Cyclam-based Cu(II) and Fe(III) complexes for antifouling coatings development

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Supplementary Information Contents

SI.1 - ^{1}H and ^{13}C{^{1}H} NMR spectra of compounds 2 and 3

7.56
7.54
7.48
7.46

4.10
4.08
4.06
4.05

3.59

3.23

2.78
2.76
2.75
2.68
2.66
2.65
2.56

1.69
1.67
1.65

1.20
1.18
1.17

4.1 ⊥
4.0 ⊥

4.0 ⊥

4.1 ⊥

4.0 ⊥

4.2 ⊥
4.1 ⊥
8.1 ⊥

5.4 ⊥

6.1 ⊥

8.0   7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0
ppm
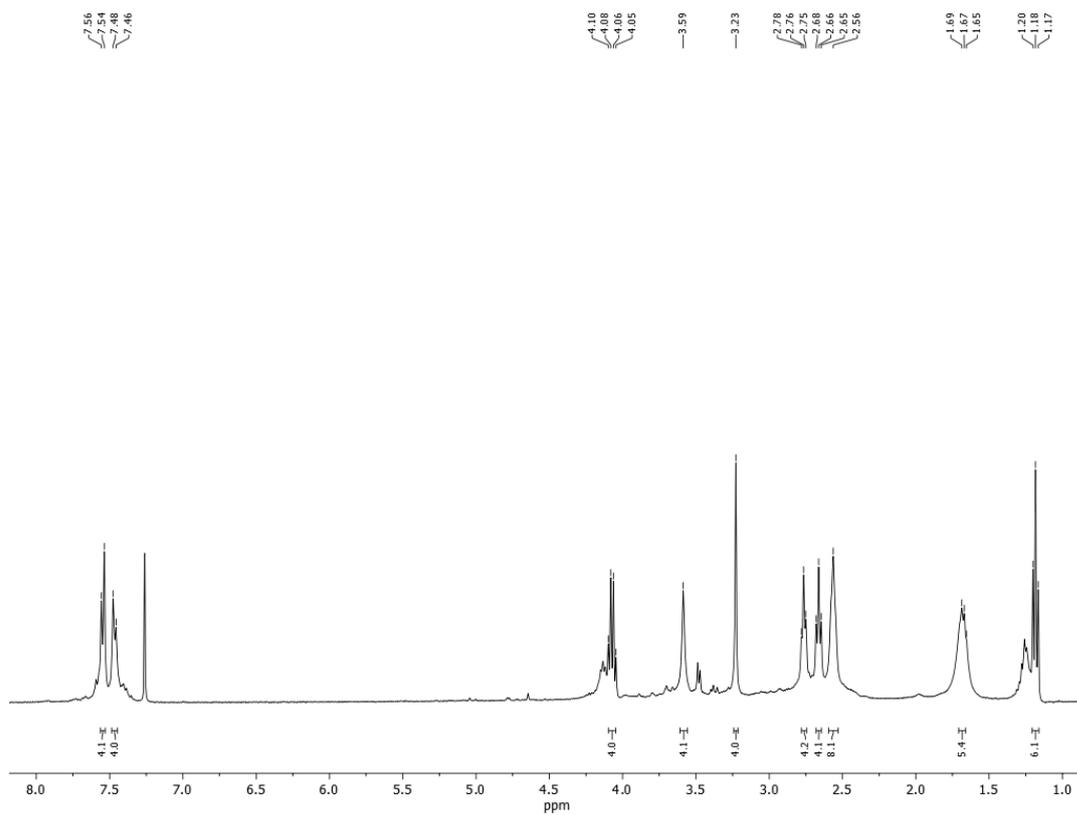
Figure S1A: ^{1}H NMR spectrum of compound **2** in CHCl$_3$.

