



Substrate/solvent dependent THPP non-covalent functionalization of polyester support: A comparative physicochemical study with mercury readout

Cristiana Longo^{a,*}, Ivana Di Bari^{a,**}, Giusy Curcuruto^b, Grazia M.L. Messina^c, Sabrina C. Carroccio^b, Emanuela T.A. Spina^b, Giuseppe D'Arrigo^a, Luigi Fabiano^c, Antonella Sciuto^{a,d}

^a Consiglio Nazionale Delle Ricerche, Istituto per la Microelettronica e Microsistemi (CNR-IMM), Catania, Italy

^b Consiglio Nazionale Delle Ricerche, Istituto per i Polimeri, Compositi e Biomateriali (CNR-IPCB), Catania, Italy

^c Università Degli Studi di Catania Dipartimento di Scienze Chimiche (DSC-UNICT), Catania, Italy

^d Centro Siciliano di Fisica Nucleare e Struttura Della Materia (CSFNSM), Catania, Italy

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ABSTRACT

The non-covalent immobilization of porphyrins onto polymeric substrates introduces complex solvent-substrate interplay governing supramolecular organization. In this comparative physicochemical investigation, synergistic effects between these factors were screened by depositing tetrakis(4-hydroxyphenyl) porphyrin (THPP) onto commercially available polyester sheets. Polyethylene terephthalate (PET), polylactic acid (PLA), and PLA/PET multilayer were employed as solid supports, while ethyl acetate (AcOEt) or a binary ethanol/diethyl ether (EtOH/Et₂O) mixture were selected as solvent system for porphyrin dispersion prior to deposition. The first is chosen as good solvent favouring the optimal solubilization of THPP, while the second one leverages the “good-bad” solvent effect, promoting controlled aggregation.

A combination of analytical techniques, including attenuated total reflectance infrared (ATR-IR) and UV-vis spectroscopy, confocal dark-field microscopy, atomic force microscopy (AFM), wettability investigation, surface free energy (SFE) measurements, and Variable Angle Spectroscopic Ellipsometry (VASE), was employed to elucidate both morphological and chemical characteristics at the interface. These structural and interfacial parameters critically dictate porphyrin aggregation mode and binding site accessibility.

The well-known selectivity of THPP for mercury ions was assessed as functional readout to compare the porphyrin response in the investigated substrate-solvent combinations. The homogeneous aggregate's distribution and smaller size found for THPP from EtOH/Et₂O on PET made this system the most responsive, allowing also to evaluate its qualitative response toward other dications.

The structure-property correlations presented in this study offer valuable design insights to guide the scalable non-covalent functionalization of porphyrin-polymer platform for a wide range of potential applications.

1. Introduction

Over the last decades porphyrins immobilization onto solid supports has received increasing attention to create active surfaces, with the aim to extend their remarkable photophysical and photochemical properties on solid-state platforms, bypassing potential complications associated with liquid phase [1–6] and enabling their integration into practical

devices.

Their unique characteristics and ability to selectively interact with several molecules made these molecules among the most studied functional species in materials science, with applicability across a wide range of fields such as biology, photophysics, photochemistry, photovoltaics, data storage, molecular recognition, catalysis and sensing [7–16].

When transferred from solution to an interface, however, porphyrin

* Corresponding author.

** Corresponding author.

E-mail addresses: cristianalongo@cnr.it (C. Longo), ivana.dibari@cnr.it, ivanadibari@hotmail.it (I. Di Bari).

¹ These authors contributed equally.

properties can change substantially and, consequently, the study and the control of parameters governing functionalization procedures becomes crucial for tuning the behaviour of the resulting platforms [17]. For this reason, to ensure robust attachment and maintain porphyrins in a more isolated or monomeric state, early immobilization approaches favoured covalent binding [18,19]. These efficient strategies always require multistep syntheses, chemical derivatization, and purification procedures, often involving hazardous solvents.

Non-covalent functionalization offers a simpler and more sustainable route for rapid and straightforward material preparation, without the need for complex synthetic procedures. However, for functional materials this method typically relies on charged porphyrins, pre-modified substrates or dispersing matrices [20–24], which may limit scalability.

Direct deposition from porphyrin solutions onto commercially available solid supports could represent an attractive alternative, overcoming preliminary modification steps. This approach is fast, low-cost, and scalable, but introduces significant physicochemical complexity: in such systems, the final material properties are governed by molecular self-organization, interfacial confinement, and solvent-substrate chemistry [25,26].

The π - π interactions, coordination bonding, hydrogen bonding, donor-acceptor interactions, van der Waals interactions, electrostatic and hydrophobic interactions collectively govern the assembly upon deposition, leading to aggregates with different orientations, shapes, sizes and nature [27,28]. Among these, the π - π interactions are responsible for different aggregation types: in H-type aggregation porphyrins stack face-to-face, causing a blue (hypsochromic) shift in Soret band compared to the monomeric form; in J-type aggregation, molecules align edge-to-edge, producing a red (bathochromic) shift [29].

In addition to intermolecular interactions, the balance between adsorbate-adsorbate and adsorbate-substrate interactions is a key factor in directing the formation of two- and three-dimensional porphyrin networks, as widely observed on metallic or semiconductor surfaces, highlighting the crucial role of substrate nature [27].

Morphological control can be further achieved through the choice of deposition and self-assembly strategies, including drop-casting, dip-coating, and spin-coating [25]. Moreover, methods such as ionic self-assembly, re-precipitation, and “good-bad” solvent protocols enable the formation of a wide variety of nanostructures, including nanotubes, nanofibers, nanosheets, nanorods, nanoprisms, and nanospheres [30, 31]. In this context, the solvent system is determinant, as its properties of polarity, hydrogen-bonding ability, ionic strength, temperature and pH [26,30–35], as well as the aging time [36], strongly influence molecular organization and surface morphology.

As a result, the features of the functionalized surface are not determined solely by the chosen porphyrin itself and its behaviour, but rather by a complex relationship among intermolecular interactions, solute-solvent effects, evaporation rates, solution viscosity, substrate surface energy, and interfacial phenomena.

Herein, we present a comparative physicochemical study of polyester supports non-covalently functionalized with tetrakis(4-hydroxyphenyl) porphyrin (THPP) via spin coating, by using two solvent systems with different and peculiar physical properties: ethyl acetate (AcOEt) and a 1:1 mixture of ethanol and diethyl ether (EtOH:Et₂O) as a “good-bad” solvent system [32].

In line with the growing interest in the development of low-cost and more sustainable functional materials, poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), and their assembly (PLA/PET) were selected as underlying rigid and transparent substrates for THPP deposition. These materials were chosen for their commercial availability, recyclable/biodegradable nature, and representative chemical differences within common polyesters. Specifically, PET is an aromatic polyester that exhibits high chemical/solvent resistance, while PLA is an aliphatic biobased and biodegradable polyester [37–39].

These differences, together with the use of THPP dispersions in different solvent systems, were exploited to assess how substrate-solvent

interactions influence THPP deposition and, consequently, its supramolecular organization on the surface, ultimately impacting the binding site accessibility. Within this framework, Hg(II) was employed as a functional probe, taking advantage of the well-known ability of THPP to selectively complex this metal ion with high binding constants and a pronounced spectral response [23]. Upon coordination, the molecular symmetry increases, leading to characteristic variations in the Soret and Q-bands associated with π - π^* electronic transitions within the porphyrin scaffold [40–42]. Due to its relatively large ionic radius, Hg(II) cannot fit into the porphyrin core to form planar metalloporphyrins; instead, it sits on the top of the molecules [43,44].

The interplay between interfacial chemistry of the selected polyesters and deposition conditions was investigated through UV-vis and Attenuated total reflectance Fourier-transform infrared (ATR-IR) spectroscopies, confocal dark-field microscopy, Atomic Force Microscopy (AFM), Surface Free Energy (SFE) measurements and Variable Angle Spectroscopic Ellipsometry (VASE). To the best of our knowledge, comprehensive comparative studies on combined solvent-substrate effect of non-covalently functionalized commercial polyester remain limited; therefore, this work provides useful insights for the rational design of future porphyrin-polymer based functional platforms.

2. Experimental

2.1. Materials

Commercial PET sheets were supplied by Buffetti S.p.a., commercial PLA sheets and pellets (4060D, MW = 106,226 D) were acquired from MP3 S.r.l. and NatureWorks LLC, respectively. Tetrahydrofuran (THF), absolute ethyl alcohol, diethyl ether, ethyl acetate, formamide, glycerol, Mercury(II)trifluoroacetate and salts of Cu²⁺, Co²⁺, Ni²⁺, Pb²⁺ and Mn²⁺ were purchased from Merck and used without any further purification. A Milli-Q water purification system was used to produce deionized water. Tetrakis(p-hydroxyphenyl)-porphyrin was prepared by the method described by Little et al. [45] starting from pyrrole and p-acetoxymethylbenzaldehyde in boiling propionic acid.

2.2. Instrumentation

UV-vis absorption spectra were acquired utilizing a JASCO V-750 spectrophotometer (JASCO Corporation, Tokyo, Japan).

Ultrasonic treatment was carried out employing an ARGO-LAB AU 32 Ultrasonic Cleaner Bath (Argo Lab Ltd, London, England).

Thermogravimetric analyses (TGA) of both PLA sheet and PLA pellets were performed using a TA Instruments Q500 thermogravimetric apparatus under a nitrogen flow (gas flow: 40 ml min⁻¹ at 10 °C min⁻¹ heating rate, up to 800 °C).

Thin films of PLA and THPP were obtained through spin-coating techniques using a KLM spin coater (Schaefer Technologie GmbH, Langen, Hessen, Germany).

Surface morphological analysis at micrometre scale were performed by a SENSOFAR S Neox Confocal Microscope (SENSOFAR's, Terrassa, Barcelona, Spain) with a 532 nm green light excitation source to acquire images over a scan area of 140 μ m $\times$ 115 μ m.

Morphological characterization at the nanometre scale was carried out by AFM using a Multimode Nanoscope IIIA (Digital Instruments, Santa Barbara, CA). Image processing and surface roughness analysis were conducted using the Nanoscope software. Measurements were performed in tapping mode with silicon tapping-mode probes (Tap300-G, BudgetSensors, Bulgaria), featuring a nominal resonant frequency of 300 kHz, a force constant of 40 N m⁻¹, and a tip radius below 10 nm. For each sample, areas of 2 μ m $\times$ 2 μ m was scanned in different regions of the substrate surface. Height images were recorded with a resolution of 512 $\times$ 512 pixels.

ATR-FTIR spectroscopy measurements were collected by using an iS50 FT-IR Thermo Scientific spectrometer (Thermo Fisher Scientific

Inc., Waltham, MA, USA).

The OCA30 instrument (Dataphysics, Filderstadt, Germany) was used at 25 °C and under 65% relative humidity for contact angle investigation. The measurements were carried out on each substrate, about 2–4 μL solvent drops were applied on different zones of each sample surface and the static contact angle was measured on both sides of the two-dimensional projection of the droplet by digital image analysis. At least three measurements were made for each sample, and values were averaged.

THPP thin films deposited on Silicon wafer, used as reference substrates, were characterized at room temperature using an M2000 ellipsometer (rotating compensator ellipsometer, J.A. Woollam Co., Inc.). Measurements were carried out over the spectral range of 350–800 nm with a wavelength step of approximately 1.5 nm, at angles of incidence of 65° and 75°. The acquired data were analysed using the WVASE32 software package.

Ellipsometry measures the complex ratio of the Fresnel reflection coefficients R_p and R_s , corresponding to p- and s-polarized light reflected from the sample surface. The experimental data are expressed in terms of the ellipsometric parameters Ψ and Δ , according to the relation:

$$P = R_p/R_s = \tan \Psi e^{i\Delta} \quad (1)$$

VASE is an indirect technique used to determine the optical constants and thickness of thin films through regression analysis of experimental data against a theoretical model. The quality of the fit is assessed by a merit function, a positive parameter that approaches zero as the agreement between experimental and calculated data improves. Herein, porphyrin thin film deposited on a silicon substrate were analysed using a Gaussian oscillator model to describe the complex dielectric function of the film. In particular, the imaginary part of the dielectric function (ϵ_2) was parameterized as a sum of three Gaussian oscillators, each associated with an electronic transition. One oscillator, centred at approximately 420 nm, was introduced to reproduce the intense Soret (B) band, while two additional oscillators in the visible range were used to account for the Q-band transitions. The fitting procedure involved the simultaneous optimization of the oscillator amplitudes, central energies, and broadenings, together with the film thickness, in order to minimize the mean square error between the calculated and experimental ellipsometric parameters (Ψ and Δ).

2.3. Platforms preparation

2.3.1. Preparation of polymeric substrates

In order to investigate the porphyrin arrangements behaviour onto polyester substrates from different solvents, we selected commercially available plastic sheets, PET and PLA, commonly used in everyday applications, as polymeric supports. A substrate incorporating both polymers, PET as support and PLA deposited on PET as a thin film, was tested to assess any synergistic or surface-mediated effects stemming from their distinct chemical structures and resultant properties.

