Curcuminoid-Based Responsive Surfaces for Fluorescent BF₃ Detection, a Fast and Reversible Approach

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Read Online Cite This: ACS Appl. Mater. Interfaces 2025, 17, 20383–20393 ACCESS Metrics & More Article Recommendations s Supporting Information ABSTRACT: The strategic design of a novel curcuminoid (CCMoid), termed PA, containing pyrene units and a terminal carboxylic group provides the necessary tools for its efficient immobilization on surfaces and its potential use as an optical chemosensor. To this end, our work provides a robust methodology for the preparation of CCMoid-based active surfaces with a fluorescent response and reusability. The covalent immobilization of the CCMoid is obtained by the reaction of the acidic groups of PA and the imidazole ends of the previously functionalized substrates. In this way, fluorescent patterned surfaces of PA, whose emission could be observed in the visible region thanks to the

printing. In addition, the coordination of BF_3 molecules (in solution and in gas phase) with the keto-enol moiety of the PAs anchored on the surfaces has been analyzed. The ability of BF_3 to modify the optical properties of the CCMoids-based surfaces, leading to emissions in the near-IR, has been identified as a fast and reversible process. Such ability is intrinsic to the final coordinated system and not to other boron-based molecules, providing unique response and sensing surfaces.

KEYWORDS: curcuminoids, curcumin derivatives, active materials, fluorescence, chemosensors, responsive surfaces, BF₃

INTRODUCTION

The growing demand for portable in situ sensing devices underlines the importance of chemical sensors,¹⁻⁴ in leadingedge applications, for environmental monitoring,⁵ in smart buildings,⁶ food screening^{7,8} and biosecurity.⁹ Among them, fluorescent chemosensors are noninvasive, thus eliminating the need for direct sample handling and allowing remote measurements, and are not susceptible to electromagnetic interference, which is a significant advantage over electrochemical detection methodologies.¹⁰ Ideally, fluorescent sensors respond in a reversible and fast way, depending on the analyte concentrations, and enable its visualization and distribution analysis due to their high spatial and temporal resolution.¹¹ These characteristics make them particularly suitable for on-site detection of toxic or hazardous compounds, where such threats require the development of highly sensitive, selective and easy to visualize sensors.¹²

pyrene groups of the CCMoid, were obtained using microcontact

Here we focus on the detection of BF₃. This molecule is an inorganic chemical found as a colorless gas, which is commercially available in liquid form stabilized in organic solvents.¹³ BF₃ is highly reactive, commonly used in isomerization,¹⁴ polymerization,¹⁵ and esterification reactions,¹⁶ among others.^{17–20} Its applications have expanded, as it is widely used in the semiconductor industry as a catalyst in chemical vapor deposition processes.^{21,22} It has been

established that the degradation of BF3 can lead to the formation of highly acidic, corrosive and toxic species that can be released into the environment in possible leaks, so appropriate plans for their rapid detection must be developed.^{23,24} BF₃ can harm both the ecosystem and the population, causing skin irritation, respiratory toxicity²⁵ and even kidney problems^{23,25} at a threshold limit of 1 ppm.²⁶ Therefore, the improvement of techniques and methodologies for BF₃ detection is a subject of interest. In recent years, the development of chemosensors for BF3 detection has emerged as an alternative to more sophisticated and expensive techniques. Although most of the new fluorescent probes are capable to detect BF₃ in solution,²⁷⁻²⁹ for their applicability in industry and gas detection, it is convenient their loading in matrixes or immobilization on substrates. Until now, the most developed strategy has been their loading on paper stripes,³⁰⁻³⁴ and it is still necessary to investigate alternatives for their incorporation in devices.

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Figure 1. (A) Chemical structure of pyrene based CCMoid, (PA) and (B) PA micropatterned surfaces (PA-LSurf).

In solution, curcumin and curcuminoids (CCM and CCMoids: a family of linear organic molecules with a diarylheptanoid skeleton) have demonstrated their capability to coordinate ion species through the 1,3-diketone unit of these systems. This has triggered their applicability in the sensory field for the detection of metallic centers, in biological or industrial processes.³⁵ This way, it is known that embedded CCM in different matrices can act as a sensor for heavy metal ions such as Pb(II),³⁶ As(III),³⁷ Fe(III).³⁸ Moreover, CCM and CCMoids have demonstrated rapid binding with BF₃ species, producing relevant optical changes.^{39–42} Their coordination causes the enhancement and bathochromic shift of their emission bands, due to the formation of donor–acceptor–donor structures.^{41,42}

Here, driven by the potential of CCMoids, as easily created molecular platforms, together with their ability to coordinate BF_{3} , we describe a straightforward strategy to create an efficient, robust, and reusable probe for solution and gas analysis. To this end, we designed a new T-Shape CCMoid with fluorescent properties (PA, Figure 1A) and immobilized it on functionalized Si(100) wafers and glass surfaces (PA-LSurf, Figure 1B). Such combination has resulted in highly reactive surfaces toward BF_3 with rapid and reversible response.