171.6

129.3
125.2
125.2

60.3
59.0
55.5
51.7
51.4
51.0

24.8

14.3

180   170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10
ppm
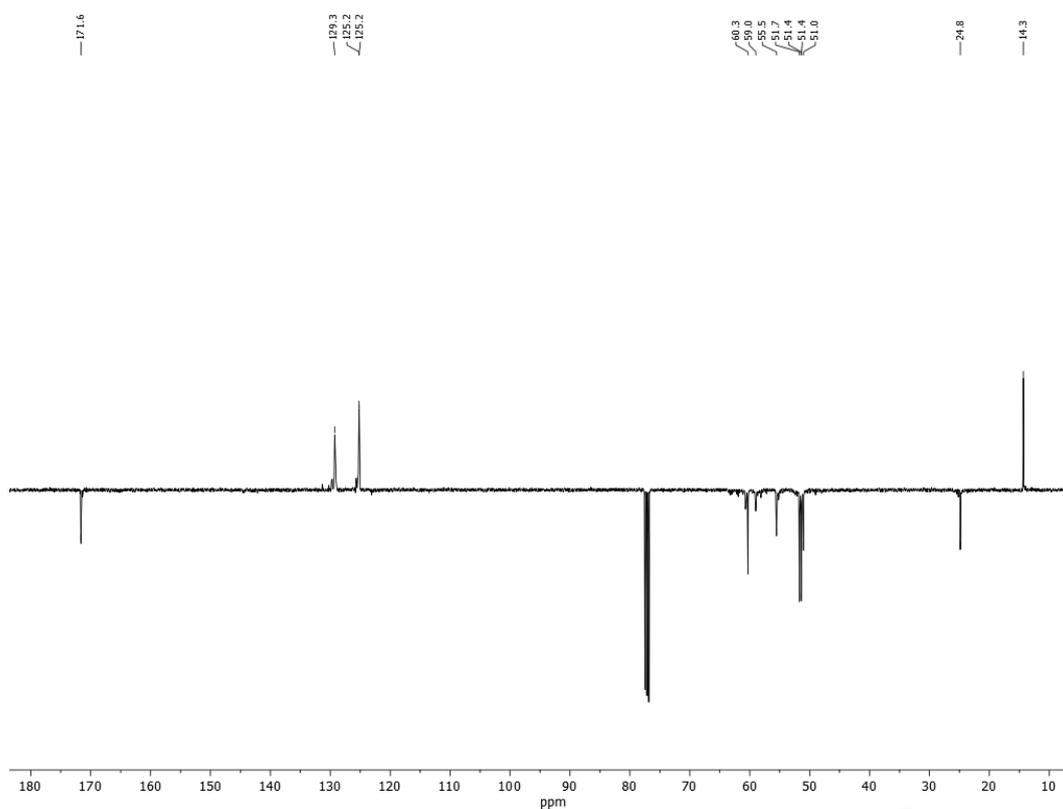
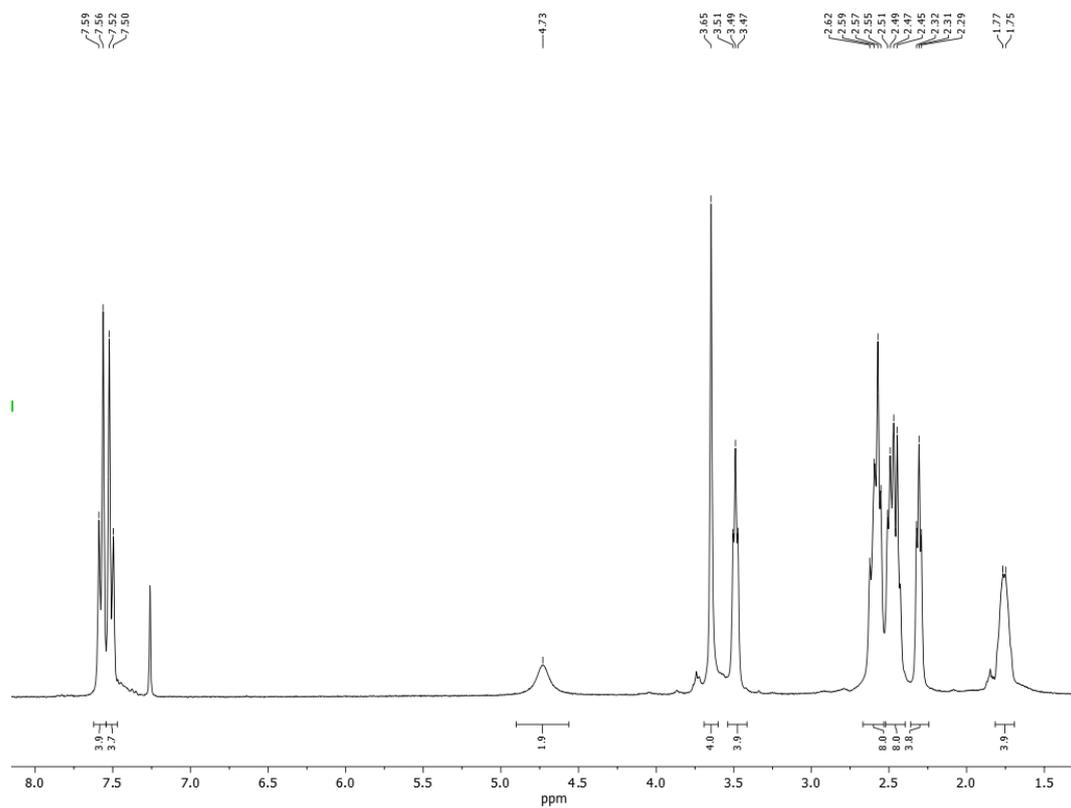**Figure S1B**: ^{13}C{^{1}H} NMR spectrum of compound **2** in CHCl$_3$.