PET and PLA squares with dimensions of $2.5 \times 2.5 \text{ cm}^2$ were cut from their respective sheets, cleaned with EtOH, and dried under a nitrogen flow. PET/PLA multilayer was prepared starting by a PLA solution obtained dissolving 1 mg of PLA pellets in 30 mL of THF and using 3 cycles of temperature-assisted sonication at 47 °C. Each ultrasound treatment cycle consisted of 6 min of sonication followed by 10 min of cooling, due to THF high volatility. 200 μL of PLA solution was used at 4 °C to form a polymeric layer onto a cleaned PET square via spin coating technique, employing an acceleration to 200 rps in 3 s, constant rotation for 180 s, and deceleration to 100 rps over 3 s followed by 60 s rotation. The sample was left overnight in air for complete drying.

2.3.2. THPP deposition on PET, PLA and PLA/PET substrates

Two different THPP solutions, at concentration 5 mM, were obtained using two solvent systems: pure AcOEt and EtOH:Et₂O mixture (1:1

ratio). For the mixed solvent system, THPP was first dissolved in EtOH and then Et₂O was rapidly added drop by drop. The resulting solution was left to age for 24 h before use. 35 μL of each porphyrin solution were deposited by spin coating on PLA, on PET and on PLA/PET substrates following Scheme 1. Spinning conditions were adopted as follows: acceleration to 100 rps over 5 s, 30 s constant speed, deceleration to 50 rps over 3 s, and 30 s final rotation. Samples were dried overnight in the dark. An additional PLA/PET sample was treated with 35 μL of AcOEt by spin coating under the same spinning conditions used for THPP deposition, prior to depositing 35 μL of THPP from the EtOH:Et₂O mixture. All obtained systems are shown in Scheme 1A, B, C and D.

2.4. Measurements procedure

Samples were cut with a width of 0.9 cm to insert them into commercial PMMA cuvettes (1 cm path length). Optical response was evaluated by immersing functionalized systems in aqueous solutions at 25 ppm in Hg²⁺ by a custom 3D-printed cup with a central groove, ensuring a fixed position (Scheme 1E). Spectra were acquired over time for 60 min by an UV-visible spectrophotometer to monitor changes in porphyrin absorption bands.

3. Results and discussion

3.1. Platforms characterization

3.1.1. Polymeric substrates characterization

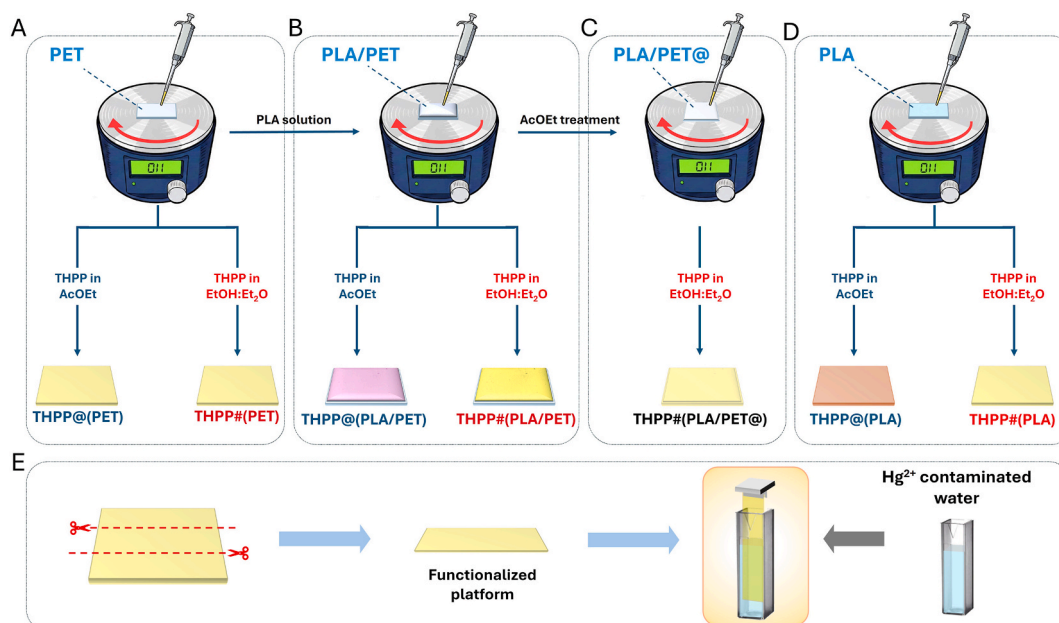
The characterization of the polymeric supports was performed by TGA, UV-vis and ATR-FTIR spectroscopy, confocal microscopy, AFM, wettability and SFE measurements.

Thermal analysis performed on PLA matrices, reported in Fig. S1, demonstrate that PLA sheet and pellets possess the same thermogravimetric profile.

UV-visible absorption spectra of PET, PLA and PLA/PET (Fig. S2), recorded after immersion for 20 min in deionized water, assess their optical transparency and no spectral overlap with characteristic THPP absorption bands exploited as monitoring signals.

Confocal microscopy analysis revealed distinct topographical features that highlight differences in polymeric substrate surfaces. PET and PLA exhibit homogeneous morphologies, consistent with the commercial extrusion process (Fig. 1A and C). In contrast, PLA/PET displays a distinct morphological organization. Spin-coating deposition of PLA onto PET resulted in a heterogeneous distribution of concurrent depressions and protrusions of variable size and irregular shape, likely arising from PLA chain arrangements relative to PET's exposed interfacial groups, visible in Fig. 1B (also confirmed by AFM measurements reported in Fig. S3A).

Morphological changes observed in the composite are further supported by ATR-FTIR analysis. Fig. 1D shows the spectra of PET, PLA, and the PLA/PET. The latter displays distinctive features reflecting both the chemical structures of the individual polymers, as evidenced by the characteristic IR signals for PET [46–48] and PLA [49,50], and the effects of processing and polymers organization in the composite. PET shows well-defined and relatively intense bands associated with its aromatic polyester structure: the carbonyl stretching vibration of the ester group appears at $\sim 1713 \text{ cm}^{-1}$, while strong C–O–C stretching bands are observed at $\sim 1245 \text{ cm}^{-1}$ (asymmetric), 1120 and 1097 cm^{-1} (symmetric), accompanied by weaker skeletal and aromatic-coupled vibrations below 1080 cm^{-1} . Additional signals at 1577 and 1504 cm^{-1} correspond to aromatic C=C stretching, and a group of signals in the range between $980 \div 840 \text{ cm}^{-1}$ is attributable to out-of-plane bending of aromatic C–H. A last characteristic band is observed at 722 cm^{-1} relative to the interaction of the polar ester group and benzene ring. PLA displays a higher C=O stretching frequency at $\sim 1745 \text{ cm}^{-1}$ due to its aliphatic ester structure, with the main asymmetric C–O–C stretching at 1262 cm^{-1} and a broader symmetric stretching contribution at 1210 and 1180 cm^{-1} ,



Scheme 1. Schematic illustration of sample labelling and preparation pathway onto PET, PLA and PLA/PET substrates.

@ denotes AcOEt; # denotes EtOH:Et₂O mixture; THPP@ denotes THPP spin-coating deposition from @ solution; THPP# denotes THPP spin-coating deposition from #.

Panel A) shows the preparation of THPP@(PET) and THPP#(PET).

Panel B) illustrates the preparation of THPP@(PLA/PET) and THPP#(PLA/PET).

Panel C) illustrates PLA/PET substrate pre-treated with @ before THPP#, to obtain THPP#(PLA/PET@).

Panel D) shows the preparation of THPP@(PLA) and THPP#(PLA).

Panel E) depicts the final step where cut sample strips are used for analysis.

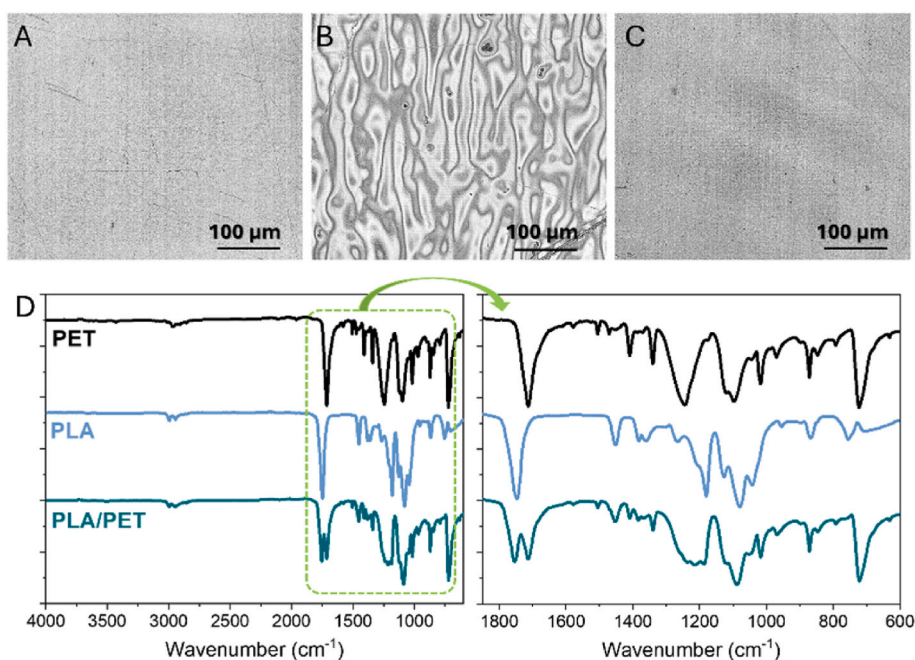


Fig. 1. Morphological and spectroscopic characterization of pristine substrates. A), B), C) Grayscale confocal microscopy images of PET, PLA/PET and PLA, respectively. D) ATR-FTIR spectra of substrates; the green dashed box shows a magnified view of the fingerprint region (1850-600 cm⁻¹).

followed by multi-peaked band (1127, 1080 and 1042 cm⁻¹) assigned to C-O-C bending and backbone skeletal vibrations. Characteristic CH₃ deformation modes appear at 1454 cm⁻¹ (asymmetric bending), 1382 and 1360 cm⁻¹ (scissoring). A weaker band at ~755 cm⁻¹ is observed, attributable to the contemporary contributes of CH₃ rocking of the pendant methyl groups along the backbone and C=O scissoring.

In the PLA/PET composite spectrum, the C=O stretching bands of PET and PLA make a double-peak profile, but the PLA band shifts to 1754 cm⁻¹. The PLA-specific ester band relative to C-O-C symmetric stretching shifts to higher wavenumbers of 1216 and 1185 cm⁻¹, respectively, as well as the bending contributes, which move to 1088 and 1047 cm⁻¹, in contrast to the PET signal at 1245 cm⁻¹ which in this

case appears at 1239 cm^{-1} . The weak CH_3 scissoring band at $\sim 755\text{ cm}^{-1}$ becomes undetectable, due to overlapping with PET signal in the closed region and because of the lower PLA thickness in the film respect to the bulk. PLA/PET composite reveals a spectrum largely dominated by PET-related signals, which are substantially unchanged, while differences in the relative intensity and position of several characteristic bands of PLA suggest distinct conformational arrangements and a decreased chain mobility of this polyester in the film. The observed spectral differences are consistent not only with the amorphous nature of the spin-coated PLA film but also provide clear insight into the effects of physical superposition, film geometry, substrate contribution and chemical interaction between the two polymers.

Additional insights into the polymeric substrate surfaces were gained through wettability investigation, which demonstrates the lower water contact angle of PLA compared to PET (Table 1).

Furthermore, surface free energy (SFE) measurements were performed using Milli-Q water, formamide, and glycerol to apply acid-base theory. The SFE was estimated by measuring the static contact angle using the three different probe liquids and applying the combining rules proposed by van Oss-Chaudhury-Good [51]. The results indicate very similar total surface free energy values for all the analysed polymeric substrates.

Nevertheless, a more detailed analysis of the SFE components, associated with the apolar and acid-base contributions, reveals some significant differences among the samples. As shown in Fig. 2, the Lifshitz-van der Waals component, which is related to the apolar character of the surface, is slightly higher for PLA/PET. The SFE contribution values and their relative standard deviations are reported in Table S1 for each substrate.

The polar acid-base (AB) contribution of the SFE, associated with the Lewis electron-acceptor (acid) and electron-donor (base) interactions, also exhibits variations. In particular, the acid component is very low for all the investigated substrates, whereas a noticeable difference is observed in the base component. Specifically, PLA shows a significantly higher base component compared to the other polymers, with a value more than twice as high. This characteristic is much less pronounced for PLA deposited on PET, indicating a partial reduction of the Lewis base character upon deposition on PET, confirming a different polymeric chains conformational arrangement.

3.1.2. Solvent effect on pristine substrates

The use of different solvents, as predictable, impacts on the chemical arrangement and consequently on the polymeric surface morphology. This effect was investigated by depositing $35\text{ }\mu\text{L}$ of pure AcOEt or $35\text{ }\mu\text{L}$ of EtOH:Et₂O mixture on pristine substrates via spin coating following the same procedure described in section 2.2.3 for the THPP deposition.