EXPERIMENTAL SECTION

Chemicals and instrumentals used are described in the Supporting Information, together with the synthesis procedures and all the characterization data of the compounds (PE, 4-acetyl-5-oxohexanoic acid, PA and PABF₂).

Immobilization of PA on Surfaces (PA-LSurf). Preparation of polydimethylsiloxane (PDMS) stamps and IM-SAMs⁴³ is described in the Supporting Information.

Printing Process (\muCP). PDMS stamps were inked with a solution of 1 mM PA in DMF for 1 h and dried with a nitrogen stream. It is important to cover them during this time to avoid degradation with light. The stamps were then brought into contact with the IM-SAM, with a weight of 10 g on them, and the whole system was kept in a vacuum desiccator, overnight. The stamps were removed, and the surfaces were rinsed with DMF and dried with a nitrogen stream. (Due to the reactivity of IM-SAMs with water, the printing process was performed with less than 30% of atmospheric humidity conditions).

DETECTION OF BF₃·O(C₂H₅)₂ WITH PA-LSURF (PABF₂-LSURF)

PABF₂-LSurf in Solution. Patterned PA surfaces were immersed in solutions of $BF_3 \cdot O(C_2H_5)_2$ in dry DCM of different concentrations for 1 min, respectively. After, the surfaces were rinsed with dry DCM and dried with a nitrogen stream.

PABF₂-LSurf in Vapor Phase. Patterned PA surfaces were placed in a closed 3D-printed setup, ^{44,45} where the surface was placed 3 cm from the bottom of the set containing different volumes (μ L) of BF₃·O(C₂H₅)₂. After 2 min, the surface was removed, washed with dry DCM and dried with a nitrogen stream.

Reusability of PA-LSurf. A solution of 30 mL of Milli-Q water with NaOH pellets was prepared until the pH reached 12. Subsequently, the PABF₂-LSurf surface was immersed in the basic solution for 4 min, washed with Milli-Q water, and dried with a nitrogen stream. Finally, the samples were kept in a vacuum desiccator overnight before inspection using a fluorescence microscope.

General Measurements: Fluorescence Quantification in Digital Imaging. Sample preparation, image acquisition parameters and data processing for fluorescence quantification of the images and measurement of the signal-to-noise ratio (SNR) are detailed in the Supporting Information.⁴⁶

RESULTS AND DISCUSSION

Synthesis of PA and PA-BF₂. The synthesis of PA T-Shape CCMoid started with certain modifications to the Pabon method described in the Supporting Information (Scheme S1).⁴⁷ Two synthetic routes were tested for this purpose, yielding PA CCMoid with a yield of 66%. On the other hand, with the objective to study the fluorescent properties of PA upon complexation with BF₃, the corresponding boron difluoride complex CCMoid (PABF₂) was also prepared (Scheme S2). The structures of PA and PABF₂ were confirmed by ¹H NMR and ¹³C NMR spectroscopy, FTIR-ATR, elemental analysis and MALDI-TOF. Moreover, the crystal structure of PE CCMoid was also resolved (See Supporting Information, Figures S1–S9, Tables S1 and S2), confirming the molecular structure of this intermediated.



Figure 2. (A) Normalized absorbance and fluorescence emission spectra of PA and PABF₂ in DCM at 10^{-5} M; (B) absorbance and fluorescence in solid state of PA and (C) PABF₂ CCMoids.



Figure 3. Preparation of PA-functionalized surfaces: (1) activation of the surface with piranha and a basic solution, (2) functionalization in vapor phase with TPEDA overnight at 70 °C (MH_2 –SAM), (3) immersion of the surfaces in saturated CDI solution with dry THF for 4 h under Ar (IM-SAM), and (4) immobilization of the PA molecule on IM-SAM by printing (μ CP) to obtain PA-LSurf.

OPTICAL PROPERTIES OF PA AND PABF₂

The electronic UV-visible absorption and fluorescence emission spectra of PA and PABF₂ were recorded in DCM solution using a concentration of 10^{-5} M, Figure 2A. The maximum of the PA absorption band appeared at $\lambda_{max} = 480$ nm (blue line), related to the typical $\pi - \pi^*$ transition of CCMoids keto-enol system; in addition, bands at 395, 347, and 305 nm also appear referring to the $\pi - \pi^*$ transitions of the pyrenes groups.^{48,49} For PABF₂ the maximum absorption band appeared at $\lambda_{max} = 586$ nm (green line), and the rest of the bands related to the pyrene groups at 424, 339, and 299 nm.