Figure S2A: ^{1}H NMR spectrum of compound **3** in CHCl$_3$.

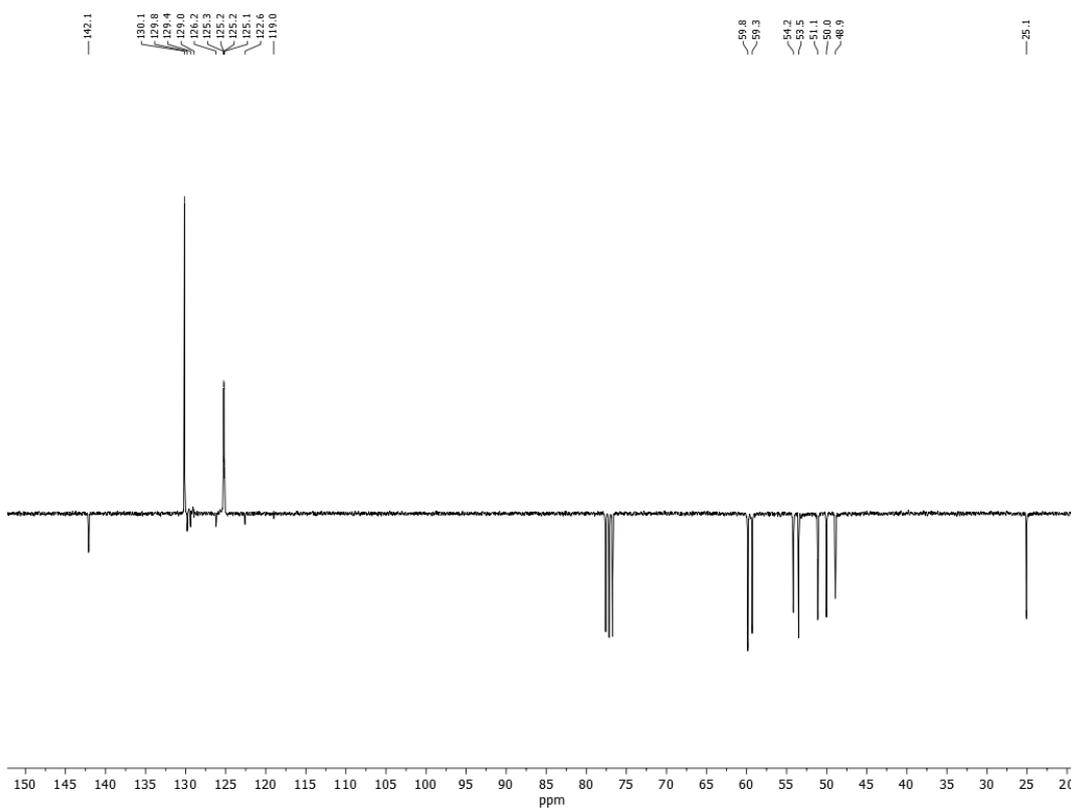**Figure S2B**: ^{13}C{^{1}H} NMR spectrum of compound **3** in CHCl$_3$.
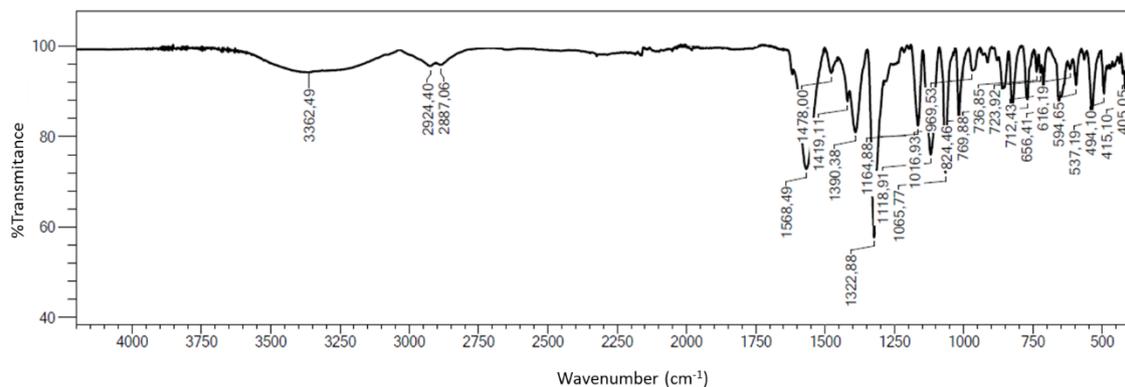
SI.2 - IR spectra of compounds 4 and 5
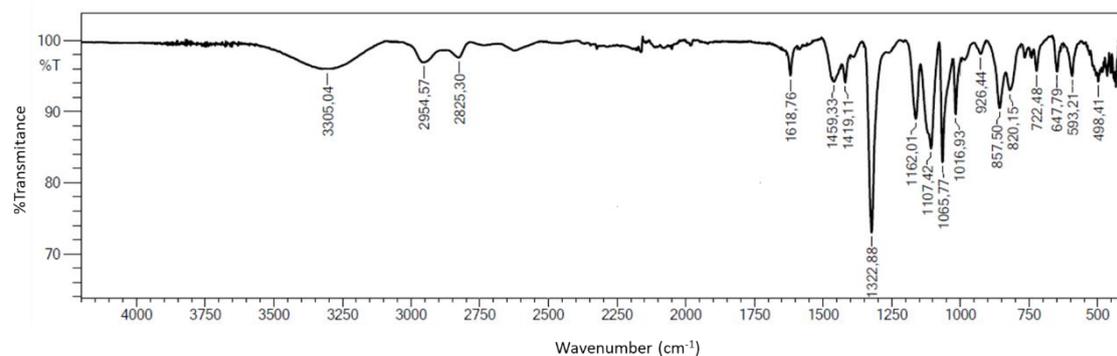