Grayscale confocal microscopy images in Fig. 3A and B and C showed that, when treated with EtOH:Et₂O mixture, all polymeric surfaces exhibited remarkable stability, preserving patterns comparable to those of untreated surfaces shown in Fig. 1A, B and C. In contrast, treatment with AcOEt altered the surfaces of PLA-containing samples, while leaving PET surface unaffected (Fig. 3A', B' and C'). Specifically, after AcOEt exposure, in PLA/PET, PLA islands coalesced into a quasi-continuous and smoother PLA film, while the initially flat PLA sheet exhibited a more textured topography, which was evident even to the naked eye, as the sample became opaque compared to the untreated one. Fig. S3 presents AFM images of the same samples, highlighting the

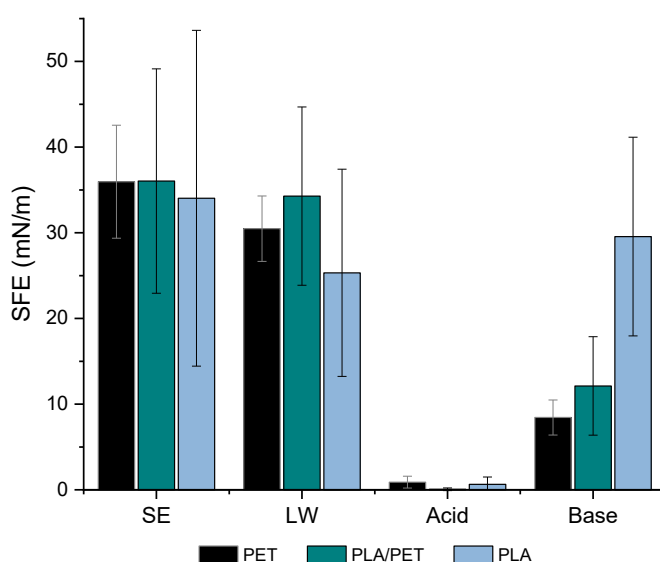


Fig. 2. Surface free energy (SFE) for PET, PLA/PET and PLA. SE, surface energy; LW, Lifshitz van der Waals term; Acid/Base polar terms: acid, Lewis electron-acceptor term; base, Lewis electron-donor term. Error bars represent the standard deviation of triplicate measurements.

changes induced at the nanometric scale by solvent treatments on PLA-containing samples.

ATR-FTIR spectra, reported in Fig. 3D and E, show that PLA as well as the composite is affected by AcOEt treatment, reflecting the interaction of this solvent with the PLA phase. In the neat PLA, the intensity of the carbonyl stretching band at 1745 cm^{-1} decreases after treatment, accompanied by a systematic attenuation of the C-O-C stretching bands at 1262 , 1180 cm^{-1} and bending at 1080 cm^{-1} . In particular, the band centred at 1080 cm^{-1} also shifts to lower wavenumbers (1074 cm^{-1}), while the signal at 1042 cm^{-1} increases in intensity and shifts to 1039 cm^{-1} . Similar solvent-induced spectral modifications have been previously reported by Paragkumar Thanki et al. [50], who associated these changes with conformational restrictions of C-O-C segments in PLA, indicative of more closely packed polymer chains.

In the PLA/PET composite, PET-related absorptions at 1713 cm^{-1} and 1239 cm^{-1} appear relatively enhanced after treatment. Since PET is not affected by AcOEt, this behaviour is attributed to partial thinning of the PLA overlayer induced by the solvent treatment, which increases the relative contribution of the underlying PET phase within the ATR probing depth. Concurrently, the PLA-related bands at 1754 , 1185 , 1088 , and 1047 cm^{-1} decrease in intensity, mirroring the conformational stiffening and the increased segmental packing observed in neat PLA. Therefore, morphological and spectroscopic changes observed after solvent treatment underscore the critical role of THPP solvent selection in determining substrate properties during the functionalization step.

3.1.3. THPP functionalized platforms characterization

THPP functionalized platforms were fabricated by depositing porphyrin onto polymeric supports using AcOEt (@) and an EtOH:Et₂O mixture (1:1, v:v) (#) as solvent systems (see Scheme 1A, B, C and D).

AcOEt and EtOH were selected as good solvents for THPP solubilization, due to their ability to establish favourable solute-solvent interactions. Particularly, AcOEt, with its relatively low boiling point and low viscosity, enables rapid solvent evaporation and the formation of homogeneous, continuous film during spin-coating deposition.

The EtOH:Et₂O mixture combines the polar character of EtOH, which favours THPP solubility, with the lower polarity of Et₂O, acting as poorer solvent. This induces a typical “good-bad” solvent effect, widely used to achieve controlled aggregation of porphyrin macrocycles: by

Table 1

Contact angle average values and relative standard deviations for PET, PLA/PET and PLA substrates.

Substrates	WCA ($\theta^\circ \pm \text{s. d.}$)
PET	78.3 ± 1.8
PLA/PET	74.3 ± 1.9
PLA	58.0 ± 4.4

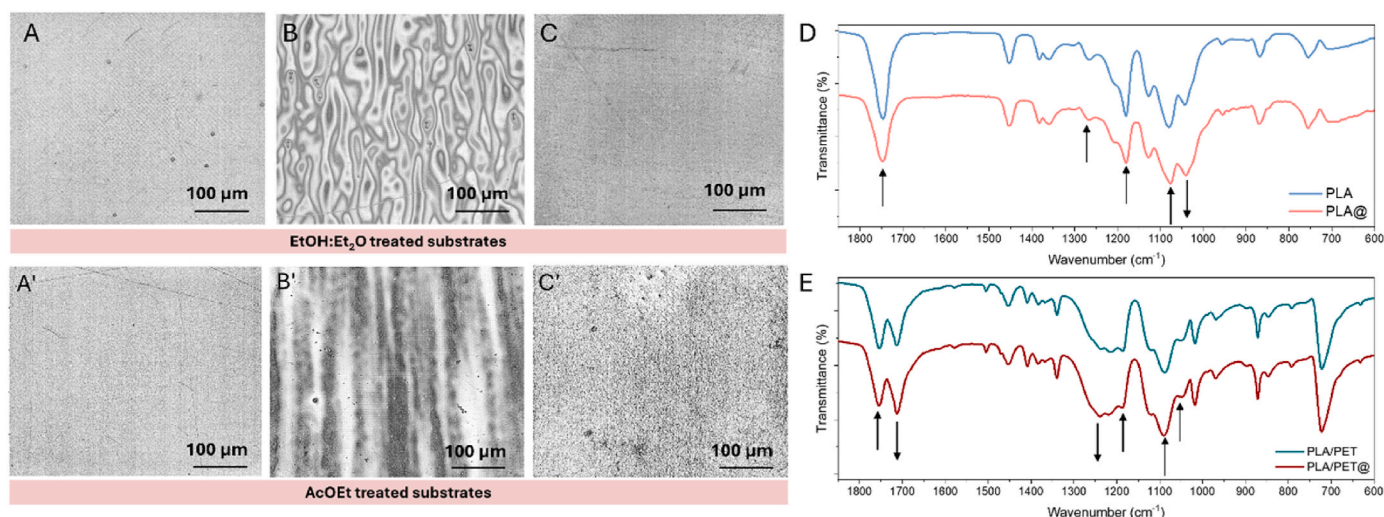


Fig. 3. On the left, morphological characterization of solvents treated substrates. Grayscale confocal microscopy images of polymeric substrates treated with EtOH:Et₂O: A) PET#, B) PLA/PET#, C) PLA#; and treated with AcOEt: A') PET@, B') PLA/PET@, C') PLA@. On the right, ATR-FTIR spectra comparison (1850-600 cm⁻¹) of PLA and PET before and after treatment with AcOEt: D) PLA and PLA@, E) PLA/PET and PLA/PET@.

dissolving THPP in the good solvent and then adding a bad solvent, solubility decreases progressively, enhancing intermolecular interactions between porphyrin rings and triggering formation of aggregated supramolecular structures [31,32]. In a previous study, authors investigated the 1:9 (v/v) EtOH:Et₂O as preliminary conditions for THPP deposition onto PLA/PET, as starting point for a non-covalent functionalization approach [52]. In the present study, the 1:1 (v/v) EtOH:Et₂O ratio was selected as optimal condition for the most uniform and continuous substrate covering. Collected pictures of platforms, obtained by screening different “good-bad” ratios for THPP deposition on PLA/PET, are reported in Fig. S4.

Fig. 4A shows that THPP@(PET), THPP#(PET), THPP#(PLA/PET),

and THPP#(PLA) appear yellow, while THPP@(PLA/PET) exhibited a salmon hue and THPP@(PLA) is pink. The samples colour appearance, already indicative of different homo- and heteromolecular interactions [29], was investigated by UV-vis spectroscopy, reported in Fig. 4D, E and F. To ensure consistent and reproducible positioning of the platforms during the measurements, minimizing potential scattering effects, platforms were centrally fixed in the cuvette using the custom 3D-printed cup with a central groove (Scheme 1E and Fig. 4B). No significant variations were observed in the overlapping UV-vis spectra of all the systems after 1 min and 20 min of immersion in water (Fig. S5).

The spectrum of the THPP solution in EtOH (Fig. 4C), reported just for comparison, shows the typical monomeric profile with a sharp Soret

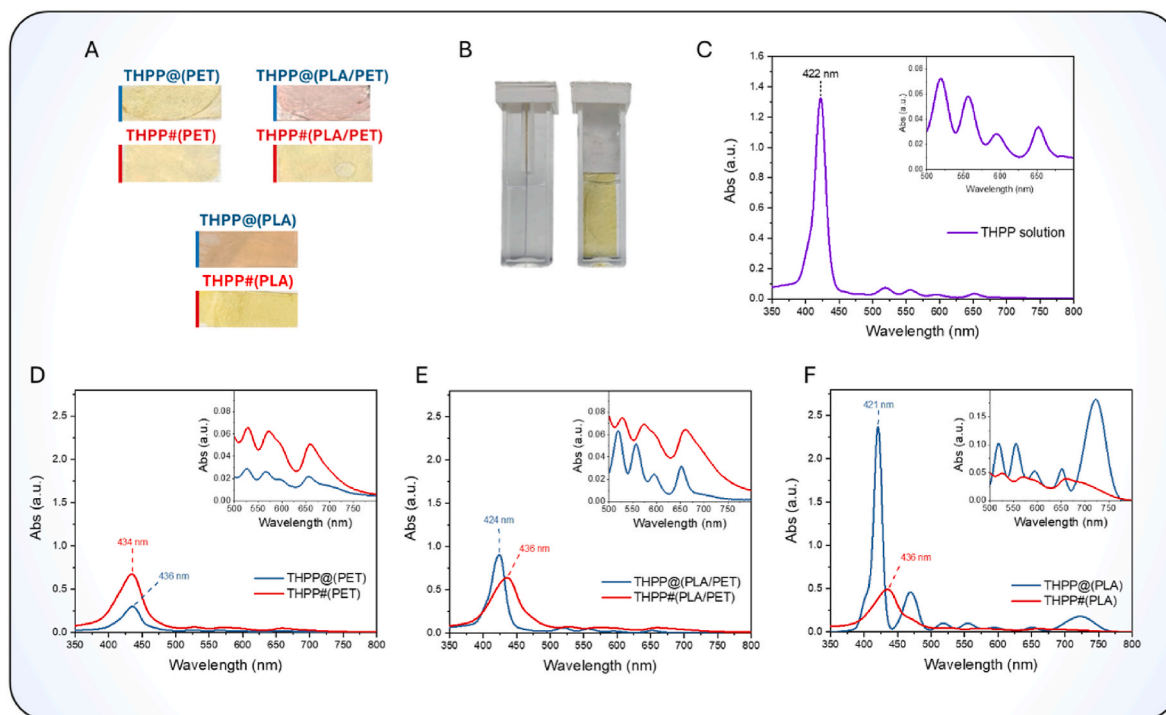


Fig. 4. A) Prepared platforms pictures. B) Lateral and frontal views of a representative system placed into a cuvette by 3D-printed cap. C) UV-Vis spectrum of THPP 10⁻⁶ M in EtOH. D) Overlapping spectra of THPP@(PET) and THPP#(PET). E) Overlapping spectra of THPP@(PLA/PET) and THPP#(PLA/PET). F) Overlapping spectra of THPP@(PLA) and THPP#(PLA). Insets in C), D), E) and F) show the Q-bands region.

band peaked at about 420 nm.

THPP#(PET), THPP#(PLA/PET) and THPP#(PLA) exhibited a red-shifted and broader Soret band peaked in the range between 434 ÷ 436 nm, and absorption Q-bands indicative of J-type aggregates. In contrast, when THPP is deposited from AcOEt, the spectroscopic characterization shows a different profile for any investigated substrate.