The fluorescence behaviors of both systems are also shown in Figure 2A. To study them, the PA solution was excited with a $\lambda_{\rm exc}$ of 485 nm, which produced the observation of an emission band that showed a maximum peak at $\lambda_{\rm em} = 563$ nm (green-yellow region, in the range of 490–580 nm, gray line). Upon excitation of the PABF₂ compound with a $\lambda_{\rm exc}$ of 587 nm, an emission band with a maximum peak at $\lambda_{\rm em} = 668$ nm was observed in the red-shift area (range 650–800 nm, orange line). Although PA and PABF₂ presented the same number of transitions, in the case of PABF₂, there was a dramatic bathochromic change (>100 nm difference) caused by the coordination with the -BF₂ group, which, together with the presence of the pyrenes, gave the molecule a D- π –A– π –Dtype structure. In addition, the incorporation of the -BF₂ group is known to increase the rigidity of the molecule and improve its photostability.^{42,50} Similarly, UV–vis absorbance characterization of PA and PABF₂ in the solid state was also performed, owing to the solvochromic character of most CCMoids in solution (Figure 2B,C). For that, samples were prepared with pellets of KBr having 0.03 mg of the respective CCMoids. The maximum absorption band of PA appeared at $\lambda_{max} = 495$ nm (green region, Figure 2B, blue line), whereas that of PABF₂ occurred at $\lambda_{max} = 601$ nm (orange region, Figure 2C, green line). Overall, the absorbance bands shifted by 10–20 nm, toward larger wavelength values, compared with those obtained in DCM.

In addition, the solid state fluorescence emission of PA was studied, exciting the sample at $\lambda_{exc} = 485$ nm detecting an emission band at $\lambda_{em} = 700$ nm (red region, Figure 2B, dark gray line). Similarly, the emission of PABF₂ in the solid state was recorded by exciting the sample at $\lambda_{exc} = 600$ nm, and an emission band was observed at $\lambda_{max} = 981$ nm (within the NIR zone, Figure 2C, orange line).

Therefore, both systems displayed absorbance and emission bands that showed clear differences in the optical properties in the solid state as well as in solution. Moreover, it is important to stress that PA in solution showed emission within the green range, and in comparison with the solid state, the latter showed a shift of approximately 200 nm toward wavelengths of the near-infrared zone. Here, coordination to the $-BF_2$ moiety and intermolecular interactions may combine to provide great displacements and therefore changes in the optical properties.



Figure 4. Fluorescent microscopy images of micropattern of PA lines on a glass surface (PA-LSurf) and intensity profiles. Conditions: low humidity, oxidized PDMS stamps 1 min with O₂ plasma, inking 1 h with 1 mM PA and μ CP overnight. Images obtained by fluorescence microscopy (×20 magnification, aperture 8). (A) 5 μ m and (B) 10 μ m lines with emission in the green region (filter 450 nm < λ ex <480 nm; λ em \geq 515 nm) and (C) 5 μ m and (D) 10 μ m lines with emission in the red region (filter 510 nm $\leq \lambda$ ex \leq 550 nm; λ em \geq 590 nm). Intensity plot profile of micropatterns of lines of (E) 5 μ m and (F) 10 μ m.

Studies of CCMoids coordinated to $-BF_2$ describe similar behavior in the solid state and propose mechanisms for the redshift based on a variety of possible CCMoid aggregations.^{51,52} Furthermore, the quantum yield (Φ) calculated for a 10^{-4} M solution of PA in DCM was 0.16 \pm 0.02, 1 order of magnitude larger than a similar CCMoid containing anthracene groups.⁵³ Therefore, the design of the PA CCMoid aims to improve its emission in the presence of pyrene groups.

PA Functionalized Surfaces (PA-LSurf). The immobilization of the PA on surfaces was performed by microconctact printing (μ CP), as schematized in Figure 3. First, an imidazoleterminated monolayer (IM-SAM)⁴³ was prepared and its formation was confirmed by contact angle measurements, fluorescence microscopy and X-ray photoelectron spectroscopy (XPS) (Figures S10-S12). Then, PDMS stamps were employed to form either patterned (stamps with lines) or full (stamps without features) monolayers of PA. The oxidized stamps were inked with a solution of PA in DMF and placed in contact with the surfaces. This solvent completely dissolves PA and is compatible with PDMS stamps.⁵⁴ Due to the contact between the stamps and the IM-SAMs, the carboxylic acid of PA reacted with the terminal imidazole group on the surface, forming an amide bond, resulting in patterned PA monolayers or full PA functionalized surfaces depending on the stamp used, with and without motifs, respectively.