Figure S3: IR spectrum of compound **4**.

Figure S4: IR spectrum of compound **5**.

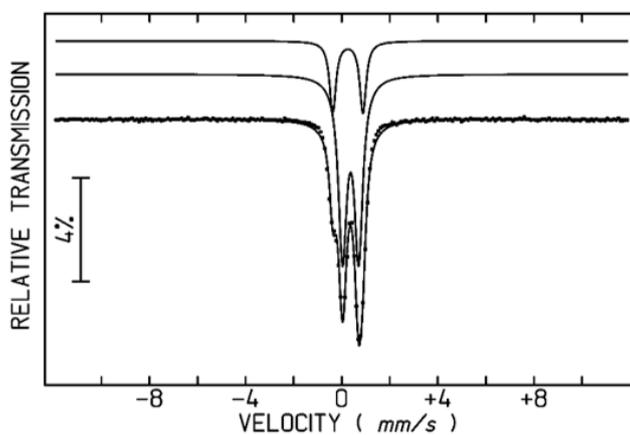## SI.3 - ^{57}Fe Mössbauer spectra and fitting parameters of compound 5

Figure S5. ^{57}Fe Mössbauer spectra, at 80 K, of compound **5**. The line on the experimental points is the sum of two doublets (Table S1), shown slightly shifted for clarity.

Table S1 – Estimated parameters from the ^{57}Fe Mössbauer spectra, at 80 K, of compounds [{H$_2$($^{4\text{-}CF3}$PhCH$_2$)$_2$Cyclam}FeCl$_2$]Cl[7g] and [{(HOCH$_2$CH$_2$)$_2$($^{4\text{-}CF3}$PhCH$_2$)$_2$Cyclam}FeCl$_2$]Cl, **5**.

Sample	Fe species	IS, mm/s	QS mm/s	I
[{H$_2$($^{4\text{-}CF3}$PhCH$_2$)$_2$Cyclam}FeCl$_2$]Cl, prepared in solution[7g]	Fe^{III} (S=5/2)	0.48	0.67	71%
	Fe^{III} (S=1/2)	0.39	1.54	29%
[{H$_2$($^{4\text{-}CF3}$PhCH$_2$)$_2$Cyclam}FeCl$_2$]Cl, prepared in the solid state[7g]	Fe^{III} (S=5/2)	0.48	0.73	75%
	Fe^{III} (S=1/2)	0.37	1.32	25%
[{(HOCH$_2$CH$_2$)$_2$($^{4\text{-}CF3}$PhCH$_2$)$_2$Cyclam}FeCl$_2$]Cl, **5**	Fe^{III} (S=5/2)	0.48	0.67	76%
	Fe^{III} (S=1/2)	0.37	1.26	24%

IS isomer shift relative to metallic α-Fe at 295 K; QS quadrupole splitting. I relative area. Estimated errors are <0.02 mm/s for IS, QS, and < 2% for I

SI.4 - Crystallographic data and refinement details for compounds 2 and 3

Table S2 - Crystal data and details of structure refinement for compounds **2** and **3**.