THPP@ (PET) spectrum seems to be similar to that observed for THPP deposited from EtOH:Et₂O mixture, but it is less intense, presents a bathochromic shift at 436 nm, and has a more defined profile in the Q-band region. THPP@ (PLA/PET) shows the same spectral trend of the monomeric porphyrin, displaying a Soret band at 424 nm and well-resolved Q-bands located at 519, 556, 595, and 652 nm (Fig. 4E).

Notably, THPP@ (PLA) spectrum displays a complex profile not attributable to a single molecular species. Specifically, the dominant Soret at 421 nm and the retention of four Q-bands indicate a major contribution from neutral free-base THPP, while additional red-shifted features at 468 nm and 723 nm respectively point to coexisting other electronic species. Several studies demonstrate that these intense red-shifted features typically arises from strong excitonic coupling, ordered intermolecular interactions, hyperporphyrin-like behavior, protonated contributions, or mixed aggregated/protonated states [35, 53–60], where porphyrin behaviors is investigated in aqueous environment at specific pH, by adding proper amount of acid and/or in presence of ionic surfactant. Under our experimental conditions (room temperature, Milli-Q water short immersion time, surface deposition from aprotic solvent) potential protonation, due to PLA hydrolysis, is not expected, as demonstrated by the lack of spectral variation of the systems between 1 and 20 min immersion in water (Fig. S5). According to literature, in fact, the hydrolytic PLA degradation is a slow process that requires extended exposure times and/or extreme pH or elevated temperatures [61–65]. Additionally, ethyl acetate only induces reversible swelling allowing chains mobility, for as long as the solvent remains present, without cleaving ester bonds [50]. By the way, AcOEt-induced crystallization of the PLA matrix promotes a molecular confinement effect, that as consequence, can result in THPP expulsion into restricted amorphous domains. This segregation could force porphyrins into close proximity with the terminal carboxylic groups of the polymer chains,

creating a local microenvironment where protonation might occur. Based on all these considerations and data reported in literature, the THPP@ (PLA) optical response might be interpreted as resulting from the combination of free-base monomer and coexisting locally protonated aggregated species, within the polymer-confined system. PLA matrix effect has been evaluated by an additional spectroscopic measurement reported in Fig. S6.

Supramolecular organization and surface topography of the platforms were assessed using confocal dark field microscopy (Fig. 5) and AFM for their complementary spatial resolutions (Fig. 6).

Confocal dark-field images of THPP@ (PET), THPP@ (PLA/PET), and THPP@ (PLA) (Fig. 5A, B and C) displayed the presence of similar and more or less homogeneous distribution of low-brightness domains, with sizes in the order of a few micrometres. At the nanometer scale, the surface morphology analysed by AFM shows clear differences among samples. In particular THPP@ (PLA/PET) (Fig. 6B) shows a flat and homogeneous topography, indicating a uniform distribution of the deposited material. This surface appears much smoother when compared to THPP@ (PLA) (Fig. 6C), which instead presents a more irregular and bumpy morphology. Considering the samples prepared by depositing THPP from AcOEt, only the PET-based platform (Fig. 6A) displays the presence of some surface aggregates. This behaviour agrees with the spectroscopic results, which show a response similar to that observed for platforms where THPP was deposited from alcoholic-ether mixture, further supporting the consistency between morphological and optical data. Surprisingly, although the THPP spectra obtained from deposition on PET, PLA and their composite from 1:1 EtOH:Et₂O display the same spectral profile, their surface morphology differs markedly. Indeed, the analyses performed at both the micro- and nanoscale reveal pronounced topographic variations among the three substrates. Confocal dark-field microscopy performed on THPP# (PET) shows a dense constellation of bright spots distributed over the entire surface (Fig. 5A'). This observation is consistent with AFM analysis, which reveals an almost homogeneous distribution of spherical aggregates with an average diameter of 115 ± 15 nm (Fig. 6A'). In the case of THPP# (PLA/PET), the bright features appear mainly localized clusters confined to specific areas (Fig. 5B'). This distribution reflects the heterogeneous

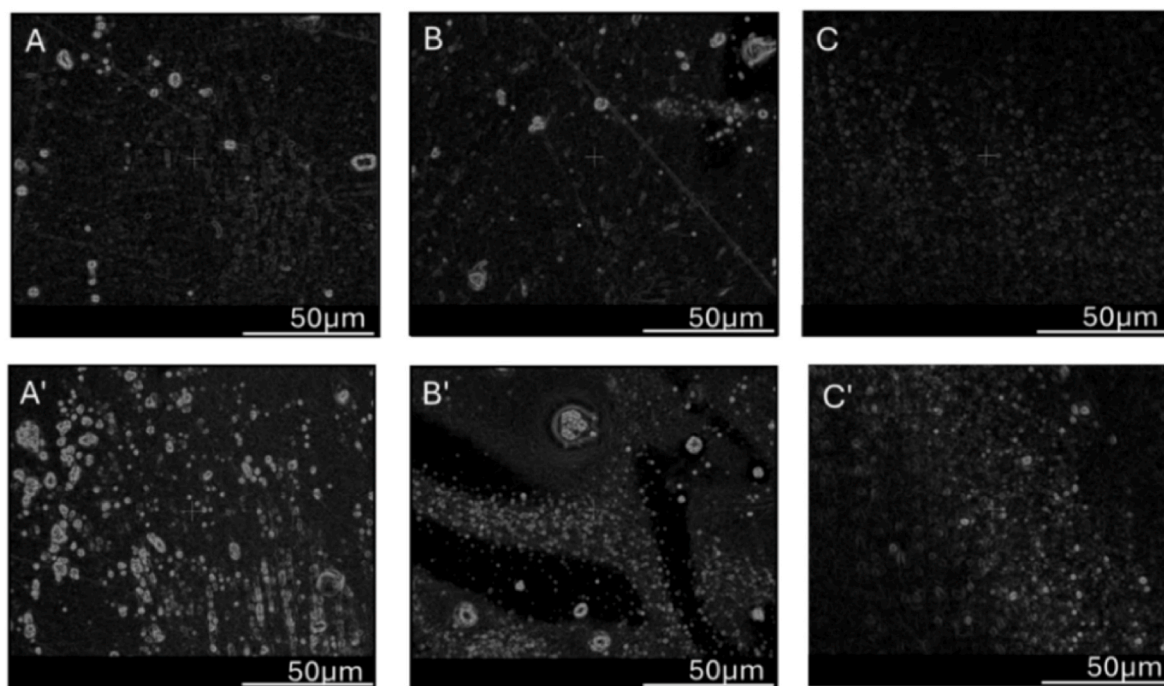


Fig. 5. Confocal dark field microscopy images of: **A)** THPP@ (PET); **A')** THPP# (PET); **B)** THPP@ (PLA/PET); **B')** THPP# (PLA/PET); **C)** THPP@ (PLA); **C')** THPP# (PLA) - Scan area: 140 μm × 115 μm.

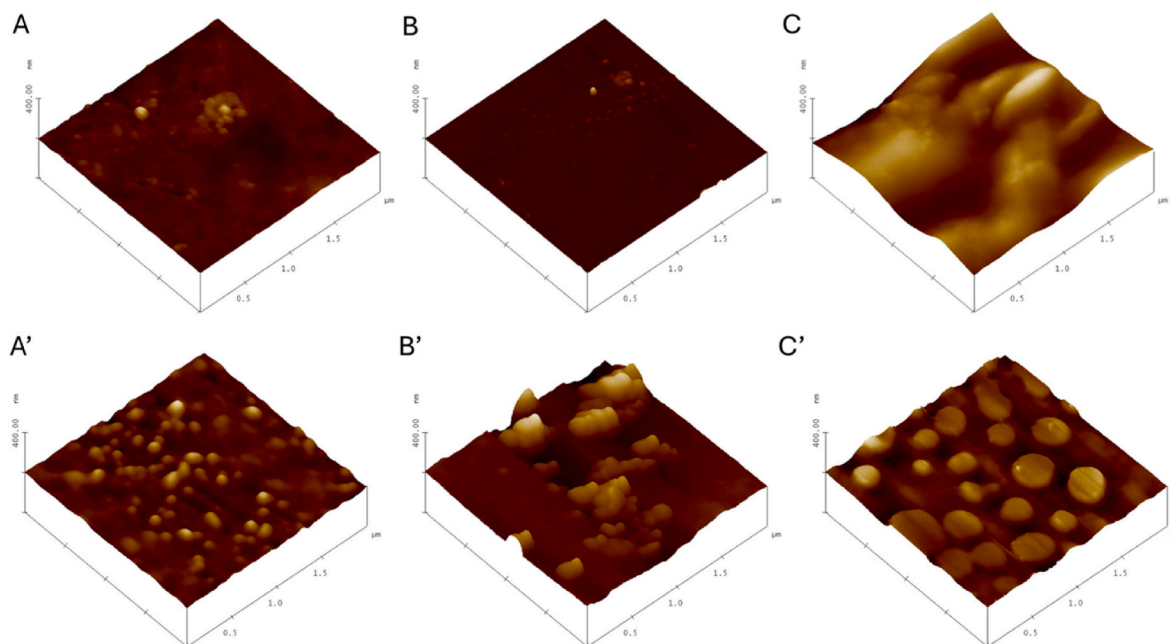


Fig. 6. 3D AFM topographic images of: **A)** THPP@(PET), **A')** THPP#(PET), **B)** THPP@(PLA/PET), **B')** THPP#(PLA/PET), **C)** THPP@(PLA), **C')** THPP#(PLA) - Scan area: $2 \times 2 \mu\text{m}^2$; Z scale: 400 nm.

morphology of the underlying PLA/PET substrate. AFM images confirm that these clusters are formed of spherical aggregates of comparable size ($130 \pm 20 \text{ nm}$) (Fig. 6B'), with the main difference from PET being their spatial arrangement rather than their dimension. A different behaviour is observed for THPP#(PLA). Dark-field images display fewer bright clusters, more uniformly distributed across the surface (Fig. 5C'). However, AFM analysis reveals the presence of larger and more isolated domains, with sizes of $350 \pm 50 \text{ nm}$ (Fig. 6C'). This distinct aggregation behaviour is likely related to the lower water contact angle of PLA compared to PET, as reported in Table 1.

Film thickness estimation was assessed through Variable Angle Spectroscopic Ellipsometry (VASE) technique. The presence of aggregates of such large dimensions, not uniformly distributed across the surface and with significant vertical dimensions, as revealed by morphological characterization (Figs. 2 and 6D AFM images reported in Fig. S7), prevents a reliable determination of thickness of the deposited layers. For these reasons, THPP thin films evaluation was performed by depositing $35 \mu\text{L}$ of porphyrin from both AcOEt and a binary EtOH:Et₂O mixture onto silicon substrates, following the same procedure already described in Section 2.3.2. Prior to deposition, the silicon surfaces were treated with UV-ozone for 10 min to remove organic contaminants and enhance surface wettability, thereby promoting the formation of uniform and homogeneous films.

The analysis of the ellipsometric data revealed distinct thicknesses depending on the solvent system employed. In particular, films obtained from the AcOEt solution (THPP@) exhibited a thickness of approximately $11.02 \pm 0.05 \text{ nm}$, whereas those prepared from the EtOH:Et₂O mixture (THPP#) showed a greater thickness of $13.32 \pm 0.10 \text{ nm}$ (Fig. S8) with a difference of about 21%. This difference suggests that the choice of solvent plays a significant role in the film formation process, likely influencing parameters such as solute-substrate interactions, evaporation rate, and molecular organization during deposition. As a result, the binary solvent system appears to promote the formation of slightly thicker films under the same preparation conditions. The obtained values agree with other porphyrin film thickness, obtained by spin coating, reported in literature [32,66].

Stability of the systems was monitored over time under both wet and dry conditions through UV-vis absorption measurements. Regarding the first condition, samples were immersed in Milli-Q water for five days,

and no absorbance variation were observed. Absorption spectrum of water was also recorded after sample removal, showing no detectable absorbance and thus confirming that the porphyrin remained attached to the substrate. The shelf-life of the platforms was monitored over a 25-day period, with absorption spectra recorded every five days while the systems were stored in the dark under dry conditions. No significant variations were observed, indicating the robustness of the systems.

3.2. Hg^{2+} response as functional readout

The well-known THPP affinity toward Hg^{2+} ions [23] was exploited as a qualitative functional readout to elucidate substrate-solvent effects on THPP supramolecular organization, aggregates distribution, and binding site accessibility. Tests were performed by immersing each functionalized platform in an aqueous solution containing 25 ppm Hg^{2+} inside a PMMA cuvette and monitoring optical signal variations. UV-visible spectra were recorded in a time frame of 1 h at room temperature, with sample fixed in the 3D-printed cup to maintain a reproducible positioning. Each experiment was conducted in triplicate to evaluate the reproducibility and reliability measurements.

