only 15.26% release observed. The relatively low leaching and high retention indicate good coating stability and strong interaction between the compound and the fabric, suggesting suitability for applications requiring prolonged functionality in aqueous environments.

5 | Conclusion

Fluoro-core polybenzoxazine coatings were successfully developed using a hexafluoropropane based diamine with different phenolic precursors (Ap-fa, Ph-fa, and Fp-fa) enabling clear structure property correlations across processing, thermal, surface and protective performances. ATR-FTIR, ^{1}H-NMR, ^{13}C-NMR and HRMS spectroscopic techniques confirmed the successful formation of the benzoxazine monomers, while XPS analysis verified surface fluorine enrichment and the presence of $-CF_3$ functionalities, confirming the formation of a low-surface-energy interface. Differential scanning calorimetry showed that curing behavior was governed by phenolic structure with Ap-fa exhibiting the lowest curing temperature of 234°C indicating

favorable processability among the series. Thermogravimetric analysis showed that all the polybenzoxazines possess excellent thermal stability with degradation temperatures above 490°C. Among them poly(Fp-fa) exhibited the highest char yield (45%) indicating the formation of a densely crosslinked network. The presence of fluorine played a key role in lowering in surface free energy and compact molecular packing. As a result, coating showed super-hydrophobicity with water contact angle reaching up to 156°. This surface property limited water and ion penetration and provided corrosion protection with inhibition efficiencies up to 99.99%. The high bond energy of the C–F linkages also contributed to good chemical durability. The coating also showed good adhesion and remained stable after exposure to acidic (pH 1) and alkaline (pH 14) conditions. This was evident from the retention of superhydrophobicity on cotton fabric even after exposure to strongly acidic (pH 1 and 5) and alkaline (pH 10 and 14) environments while maintaining stable oil–water separation efficiencies above 95%. Among the polymers, poly(Fp-fa) exhibited the highest lap shear strength (2.39 MPa), which corresponds to a maximum force of 1490 N, which showed a good adhesive strength. In addition, the low surface energy fluorinated interface reduced bacterial adhesion resulting in significant antibacterial activity with inhibition zones of 25 mm against *Escherichia coli* and *Staphylococcus aureus*. In comparison with control of neat cotton fabric (0 mm) compared into Fp-fa coated cotton fabric possess 17.5 mm, confirmed the activity against both *Staphylococcus aureus* ATCC 6538 and *Klebsiella pneumoniae* ATCC 4352 with the relatively low leaching and high retention indicate sustained functional activity. From a materials design perspective the superior performance of poly(Fp-fa) highlights the importance of fluorine incorporation in developing polybenzoxazine networks that combine durable surface repellence thermal robustness and corrosion resistance required for long-term marine coating applications without relying on multilayer systems or additive-based approaches.

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The authors have nothing to report.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Section S1** Instrumentation and measurements. **Section S2:** Antibacterial activity evaluation. **Section S3:** Assessment of comparison with control and leaching behavior. **Section S4:** Preparation of polybenzoxazine-coated mild steel. **Section S5:** Preparation of poly(Fp-fa) coated cotton fabric. **Figure S1:** HRMS of Ap-fa. **Figure S2:** HRMS of Ph-fa. **Figure S3:** HRMS of Fp-fa. **Figure S4:** Images of fluoro-core polybenzoxazines coated mild steel, (a) immersion setup in acidic (pH-1) and alkaline (pH-14) media, (b) surface appearance of the coating before and after exposure to pH-1 and pH-14, and (c) cross-hatch adhesion performance before and after the tape test. **Figure S5:** (a) Salt spray exposure of fluoro-core polybenzoxazine-coated mild steel. (b) Photographs of fluoro-core polybenzoxazine-coated mild steel before and after salt spray testing for 336 h (14 days). **Figure S6:** Lap shear test of fluoro-core polybenzoxazine-coated mild steel. **Figure S7:** Lap shear test of fluoro-core poly(Ap-fa), poly(Ph-fa) and poly(Fp-fa) coated mild steel. **Figure S8:** Bacteriostatic activity of uncoated and Fp-fa coated cotton fabric. **Table S1:** Oil–water separation efficiency of benzoxazine and related systems compared with literature. **Table S2:** Swelling ratio and gel content of fluoro-core polybenzoxazines.