	2	3
Empirical formula	$C_{34}H_{46}F_6N_4O_4$	$C_{30}H_{42}F_6N_4O_2$
Formula weight	688.75	604.68
Crystal system, space group	Triclinic, P-1	Triclinic, P -1
a, (Å)	5.3622(7)	8.930(1)
b, (Å)	8.688(1)	9.2703(9)
c, (Å)	19.054(2)	9.6657(9)
α, (°)	95.539(8)	91.972(5)
β, (°)	91.382(8)	106.372(6)
γ, (°)	105.270(7)	101.663(5)
Volume (Å^3)	851.19(18)	748.30(13)
Z	1	1
Calculated density (g cm^{-3})	1.344	1.342
Absorption coefficient (mm^{-1})	0.110	0.110
F (000)	364	320
Crystal size (mm)	0.200 x 0.160 x 0.060	0.140 x 0.120 x 0.080
θ range for data collection (°)	1.075 to 25.755	2.207 to 26.467
Limiting indices	-6≤h≤6; -10≤k≤10; -23≤l≤23	-11≤h≤11; -10≤k≤11; -12≤l≤10
Reflections collected/unique	5551/3269 [R_{int} = 0.0456]	6863 / 3093 [R_{int} = 0.0455]
Completeness to θ = 25.242	93.2	99.8
Data/restraints/parameters	3269 / 0 / 218	3093 / 0 / 194
Goodness-of-fit on F^2	1.053	1.077
Final R indices [I > 2σ(I)][a]	R_1 = 0.0993, wR_2 = 0.2686	R_1 = 0.0633, wR_2 = 0.1540
Final R índices (all data)[a]	R_1 = 0.1745, wR_2 = 0.3110	R_1 = 0.0969, wR_2 = 0.1671
Largest diff. peak and hole (e Å^{-3})	0.597 and -0.671	0.616 and -0.528

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

SI.5 - Coatings characterization: FTIR, Optical Imaging, and AFM

FTIR analysis of polyurethane-based coatings under various exposure conditions

The coatings analysed under the various experimental conditions, along with their corresponding designations, are listed in Table S3.

Table S3 - Marine cyclam-based coating surfaces designations for different exposure conditions.