When THPP was deposited from AcOEt solution, the resulting platforms showed no detectable activity as visible in Fig. S9. Although the absorption spectrum of THPP@(PET) shows J-type aggregates, as well as for systems where deposition has carried out from mixture, the porphyrin chelating sites by using AcOEt seem to be inaccessible, preventing Hg^{2+} complexation. In this case the chelation ability differs because solvents influence the structure of the deposited aggregates (see Fig. 5A and A', Fig. 6A and A') which modulate accessibility, without altering the main optical transition. On PLA and PLA/PET substrates, AcOEt induces PLA swelling, bringing THPP to enter within the PLA matrix. This trapping prevents effective coordination with Hg^{2+} ions, resulting once again in inactive surfaces.

In contrast, as shown in Fig. 7, THPP deposited from EtOH:Et₂O mixture yielded, at first glance, active platforms. Fig. 7A, B and C show the response of these platforms to Hg^{2+} in water, featuring bathochromic and hypochromic effects of the Soret band and the growth of a new absorption signal around 465 nm, accompanied by an isosbestic point at 451 nm, indicative of an equilibrium between free-porphyrins and metalloporphyrins. Modifications in the Q-bands are also

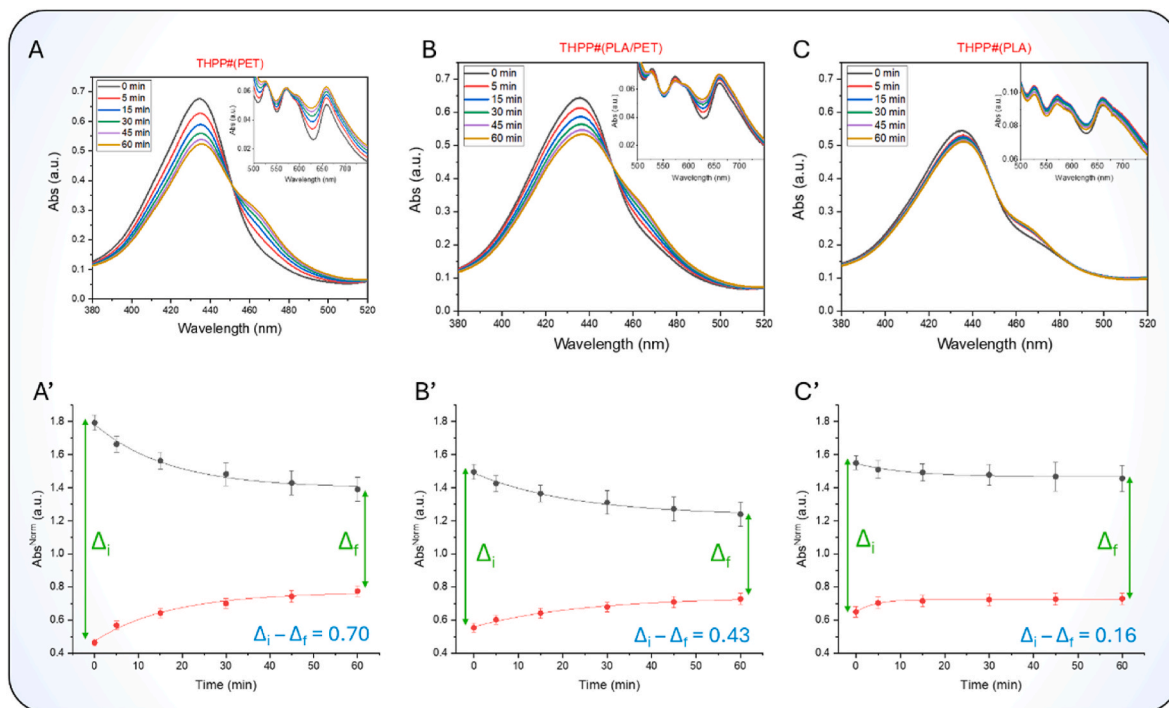


Fig. 7. On the top, UV-vis absorption spectra of **A)** THPP#(PET), **B)** THPP#(PLA/PET), and **C)** THPP#(PLA) under 1 h 25 ppm mercury exposure. The inset highlights the spectral region between 500 and 750 nm, corresponding to the Q-bands of the porphyrin. On the bottom, normalized absorbance values for the Soret band reduction (in black), and for the growing 465 nm signal (in red) for **A')** THPP#(PET), **B')** THPP#(PLA/PET), and **C')** THPP#(PLA), under 1 h mercury exposure. Error bars represent the standard deviation of three independent measurements per sample type.

observed, consistent with the complexation phenomenon.

Fig. 7A', B' and C' present normalized absorbance trends of two signals for each platform with their relative standard deviations: the exponential decay of the Soret band intensity (black points) and the growth of the signal at 465 nm (red points). Absorbance data were normalized according to Equation (2):

$$Abs^{Norm}(\lambda, t) = \frac{Abs_{MAX}(t)}{Abs_{451}} \quad (2)$$

where, as maximum absorbance over the time, $Abs_{MAX}(t)$ corresponds the higher value of the B band and to the absorbance at 465 nm to monitor the Soret signal decreasing and the new growing signal,

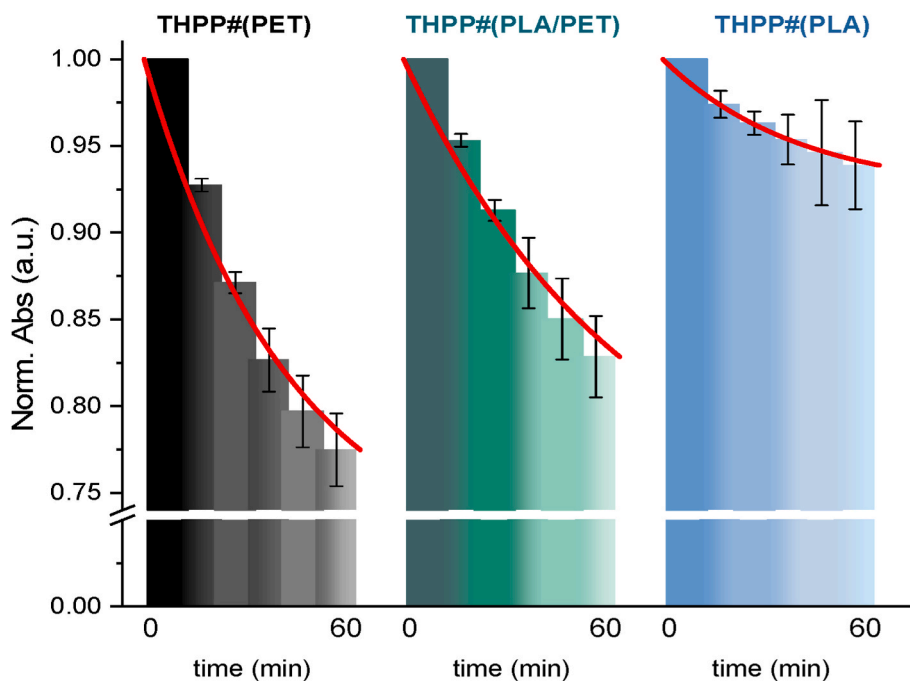


Fig. 8. Time-dependent trend of the normalized Soret band maximum absorbance for THPP#(PET), THPP#(PLA/PET) and THPP#(PLA) under 1 h mercury exposure. Error bars represent the standard deviation of three independent measurements per sample type.

respectively. Abs_{451} corresponds to the absorbance value at the isosbestic point.

To evaluate the overall spectral evolution, a parameter $\Delta_i - \Delta_f$ was estimated for each system as in Equation (3):

$$\Delta_i - \Delta_f = [Abs_{(Soret,t=0')}^{Norm} - Abs_{(465,t=0')}^{Norm}] - [Abs_{(Soret,t=60')}^{Norm} - Abs_{(465,t=60')}^{Norm}] \quad (3)$$

Fig. 7A', B' and C' show that $\Delta_i - \Delta_f$ progressively decreases when moving from PET to PLA/PET and finally to PLA substrates, indicating a reduced extent of porphyrin metallation and a decreasing response on supports with increasing PLA content.

Temporal evolution of the Soret band decay of the three systems upon mercury exposure, reported as normalized data with the initial absorbance value set to 1, is shown in Fig. 8. Considering the spectral changes observed during 1 h of immersion, a % decay of about 22%, 17% and 6% was observed suggesting a ranking $PET > PLA/PET \gg PLA$. Since the optical response was monitored in the defined time-frame, without reaching a stable plateau, the reported relative ranking should be interpreted as time-dependent descriptors of the systems response under the chosen observation window.

The very slight observed variations for THPP#(PLA) seem to be consistent with a nearly total absence of response, while the other two platforms exhibit appreciable decay. Observed behaviours are directly related to spatial distribution, surface density of aggregates and

accessible coordination sites dictated by the different substrates. Undoubtedly, the homogeneous aggregates distribution in THPP#(PET) results in more disposability sites if compared to the more heterogeneous morphology of THPP#(PLA/PET) featuring “grape cluster” like. This latter is attributable to the PLA chains arrangements in presence of PET, as suggested by IR and WCA measurements.

Assumed THPP morphology results in a reduced sites disposability, partially hindering mercury interactions. Meanwhile, the large aggregates observed in THPP#(PLA), showed negligible response. The surface PLA characteristics probably drive porphyrin aggregates to assume an assessment where core is not disposable to interact with ions. However, the aggregate size also plays a crucial role, as it is directly related to the active surface area: smaller aggregates provide a larger effective active area, thereby enhancing the response of the surface.

An additional experiment was conducted using a PLA/PET substrate pretreated with AcOEt, followed by the deposition of THPP from the EtOH:Et₂O mixture. As previously shown in Fig. 1B', AcOEt redistributes PLA on PLA/PET surface and chemically alters its surface. The picture and the UV-vis spectrum in Fig. 9A indicate the presence of J-type aggregates on THPP#(PLA/PET@) sample. The 3D AFM image in Fig. 9B confirms a heterogeneous distribution of aggregates, resembling the pattern seen on untreated PLA/PET, yet distinctly different from the larger, more isolated structures observed on untreated PLA. In this case, the THPP aggregates formed through the “good-bad” solvent approach interact with a different PLA chains conformation induced by the AcOEt

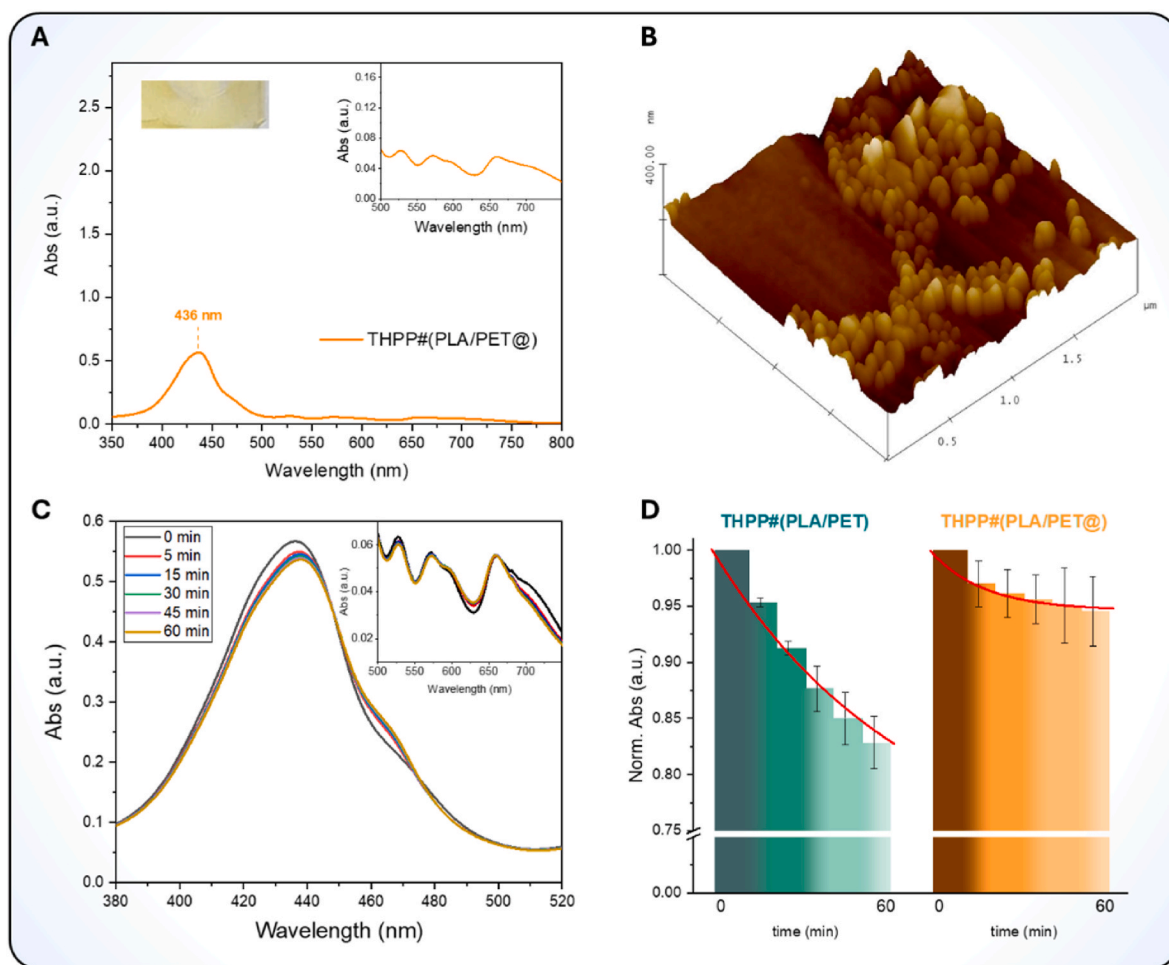


Fig. 9. UV-vis absorption spectra of THPP#(PLA/PET@), A) in water and C) under 1 h 25 ppm mercury exposure. Inset on the left in A) shows a picture of the platform. Insets on the right in A) and C) show the Q-bands region. B) 3D AFM topographic image of THPP#(PLA/PET@) - Scan area: $2 \times 2 \mu m^2$; Z scale: 400 nm. D) Time-dependent trend of the normalized Soret band maximum absorbance of THPP#(PLA/PET@) under 1 h mercury exposure. THPP#(PLA/PET) observed trend is reported just for comparison. Error bars represent the standard deviation of three independent measurements.

treatment. Upon exposure to Hg^{2+} , THPP#(PLA/PET@) shows a very negligible response (Fig. 9C), as well as the THPP#(PLA) (Fig. 7C), compared to THPP#(PLA/PET) (Fig. 9D). This finding confirms that AcOEt modifies not only the surface morphology, but also the physico-chemical properties of the substrate (as suggested by IR analysis), ultimately impairing the interactions with the tested metal ion.