Coating formulation	56 days of exposure to ultrapure water	56 days of exposure to bacterial biofilm formation
PU (control)	PU (control) 56D Water	PU (control) 56D biofilm
PU/Cy	PU/Cy 56D Water	PU/Cy 56D biofilm
PU/CuCy	PU/CuCy 56D Water	PU/CuCy 56D biofilm
PU/FeCy	PU/FeCy 56D Water	PU/FeCy 56D biofilm
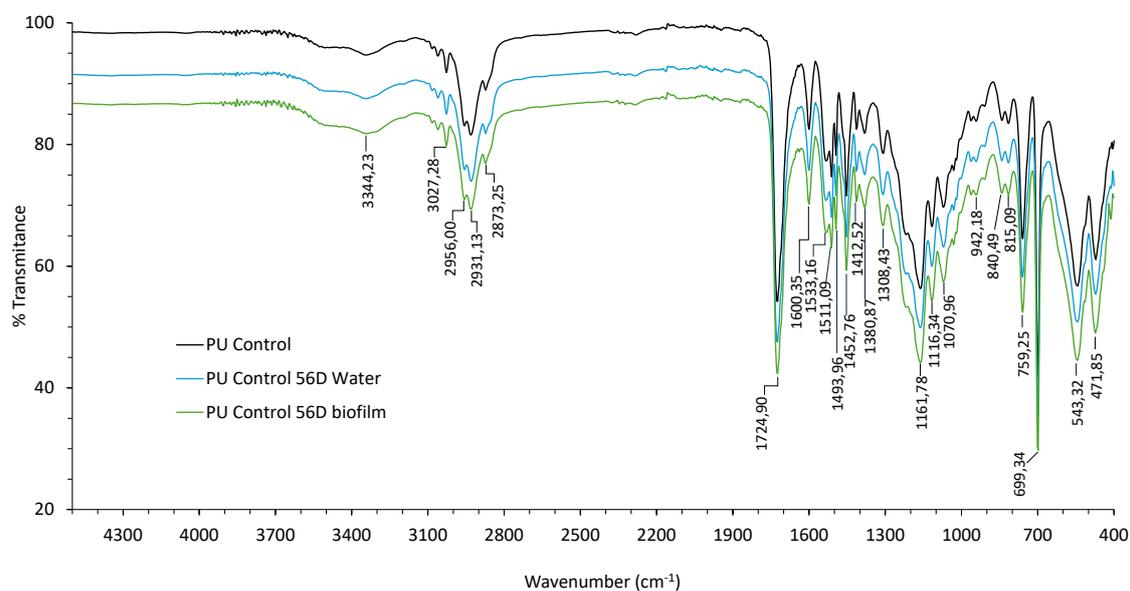
Figure S6: FTIR-ATR spectra of polyurethane commercial coating surfaces (**PU** (control)) before and after 56 days of bacterial biofilm exposure (bioassay, followed by washing).
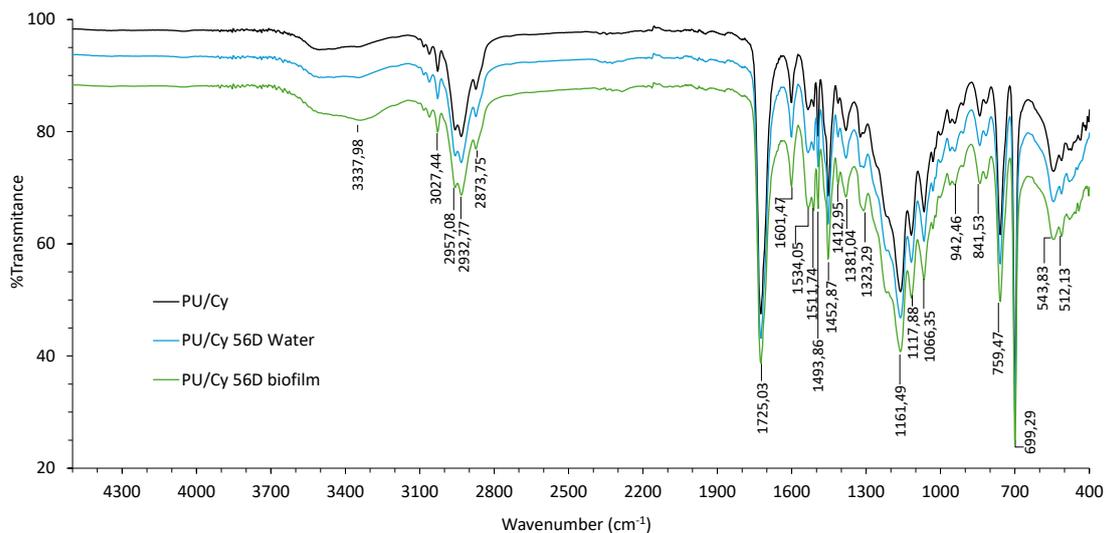
Figure S7: FTIR-ATR spectra of polyurethane coating surfaces modified with cyclam (**PU/Cy**) before and after 56 days of bacterial biofilm exposure (bioassay, followed by washing).
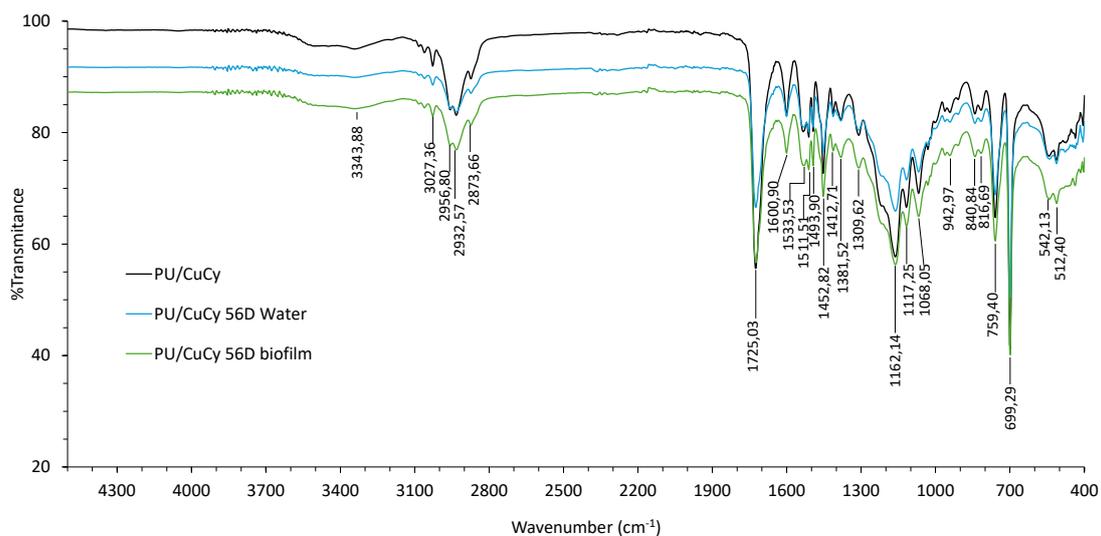
Figure S8: FTIR-ATR spectra of polyurethane coating surfaces modified with cyclam-based Cu(II) complex (**PU/CuCy**) before and after 56 days of bacterial biofilm exposure (bioassay, followed by washing).
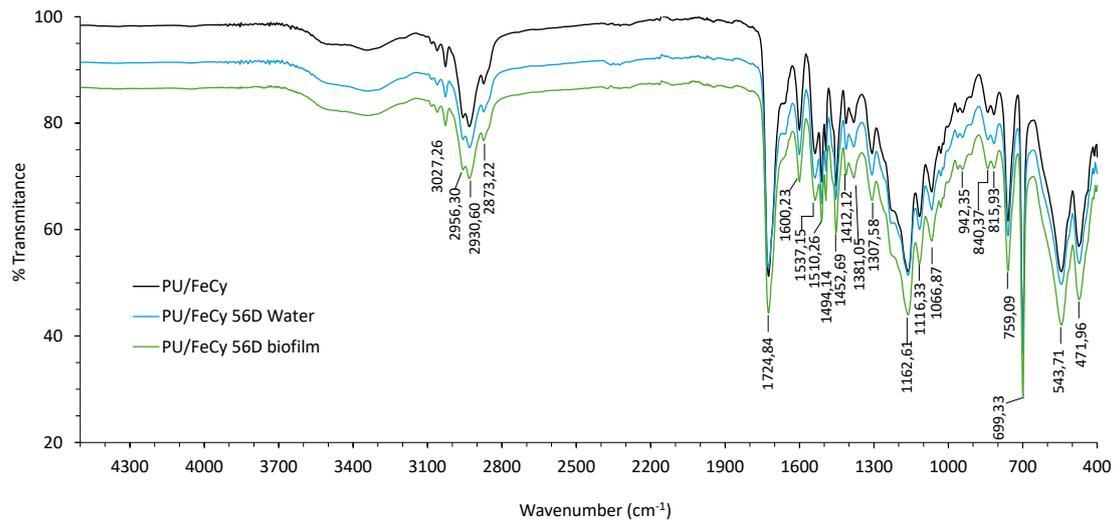
Figure S9: FTIR-ATR spectra of polyurethane coating surfaces modified with cyclam-based Fe(III) complex (**PU/FeCy**) before and after 56 days of bacterial biofilm exposure (bioassay, followed by washing).