Table 2 summarizes the optical THPP observed species, distribution and average size at nanoscale, and qualitative mercury readout for all substrate-solvent combinations described in the previous pages. Overall, the observed trends highlight the crucial interplay between solvent-induced porphyrin aggregation and substrate properties in determining response: AcOEt deposition leads to inactive surfaces, whereas aggregates formed in the EtOH:Et₂O mixture exhibit different activities depending on the PLA content. These results indicate that the physico-chemical properties of PLA are likely critical in driving molecular organization at the surface, especially for pristine PLA, which exhibits a pronounced Lewis base character. This latter high base contribute appears to inhibit active chromophores which could interact with mercury ions.

3.2.1. THPP#(PET) as optimal platform: qualitative comparison response of Hg^{2+} vs other dication

The homogeneous surface distribution, aggregate size, and positive Hg^{2+} response in 1 h identify the system featuring PET as substrate and porphyrin deposition from the EtOH:Et₂O mixture as the optimal substrate-solvent combination for non-covalent THPP deposition onto a polyester substrate, among the investigated platforms. For this reason, THPP#(PET) was also exposed to other dications to qualitative evaluate the preservation of THPP specificity towards mercury even in aggregate form. The active platform was tested separately in various solutions, each containing 25 ppm of the following individual metals: Cu^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Mn^{2+} and compared to the Hg^{2+} response. Fig. 10 shows a comparison between the spectral response at $t = 0$ min (Fig. 10A) and after 1 h immersion in metal solutions (Fig. 10B). Negligible absorbance

Table 2

Summary of THPP substrate/solvent deposition conditions, spectroscopically assigned species, surface morphology, and qualitative Hg^{2+} response after 1 h of exposure.

Substrate	THPP Solvent	THPP species Spectroscopically identified	Morphological surface shape, Average Size (nm) $\pm$ SD and surface distribution	Response towards Hg^{2+} in 1 h
PET	AcOEt	J-type aggregates	Bumpy and irregular	Absent
	EtOH: Et ₂ O	J-type aggregates	Spherical aggregates 115 $\pm$ 15 Homogeneous	Very Good
PLA/PET	AcOEt	Monomeric	Flat and homogenous	Absent
	EtOH: Et ₂ O	J-type aggregates	Spherical aggregates 130 $\pm$ 20 Grape-like Cluster	Good
PLA	AcOEt	Coexisting of monomeric and locally protonated aggregated species	Bumpy and irregular	Absent
	EtOH: Et ₂ O	J-type aggregates	Spherical-like 350 $\pm$ 50 Isolated	Negligible
PLA/PET@	EtOH: Et ₂ O	J-type aggregates	Spherical 125 $\pm$ 20 Clustered	Negligible

reductions were observed for Mn^{2+} , Pb^{2+} and Ni^{2+} , and very small variations for Cu^{2+} and Co^{2+} . Only Hg^{2+} induces the characteristic absorbance changes previously described, as clearly displayed in the bar chart reported in Fig. 10C.

A selectivity estimation percentage through single ions (SI) test was calculated applying Equation (4):

$$\text{Selectivity}_{SI} (\%) = \frac{|\Delta Abs_{Hg}|}{|\Delta Abs_{Hg}| + \sum |\Delta Abs_{Metals}|} \times 100 \quad (4)$$

where $|\Delta Abs_{Hg}|$ is defined as the absolute change in absorbance due to Hg^{2+} , and $\sum |\Delta Abs_{Metals}|$ is the summation of absolute change in absorbance from all the other metals tested. $\text{Selectivity}_{SI} (\%)$ of about 83% confirms that the supramolecular organization of THPP on PET provides selective accessibility to the porphyrin core preferentially for mercury ions.

The response of THPP#(PET) was further evaluated under competitive conditions by exposing the platform to a mixed-ions solution (MIX) containing Cu^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Mn^{2+} , each at 25 ppm. The MIX alone induces a minor perturbation of the Soret band 1 h after immersion, respect to the pure water used as background (Fig. 11A).

The system was later tested in five different solutions containing the MIX and Hg^{2+} concentrations of 5, 10, 15, 20 and 25 ppm, respectively. A clearly marked hypochromic evolution of the Soret band was observed concomitantly with Hg^{2+} increasing concentration and is still perceptible even at the lowest tested of 5 ppm, despite competing ions.

In this case, a competitive (COMP) selectivity percentage was estimated for each Hg^{2+} concentration in MIX, after 1 h exposure, through Equation (5):

$$\text{Selectivity}_{COMP} (\%) = \frac{|\Delta Abs_{Hg+MIX}|}{|\Delta Abs_{Hg+MIX}| + |\Delta Abs_{MIX}|} \times 100 \quad (5)$$

where $|\Delta Abs_{Hg+MIX}|$ is defined as the absolute change in absorbance due to MIX + Hg^{2+} solution respect to the signal in water. $|\Delta Abs_{MIX}|$ is the absolute change in absorbance after exposure to only MIX solution, respect to the absorbance collected in pure water.

Fig. 11B illustrates $\text{Selectivity}_{COMP} (\%)$ as a function of Hg^{2+} concentration (5 $\div$ 25 ppm) in the presence of the MIX. $\text{Selectivity}_{COMP}$ values increase proportionally with the mercury ions concentration, with a mean value of $84 \pm 8\%$. This value is fully in agreement with the previous $\text{Selectivity}_{SI} (\%)$, confirming THPP#(PET) ability to preferentially coordinates Hg^{2+} despite a 25:1 interferent-to-target ratio.

To rationalize the behaviour within the selected observation period, the ΔAbs variation, collected at 1 h in the presence of the competitive mixture, were plotted respect to the increasing mercury concentration. The signal variation was defined as:

$$\Delta Abs = Abs(\text{water}) - Abs(\text{MIX} + n \text{ ppm Hg(II)}) \quad (6)$$

where $Abs(\text{water})$ represents the Soret band absorbance after 1 h immersion in pure water, and $Abs(\text{MIX} + n \text{ ppm Hg}^{2+})$ is the maximum of Soret absorbance after exposure to the competitive mixture plus Hg^{2+} at concentrations of 5, 10, 15, 20, and 25 ppm, respectively.

The linear fit reported in Fig. 12 shows a direct proportionality between the recorded absorbance variation and increasing mercury ion concentrations in MIX, measured during 1 h of sample exposure, with an R^2 value of 0.99456 and a slope of $0.0078 \pm 0.0003 \text{ Abs/ppm}$. The non-zero intercept also reflects the minor response of the system in a complex matrix, consistently with the previously discussed $\text{Selectivity}_{COMP} (\%)$ ($\sim 84\%$). These parameters are therefore valid within the specific measurement window and experimental conditions adopted in this study, describing the responsivity performance of the platform under competitive conditions where Hg^{2+} concentration is varied in the presence of fixed interferents, rather than a time-independent equilibrium response.

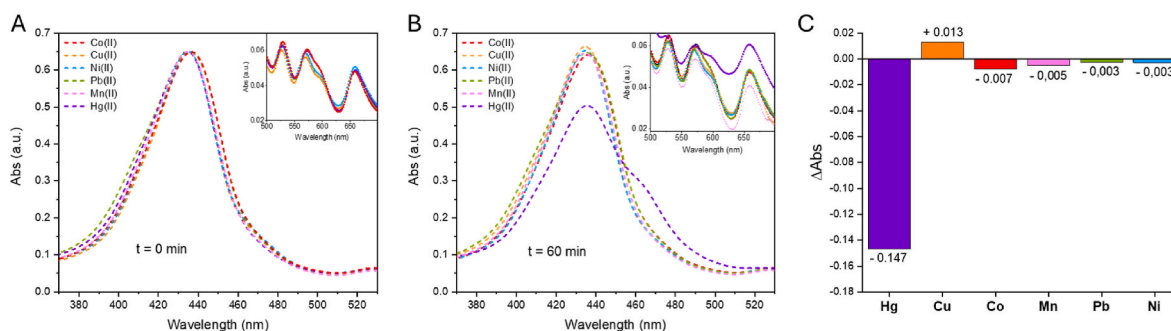


Fig. 10. UV-vis absorption spectra of THPP#(PET) recorded **A)** at $t = 0$ min and **B)** 1 h after immersion in 25 ppm aqueous solutions of different metal ions, Cu^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Mn^{2+} , Hg^{2+} . **C)** Absorbance variation (ΔAbs) at 1-h immersion in aqueous solutions containing 25 ppm of individual metal ions (Hg, Cu, Co, Mn, Pb, and Ni).

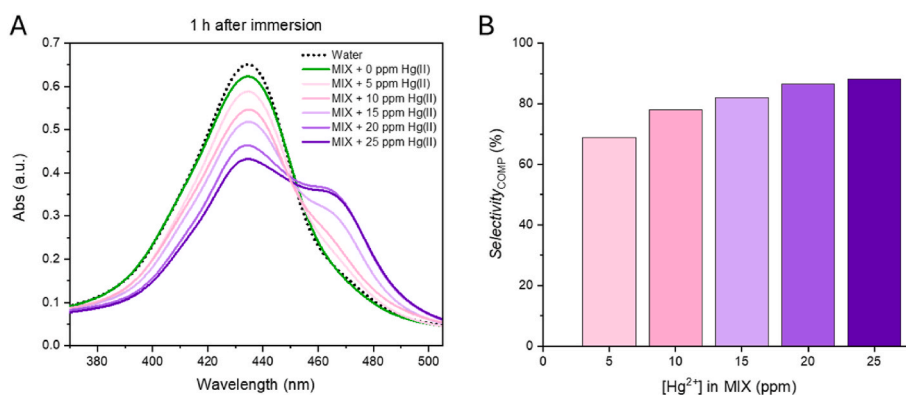


Fig. 11. **A)** UV-vis absorption spectra of THPP#(PET) recorded after 1 h immersion in Milli-Q water, in a mixed-ions solution (MIX, 25 ppm each) and in MIX plus increasing Hg^{2+} concentrations (5, 10, 15, 20 and 25 ppm). **B)** Column plot of $\text{Selectivity}_{\text{COMP}} (\%)$ vs $[\text{Hg}^{2+}]$ in the MIX solution.

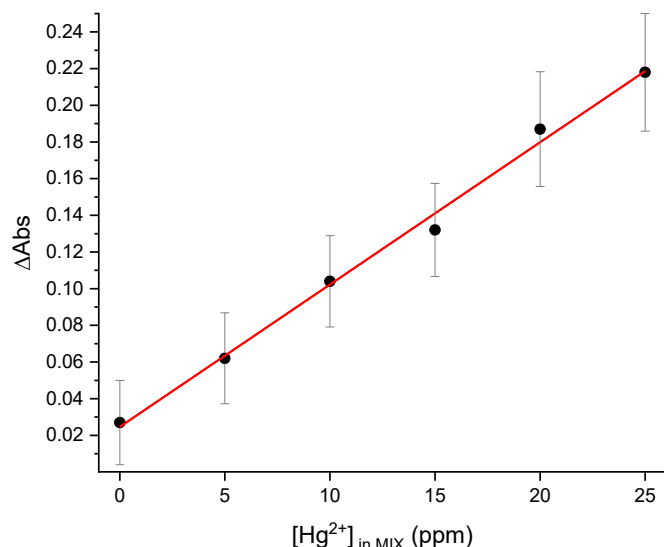


Fig. 12. Linear fit of collected ΔAbs variations in MIX solution at different Hg^{2+} concentrations (0, 5, 10, 15, 20 and 25 ppm, respectively). Error bars represent the standard deviation of three independent measurements.

4. Conclusion

The non-covalent functionalization of PET, PLA/PET and PLA via THPP deposition was employed to investigate how both the intrinsic properties of the polymeric substrate and the solvents used for porphyrin deposition play critical roles in governing the supramolecular organization of the macrocyclic layer, thereby impacting its well-known mercury affinity. A functional read-out of all prepared platforms was carried out by direct immersion in 25 ppm Hg^{2+} aqueous solutions.

Specifically, spin-coating porphyrin deposition from AcOEt results in poorly defined aggregates on PET, monomeric species on PLA/PET, with also the presence of different species on PLA substrate, as evidenced by morphological characterization and UV-vis spectroscopy. These structural features correspond to a responsivity absence when these platforms are exposed to aqueous mercury solutions. Particularly, for platform containing PLA the inactive surface is attributable to chromophore entrapment within the polymeric matrix.

In contrast, deposition from EtOH:Et₂O led to aggregated species with accessible coordination sites depending on the substrate, thereby enabling active surface towards Hg^{2+} . Surface Free Energy measurements, corroborated by shape and size of THPP aggregates, demonstrate that in this case the chemical-physical characteristic of the substrate play a key role in the organization of aggregates, leading to different activities. The neat PLA substrate, owing to its significant SFE base component, promotes aggregate orientations that do not expose binding sites, resulting in negligible Hg^{2+} recognition. This SFE component

decreases when PLA is laminated onto PET, indicating a conformational change also supported by IR analysis. This structural rearrangement leads to smaller THPP aggregates and activity enhancement. The best covering in terms of homogeneity and aggregate size was achieved by combining the ether-alcohol mixture as THPP solvent with PET as substrate. This configuration produced a uniform distribution of aggregates on the polymer surface, with an average size of approximately 115 nm, resulting in a faster mercury trapping within a 1-h time window. This latter has shown mercury selectivity of about 84% even in presence of other metal ions.

The findings of this study underscore that porphyrin arrangements are governed by the intricate interplay between polymeric substrate chemistry and solvent dynamics, which also drive the coordination sites disposability. Collectively, these insights advance the current understanding of the multifaceted parameters that must be addressed to design an effective, economically viable heterogeneous platform using a simply non-covalent functionalization strategy.

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CRediT authorship contribution statement

Cristiana Longo: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **Ivana Di Bari:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Giusy Curcuruto:** Conceptualization, Investigation, Methodology, Resources, Visualization, Writing – review & editing. **Grazia M.L. Messina:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing – review & editing. **Sabrina C. Carroccio:** Conceptualization, Formal analysis, Methodology, Resources, Supervision, Visualization, Writing – review & editing. **Emanuela T.A. Spina:** Conceptualization, Methodology, Resources, Visualization, Writing – review & editing. **Giuseppe D'Arrigo:** Investigation, Resources, Visualization, Writing – review & editing. **Luigi Fabiano:** Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – review & editing. **Antonella Sciuto:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Resources, Supervision, Visualization, Writing – review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtadv.2026.100840>.

Data availability

Data will be made available on request.

References

- [1] M. Plaschke, R. Czolk, H.J. Ache, Fluorimetric determination of mercury with a water-soluble porphyrin and porphyrin-doped sol-gel films, *Anal. Chim. Acta* 304 (1) (1995) 107–113, [https://doi.org/10.1016/0003-2670\(94\)00568-7](https://doi.org/10.1016/0003-2670(94)00568-7).
- [2] G. Sallam, S.Y. Shaban, A. Nassar, M.E. El-Khouly, Water soluble porphyrin as optical sensor for the toxic heavy metal ions in an aqueous medium, *Spectrochim. Acta Mol. Biomol. Spectrosc.* 241 (2020) 118609, <https://doi.org/10.1016/j.saa.2020.118609>.
- [3] G. Feng, H. Mi, Q. Fei, H. Shan, B. Wang, H. Xu, G. Li, F. Chen, Y. Huan, A facile fluorescent chemosensor based on a water-soluble porphyrin for Mo 6+ in aqueous solution, *Spectrochim. Acta Mol. Biomol. Spectrosc.* 167 (2016) 122–126, <https://doi.org/10.1016/j.saa.2016.05.039>.
- [4] K.-K. Liu, L.-N. Zhang, L.-N. Zhu, R. Zhang, X.-Z. Li, D.-M. Kong, A water-soluble, cationic bis-porphyrin exhibiting a more sensitive fluorescent response to Cu2+ relative to its monomeric counterpart, *Sensor. Actuator. B Chem.* 247 (2017) 179–187, <https://doi.org/10.1016/j.snb.2017.03.016>.
- [5] P.P. Namitha, A. Saji, S. Francis, L. Rajith, Water soluble porphyrin for the fluorescent determination of cadmium ions, *J. Fluoresc.* 30 (3) (2020) 527–535, <https://doi.org/10.1007/s10895-020-02514-1>.
- [6] B.B. Beyene, A.W. Yibeltal, M.T. Ayana, Colorimetric and fluorescent on-off detection of Cu2+, Sn2+ and Zn2+ by a water-soluble porphyrin: electronic absorption and emission study, *Results Chem.* 2 (2020) 100058, <https://doi.org/10.1016/j.rechem.2020.100058>.
- [7] R. Purrello, R. Gurrieri, R. Laueri, Porphyrin assemblies as chemical sensors, *Coord. Chem. Rev.* 190–192 (1999) 683–706, [https://doi.org/10.1016/S0010-8545\(99\)00106-X](https://doi.org/10.1016/S0010-8545(99)00106-X).
- [8] O. Özbek, Ö. Isildak, C. Berkel, The use of porphyrins in potentiometric sensors as ionophores, *J. Inclusion Phenom. Macrocycl. Chem.* 98 (1–2) (2020) 1–9, <https://doi.org/10.1007/s10847-020-01004-y>.
- [9] C.C. Negut, R.-I. Stefan - Van Staden, J.F. Van Staden, Porphyrins-as active materials in the design of sensors. An overview, *ECS J. Solid State Sci. Technol.* 9 (5) (2020) 051005, <https://doi.org/10.1149/2162-8777/ab9a5d>.
- [10] D. Duc La, H.M. Khong, X.Q. Nguyen, T.-D. Dang, X.T. Bui, M.K. Nguyen, H.H. Ngo, D.D. Nguyen, A review on advances in graphene and porphyrin-based electrochemical sensors for pollutant detection, *Sustain. Chem. One World* 3 (2024) 100017, <https://doi.org/10.1016/j.scowo.2024.100017>.
- [11] R. Dhir, M. Kaur, A.K. Malik, Porphyrin metal-organic framework sensors for chemical and biological sensing, *J. Fluoresc.* 35 (4) (2024) 1895–1917, <https://doi.org/10.1007/s10895-024-03674-0>.
- [12] E.A.M. Saleh, M.M. Moharam, M.S. Jabir, I. Ahmad, R. Roopashree, A. Kashyap, T. Krithiga, S. Ray, I.A. Mohammed, H.A. Jasim, Recent advances in photo/electrochemical biosensing of chemical food contaminants based on the porphyrin-MOFs nanohybrids, *Microchem. J.* 213 (2025) 113671, <https://doi.org/10.1016/j.microc.2025.113671>.
- [13] A.S. Khune, N.N. Ingle, B.S. Killare, R.P. Bongane, A.C. Khandare, A. Singh, M. D. Shirsat, Chemiresistive NO2 sensor: a comparative study of rGO/MCPTTP and rGO/TPTP/MCPTTP composite, *Sensor Actuator Phys.* 378 (2024) 115818, <https://doi.org/10.1016/j.sna.2024.115818>.
- [14] Y.A. Waghmare, N.N. Ingle, V.N. Narwade, M.-L. Tsai, T. Hianik, M.D. Shirsat, Reduced graphene oxide functionalized zinc octaethyl porphyrin (rGO/Zn OEP) for selective detection of carbon monoxide in chemiresistive modality, *J. Mater. Sci. Mater. Electron.* 35 (23) (2024) 1602, <https://doi.org/10.1007/s10854-024-13271-3>.
- [15] R. Paolesse, S. Nardis, D. Monti, M. Stefanelli, C. Di Natale, Porphyrinoids for chemical sensor applications, *Chem. Rev.* 117 (4) (2017) 2517–2583, <https://doi.org/10.1021/acs.chemrev.6b00361>.
- [16] Y. Ding, W.-H. Zhu, Y. Xie, Development of ion chemosensors based on porphyrin analogues, *Chem. Rev.* 117 (4) (2017) 2203–2256, <https://doi.org/10.1021/acs.chemrev.6b00021>.
- [17] Z.-L. Qi, Y.-H. Cheng, Z. Xu, M.-L. Chen, Recent advances in porphyrin-based materials for metal ions detection, *IJMS* 21 (16) (2020) 5839, <https://doi.org/10.3390/ijms21165839>.