Optical Microscopy analysis of polyurethane-based coatings under various exposure conditions

Table S4 - Optical Microscope images of polyurethane (PU)-based coatings after different exposure conditions: **PU** (control), **PU/Cy**, **PU/CuCy,** and **PU/FeCy** surfaces - reference samples; after 56 days of water immersion; and after 56 days of bacterial exposure (biofilm formation bioassay), followed by washing. Scale bars are included in each image and correspond to 50 μm.

Polyurethane-based coatings	Reference Surface (free of water/biofilm exposure)	56 days submerged in water	56 days of bacterial biofilm exposure
PU (control)			
PU/Cy			
PU/CuCy			
PU/FeCy			
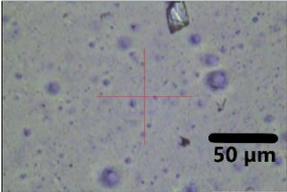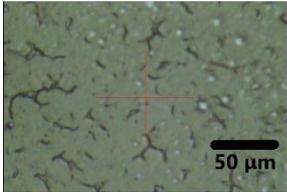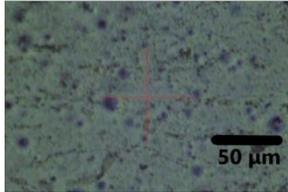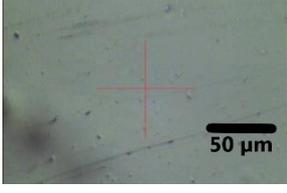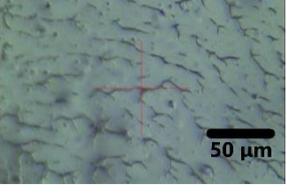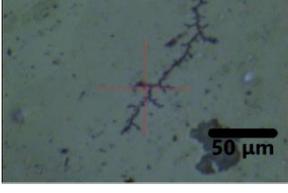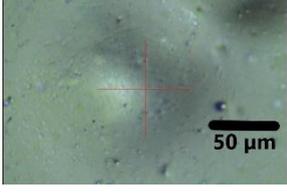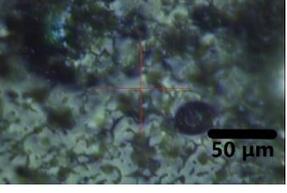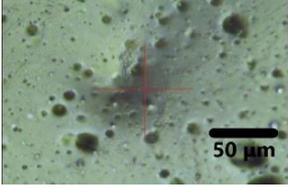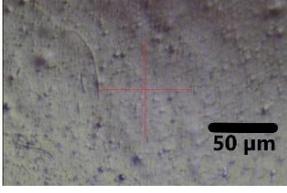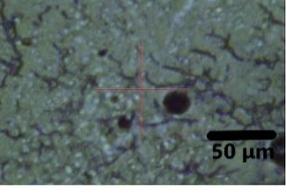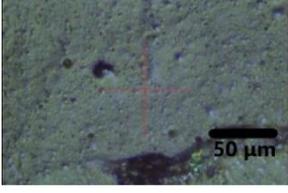
Table S5 - Two-dimensional and three-dimensional AFM images of polyurethane (PU)-based coatings after different exposure conditions: **PU** (control), **PU/Cy**, **PU/CuCy,** and **PU/FeCy** surfaces - reference samples; after 56 days of water immersion; and after 56 days of bacterial biofilm exposure (bioassay), followed by washing. All images correspond to a 5 × 5 μm² surface area.