- [18] X. Liu, X. Liu, M. Tao, W. Zhang, A highly selective and sensitive recyclable colorimetric Hg^{2+} sensor based on the porphyrin-functionalized polyacrylonitrile fiber, *J. Mater. Chem. A* 3 (25) (2015) 13254–13262, <https://doi.org/10.1039/C5TA02491A>.
- [19] E.C. Atayde, Y. Takenaka, H. Abe, M.-R. Wu, K.C.-W. Wu, Porphyrin-grafted Poly (ethylene terephthalate) as a reusable and highly selective colorimetric probe for mercuric ion contaminants in aqueous samples, *ACS Appl. Mater. Interfaces* 16 (30) (2024) 39195–39205, <https://doi.org/10.1021/acsami.4c03846>.
- [20] L. Zhang, Y.-H. Zhao, R. Bai, Development of a multifunctional membrane for chromatic warning and enhanced adsorptive removal of heavy metal ions: application to cadmium, *J. Membr. Sci.* 379 (1–2) (2011) 69–79, <https://doi.org/10.1016/j.memsci.2011.05.044>.
- [21] L. Zhao, M. Li, M. Liu, Y. Zhang, C. Wu, Y. Zhang, Porphyrin-functionalized porous polysulfone membrane towards an optical sensor membrane for sorption and detection of cadmium(II), *J. Hazard. Mater.* 301 (2016) 233–241, <https://doi.org/10.1016/j.jhazmat.2015.08.044>.
- [22] F. Caroleo, G. Magna, C. Damiano, M. Cavalleri, E. Gallo, C. Di Natale, R. Paolesse, Colour Catcher® sheet beyond the laundry: a low-cost support for realizing porphyrin-based mercury ion sensors, *Sensor. Actuator. B Chem.* 364 (2022) 131900, <https://doi.org/10.1016/j.snb.2022.131900>.
- [23] R. Zare-Dorabei, R. Rahimi, A. Koohi, S. Zargari, Preparation and characterization of a novel tetrakis(4-hydroxyphenyl)porphyrin-graphene oxide nanocomposite and application in an optical sensor and determination of mercury ions, *RSC Adv.* 5 (113) (2015) 93310–93317, <https://doi.org/10.1039/C5RA17047H>.
- [24] M.M. Langari, F. Mandoj, G. Pomarico, M.M. Antxustegi, R. Paolesse, J. Labidi, L. Lvova, Cellulose nanofibers as effective mediator for optical chemical sensors for heavy metal ions detection, *Carbohydr. Polym.* 368 (2025) 124028, <https://doi.org/10.1016/j.carbpol.2025.124028>.
- [25] E.V. Ermakova, A. Bessmertnykh-Lemeune, The optical sensing of volatile organic compounds using porphyrins, *Chemosensors* 12 (12) (2024) 253, <https://doi.org/10.3390/chemosensors12120253>.
- [26] D. Monti, M. Venanzi, M. Russo, G. Bussetti, C. Goletti, M. Montalti, N. Zaccaroni, L. Prodi, R. Rella, M.G. Manera, G. Mancini, C. Di Natale, R. Paolesse, Spontaneous deposition of amphiphilic porphyrin films on glass, *New J. Chem.* 28 (9) (2004) 1123, <https://doi.org/10.1039/b403591g>.
- [27] S. Mohnani, D. Bonifazi, Supramolecular architectures of porphyrins on surfaces: the structural evolution from 1D to 2D to 3D to devices, *Coord. Chem. Rev.* 254 (19–20) (2010) 2342–2362, <https://doi.org/10.1016/j.ccr.2010.05.006>.
- [28] G. Lu, X. Zhang, X. Cai, J. Jiang, Tuning the morphology of self-assembled nanostructures of amphiphilic tetra(p-hydroxyphenyl)porphyrins with hydrogen bonding and metal–ligand coordination bonding, *J. Mater. Chem.* 19 (16) (2009) 2417, <https://doi.org/10.1039/b820127g>.
- [29] C. Oliveras-González, F. Di Meo, A. González-Campo, D. Beljonne, P. Norman, M. Simón-Sorbed, M. Linares, D.B. Amabilino, Bottom-Up hierarchical self-assembly of chiral porphyrins through coordination and hydrogen bonds, *J. Am. Chem. Soc.* 137 (50) (2015) 15795–15808, <https://doi.org/10.1021/jacs.5b08081>.
- [30] D.D. La, H.H. Ngo, D.D. Nguyen, N.T. Tran, H.T. Vo, X.H. Nguyen, S.W. Chang, W. J. Chung, M.D.-B. Nguyen, Advances and prospects of porphyrin-based nanomaterials via self-assembly for photocatalytic applications in environmental treatment, *Coord. Chem. Rev.* 463 (2022) 214543, <https://doi.org/10.1016/j.ccr.2022.214543>.
- [31] G. Magna, D. Monti, C. Di Natale, R. Paolesse, M. Stefanelli, The assembly of Porphyrin systems in well-defined nanostructures: an update, *Molecules* 24 (23) (2019) 4307, <https://doi.org/10.3390/molecules24234307>.
- [32] E. Nikoloudakis, K. Karikis, J. Han, C. Kokotidou, A. Charisiadis, F. Folias, A. M. Douvas, A. Mitrali, G. Charalambidis, X. Yan, A.G. Coutsolelos, A self-assembly study of PNA-porphyrin and PNA-BODIPY hybrids in mixed solvent systems, *Nanoscale* 11 (8) (2019) 3557–3566, <https://doi.org/10.1039/C8NR05667F>.
- [33] L. Đorđević, N. Demitri, D. Bonifazi, Solvent-dependent moulding of porphyrin-based nanostructures: solid state, solution and on surface self-assembly, *Supramol. Chem.* 28 (9–10) (2016) 753–761, <https://doi.org/10.1080/10610278.2016.1158407>.
- [34] F. Song, J. Jia, J. Yu, C. Chen, J. Feng, P. Zhu, Morphology controlled nanostructures of a porphyrin dendrimer complex: solvent effect on the self-assembly behavior, *Inorg. Chem. Commun.* 61 (2015) 149–151, <https://doi.org/10.1016/j.inoche.2015.06.035>.
- [35] M. Zannotti, R. Giovannetti, B. Minofar, D. Řeha, L. Placková, C.A. D'Amato, E. Rommozzi, H.V. Dudko, N. Kari, M. Minicucci, Aggregation and metal-complexation behaviour of THPP porphyrin in ethanol/water solutions as function of pH, *Spectrochim. Acta Mol. Biomol. Spectrosc.* 193 (2018) 235–248, <https://doi.org/10.1016/j.saa.2017.12.021>.
- [36] Y. Qiu, P. Chen, M. Liu, Evolution of various porphyrin nanostructures via an Oil/aqueous medium: controlled self-assembly, further organization, and supramolecular chirality, *J. Am. Chem. Soc.* 132 (28) (2010) 9644–9652, <https://doi.org/10.1021/ja1001967>.
- [37] T. Muringayil Joseph, S. Azat, Z. Ahmadi, O. Moini Jazani, A. Esmaeili, E. Kianfar, J. Haponiuk, S. Thomas, Polyethylene terephthalate (PET) recycling: a review, *Case Stud. Chem. Environ. Eng.* 9 (2024) 100673, <https://doi.org/10.1016/j.csee.2024.100673>.
- [38] L. Mou, J. Li, Y. Lu, G. Li, J. Li, Poly(lactic acid): a future universal biobased polymer with multifunctional performance—from monomer synthesis, and processing to applications: a review, *J. Hazard. Mater. Adv.* 18 (2025) 100757, <https://doi.org/10.1016/j.hazadv.2025.100757>.
- [39] M. Yanat, E. Voortman, C. Buijsse, K. Schroeën, Life cycle assessment (LCA) of chitin nanocrystal reinforced polylactic acid (ChNC/PLA) and polyethylene terephthalate (PET) packaging material, *Carbohydr. Polym.* 348 (2025) 122927, <https://doi.org/10.1016/j.carbpol.2024.122927>.
- [40] M.-S. Liao, S. Scheiner, Electronic structure and bonding in metal porphyrins, metal=Fe, Co, Ni, Cu, Zn, *J. Chem. Phys.* 117 (1) (2002) 205–219, <https://doi.org/10.1063/1.1480872>.
- [41] M. Lan, H. Zhao, H. Yuan, C. Jiang, S. Zuo, Y. Jiang, Absorption and EPR spectra of some porphyrins and metalloporphyrins, *Dyes Pigments* 74 (2) (2007) 357–362, <https://doi.org/10.1016/j.dyepig.2006.02.018>.
- [42] W. Zheng, N. Shan, L. Yu, X. Wang, UV–visible, fluorescence and EPR properties of porphyrins and metalloporphyrins, *Dyes Pigments* 77 (1) (2008) 153–157, <https://doi.org/10.1016/j.dyepig.2007.04.007>.
- [43] M. Biesaga, K. Pryzyska, M. Trojanowicz, Porphyrins in analytical chemistry. A review, *Talanta* 51 (2) (2000) 209–224, [https://doi.org/10.1016/S0039-9140\(99\)00291-X](https://doi.org/10.1016/S0039-9140(99)00291-X).
- [44] R. Pratiwi, S. Ibrahim, D.H. Tjahjono, Reactivity and stability of metalloporphyrin complex formation: DFT and experimental study, *Molecules* 25 (18) (2020) 4221, <https://doi.org/10.3390/molecules25184221>.
- [45] R.G. Little, J.A. Anton, P.A. Loach, J.A. Ibers, The synthesis of some substituted tetraarylporphyrins, *J. Heterocycl. Chem.* 12 (2) (1975) 343–349, <https://doi.org/10.1002/jhet.5570120226>.
- [46] J. Štokr, B. Schneider, D. Doskočilová, J. Lövy, P. Sedláček, Conformational structure of poly(ethylene terephthalate), Infra-red, Raman and n.m.r spectra, *Polymer* 23 (5) (1982) 714–721, [https://doi.org/10.1016/0032-3861\(82\)90057-X](https://doi.org/10.1016/0032-3861(82)90057-X).
- [47] M. Mecozzi, L. Nisini, The differentiation of biodegradable and non-biodegradable polyethylene terephthalate (PET) samples by FTIR spectroscopy: a potential support for the structural differentiation of PET in environmental analysis, *Infrared Phys. Technol.* 101 (2019) 119–126, <https://doi.org/10.1016/j.infrared.2019.06.008>.
- [48] A.P.D.S. Pereira, M.H.P.D. Silva, É.P. Lima Júnior, A.D.S. Paula, F.J. Tommasini, Processing and characterization of PET composites reinforced with geopolymer concrete waste, *Math. Res.* 20 (suppl 2) (2017) 411–420, <https://doi.org/10.1590/1980-5373-mr-2017-0734>.
- [49] G. Kister, G. Cassanas, M. Vert, Effects of morphology, conformation and configuration on the IR and Raman spectra of various poly(lactic acid)s, *Polymer* 39 (2) (1998) 267–273, [https://doi.org/10.1016/S0032-3861\(97\)00229-2](https://doi.org/10.1016/S0032-3861(97)00229-2).
- [50] T. Paragkumar N, D. Edith, J.-L. Six, Surface characteristics of PLA and PLGA films, *Appl. Surf. Sci.* 253 (5) (2006) 2758–2764, <https://doi.org/10.1016/j.apsusc.2006.05.047>.
- [51] C.J. Van Oss, R.J. Good, M.K. Chaudhury, The role of van der Waals forces and hydrogen bonds in “hydrophobic interactions” between biopolymers and low energy surfaces, *J. Colloid Interface Sci.* 111 (2) (1986) 378–390, [https://doi.org/10.1016/0021-9797\(86\)90041-X](https://doi.org/10.1016/0021-9797(86)90041-X).
- [52] C. Longo, I. Di Bari, G. Curcuruto, E.T.A. Spina, G.M.L. Messina, S.C. Carroccio, G. D'Arrigo, A. Sciuto, Easy non-covalent functionalization of PLA film with porphyrin for heavy metals optical sensing in water: a preliminary study, in: 2025 IEEE International Workshop on Metrology for Green Technologies, Renewable Energy and Ecological Sustainability (Metrogreenst), 2025, pp. 157–162, <https://doi.org/10.1109/MetroGREENST67435.2025.11428849>.
- [53] M.A. Gradova, O.V. Gradov, A.V. Bychkova, M.V. Motyakin, I.S. Ionova, A. V. Lobanov, Interaction between meso-tetra-(4-hydroxyphenyl)porphyrin and SDS in aqueous solutions: premicellar porphyrin-surfactant J-aggregate formation, *Chem. Phys.* 562 (2022) 111655, <https://doi.org/10.1016/j.chemphys.2022.111655>.
- [54] S. Okada, H. Segawa, Substituent-control exciton in J-Aggregates of protonated water-insoluble porphyrins, *J. Am. Chem. Soc.* 125 (9) (2003) 2792–2796, <https://doi.org/10.1021/ja017768j>.
- [55] X. Li, D. Li, M. Han, Z. Chen, G. Zou, Neutral porphyrin J-aggregates in premicellar SDS solution, *Colloids Surf. A Physicochem. Eng. Asp.* 256 (2–3) (2005) 151–156, <https://doi.org/10.1016/j.colsurfa.2005.01.006>.
- [56] H. Ma, S. Sun, X. Chen, D. Wu, P. Zhu, B. Du, Q. Wei, Spectroscopic studies of aggregation behavior of meso-tetra(4-hydroxyphenyl)porphyrin in aqueous AOT solution, *J. Porphyr. Phthalocyanines* 12 (2) (2008) 101–108, <https://doi.org/10.1142/S1088424608000133>.
- [57] L. Hanna, E. Movsesian, M. Orozco, A.R. Bernot Jr., M. Asadinamin, L. Shenje, S. Ullrich, Y. Zhao, N. Marshall, J.A. Weeks, M.B. Thomas, J.A. Teprovich Jr., P. A. Ward, Spectroscopic investigation of the electronic and excited state properties of para-substituted tetraphenyl porphyrins and their electrochemically generated ions, *Spectrochim. Acta Mol. Biomol. Spectrosc.* 278 (2022) 121300, <https://doi.org/10.1016/j.saa.2022.121300>.
- [58] X. Li, Z. Zheng, M. Han, Z. Chen, G. Zou, Tuning J-Aggregates of tetra(p-hydroxyphenyl)porphyrin by the headgroups of ionic surfactants in acidic nonionic micellar solution, *J. Phys. Chem. B* 111 (17) (2007) 4342–4348, <https://doi.org/10.1021/jp067148a>.
- [59] G. De Luca, A. Romeo, L.M. Scolaro, Aggregation properties of hyperporphyrins with hydroxyphenyl substituents, *J. Phys. Chem. B* 110 (29) (2006) 14135–14141, <https://doi.org/10.1021/jp0619179>.
- [60] V.N. Mironyuk, O.A. Hassoon, A.I. Smirnova, T.Ya Karatysheva, A.J.K. Al-Alwani, N.V. Usol'tseva, E.G. Glukhovskoy, Protonation and aggregation of the A3B-type porphyrin in floating layers and thin films, *Supramolecular Materials* 4 (2025) 100104, <https://doi.org/10.1016/j.supmat.2025.100104>.
- [61] S. Li, S. McCarthy, Further investigations on the hydrolytic degradation of poly (DL-lactide), *Biomaterials* 20 (1) (1999) 35–44, [https://doi.org/10.1016/S0142-9612\(97\)00226-3](https://doi.org/10.1016/S0142-9612(97)00226-3).
- [62] A. Apicella, K.V. Malafeev, P. Scarfato, L. Incarnato, Generation of microplastics from biodegradable packaging films based on PLA, PBS and their blend in

- freshwater and seawater, *Polymers* 16 (16) (2024) 2268, <https://doi.org/10.3390/polym16162268>.
- [63] R. Vaid, E. Yildirim, M.A. Pasquinelli, M.W. King, Hydrolytic degradation of polylactic acid fibers as a function of pH and exposure time, *Molecules* 26 (24) (2021) 7554, <https://doi.org/10.3390/molecules26247554>.
- [64] F. Tollini, S. Di Bartolo, G. Storti, M. Sponchioni, D. Moscatelli, Influence of pH and temperature on the kinetics of polylactic acid hydrolysis, *Ind. Eng. Chem. Res.* 64 (24) (2025) 11733–11747, <https://doi.org/10.1021/acs.iecr.5c00540>.
- [65] M.A. Elsayy, K.-H. Kim, J.-W. Park, A. Deep, Hydrolytic degradation of polylactic acid (PLA) and its composites, *Renew. Sustain. Energy Rev.* 79 (2017) 1346–1352, <https://doi.org/10.1016/j.rser.2017.05.143>.
- [66] K. Tomita, N. Shioya, T. Shimoaka, K.K. Okudaira, H. Yoshida, T. Koganezawa, T. Hasegawa, Substrate-independent control of polymorphs in tetraphenylporphyrin thin films by varying the solvent evaporation time using a simple spin-coating technique, *Cryst. Growth Des.* 21 (9) (2021) 5116–5125, <https://doi.org/10.1021/acs.cgd.1c00500>.