PU-based coating formulations	Reference Surface (free of water/biofilm exposure)	56 days submerged in water	56 days of bacterial biofilm exposure
PU (control)			
PU/Cy			
PU/CuCy			

Table S5 (continued)

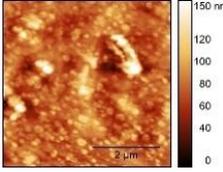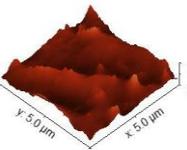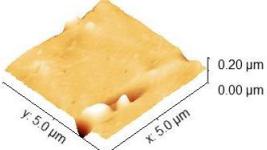| PU-based coating formulations	Reference Surface (free of water/biofilm exposure)	56 days submerged in water	56 days of bacterial biofilm exposure
PU/FeCy			
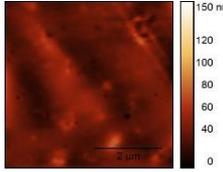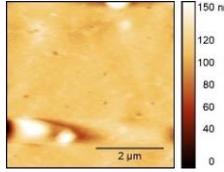
Atomic Force Microscopy analysis of polyurethane-based coatings under various exposure conditions

Table S6 - Atomic Force Microscopy obtained roughness parameters ($R_a{}^1$ and $R_q{}^2$) for polyurethane (PU)-based coatings, **PU** (control), **PU/Cy**, **PU/CuCy**, and **PU/FeCy** surfaces - reference samples; after 56 days of water immersion; and after 56 days of bioassay (biofilm formation), followed by washing.
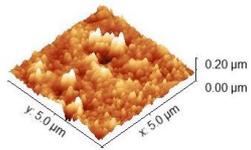
Polyurethane-based coating	Reference Surface (free of water/biofilm exposure)	56 days submerged in water	56 days of bacterial biofilm exposure
PU (control)	$R_a = 12.70 \pm 6.11$ nm $R_q = 15.69 \pm 7.11$ nm	$R_a = 9.34 \pm 2.70$ nm $R_q = 12.25 \pm 4.02$ nm	$R_a = 21.16 \pm 5.30$ nm $R_q = 27.82 \pm 9.35$ nm
PU/Cy	$R_a = 1.32 \pm 0.52$ nm $R_q = 2.82 \pm 1.45$ nm	$R_a = 6.83 \pm 6.76$ nm $R_q = 10.58 \pm 10.33$ nm	$R_a = 11.58 \pm 1.07$ nm $R_q = 14.75 \pm 1.43$ nm
PU/CuCy	$R_a = 7.62 \pm 4.27$ nm $R_q = 10.04 \pm 4.71$ nm	$R_a = 13.71 \pm 3.17$ nm $R_q = 15.75 \pm 5.30$ nm	$R_a = 24.13 \pm 1.78$ nm $R_q = 30.65 \pm 1.46$ nm
PU/FeCy	$R_a = 14.57 \pm 6.12$ nm $R_q = 18.49 \pm 5.58$ nm	$R_a = 7.52 \pm 1.31$ nm $R_q = 9.46 \pm 1.75$ nm	$R_a = 13.78 \pm 1.31$ nm $R_q = 17.72 \pm 1.40$ nm

[1] R_a is the arithmetical mean roughness and is defined according to ISO 4287 as the arithmetic average of the absolute values of the profile height deviations from the mean line over the evaluation length.

[2] R_q is the square root of the mean of the squared profile height deviations from the mean line over the evaluation length.