After removing the stamp and washing the surfaces, the resulting line patterns of PA-LSurf on glass slides were inspected by fluorescence microscopy, which also allowed the optimization of several parameters of the printing process, such as the concentration of the PA ink solution, printing time, oxidation of the stamps, and the influence of atmospheric humidity.⁵⁵ The fluorescent patterns of PA clearly showed a sharp, uniform contrast between the CCMoid areas and the

background when a blue filter (450 nm < λ_{ex} < 480 nm; $\lambda_{em} \ge$ 515 nm) was used (Figure 4A,B,E,F).

When the surface was irradiated and a green filter was used (510 nm $\leq \lambda_{\rm ex} \leq$ 550 nm; $\lambda_{\rm em} \geq$ 590 nm), almost no patterns were detected (Figure 4C–F). In the latter, the low intensity existing is due to the fact that the surface PA emits in a wide range from 450 to 650 nm, with a maximum peak at 408 nm, and a small part of the emission is still collected. Nevertheless, this fact was considered negligible compared to the subsequent response of the surfaces.

In order to achieve the optimal printing conditions, a series of printing experiments were performed modifying the ink concentration and the printing time (see Supporting Information, Figures S13 and S14). First, the better results were obtained with 10^{-3} M inking solution concentration, showing homogeneous patterns and without aggregates (Figure S13). On the other hand, for the printing time optimization study, the surfaces were stored in a vacuum desiccator during the printing to regulate the humidity and prevent degradation of the terminal imidazole groups of the IM SAMs. Although, after 3 h of printing, patterns were observed with the maximum intensity, longer printing times allowed more homogeneous and reproducible patterns with good contrasts (Figure S14).

Characterization of PA-LSurf. The fluorescence emission of the PA-LSurf glass surfaces and their stability were monitored by confocal microscopy. For this, a selected area of the surface was excited at 405 nm. After scanning, the emission spectrum showed a broad band from 440 to 750 nm. with a maximum signal at approximately 476 nm (Figure 5A,B (blue line)).

The comparison of the optical properties of the PA-LSurf with those of PA CCMoid in solution (Figure 5, green line) and in the solid state (Figure 5, orange line) clearly showed



Figure 5. Study of the fluorescence emission of PA on the surface (PA-LSurf) using confocal microscopy. (A) Image of the PA-LSurf study area. (B) Normalized emission spectrum of PA-LSurf (blue), PA in solution (green), and PA in solid state (orange).

how the environment has a great effect on the final emission. To some extent, all CCMoids are solvochromic compounds, while in the solid state (bulk), aggregates are formed displaying a broad emission band in the NIR. PA-LSurf showed a significant shift of the emission of the PA toward much lower wavelengths. Such displacement, which is even lower to that of PA in solution (DCM), it is closer to the emission observed for pyrene monomers and relates to the distribution of PA on the surface.^{49,56,57} This would reinforce the idea of the absence of aggregates or the formation of compact layers that could display strong intermolecular interactions between the CCMoids.

In addition, the stability of the PA-LSurf surface over time was examined in two ways. First, a fresh PA-LSurf surface was prepared, and an emission image was taken. Then, it was stored under nitrogen and shielded from light for two weeks. No intensity loss was observed afterward, proving that this storage method was effective (Figure S15). Second, the extinction time of the PA-LSurf emission was studied when it was continuously irradiated by a laser applying 100% of its power, causing photobleaching of the sample. As shown in Figure 6, the emission faded exponentially after 600 s, probably



Figure 6. Study of the extinction of PA emission in PA-LSurf, using confocal microscopy. Image of the study area and graph of the intensity over the irradiation time of the sample.

due to the photon-induced chemical damage of the pyrene groups of the system. This indicates that the degradation of the surface requires long irradiation times when using a powerful laser.

The formation of PA-LSurf was additionally confirmed using contact angle measurements and X-ray photoelectron spectroscopy measurements; see Supporting Information (Figures S10 and S12).

PA-LSurf as a BF₃ Detector. Once the PA-LSurf was fully characterized, to assess its feasibility for the detection of BF₃ in solution and in gas phase two approaches were followed: (1) the immersion of the PA-LSurf surface in solution with different concentrations of BF₃·O(C_2H_5)₂, in dry DCM, to prevent rapid degradation of BF₃ (Figure 7A) and (2) the exposure of PA-LSurf to the vapors generated by BF₃·O(C_2H_5)₂ (Figure 7B). Vapor-phase tests were performed using a homemade sublimation setup, with it has possible to perform a small vacuum at first and to keep later the experiment close for short periods of time.^{44,45}

Upon exposure of PA-LSurf to $BF_3 \cdot O(C_2H_5)_2$ a change in the emission of the PA patterns was observed in both methodologies, demonstrating the detection capacity of the fluorescence surface. The reaction between the keto–enol group of immobilized PA CCMoids and BF_3 is a fast coordination process, resulting in the formation of BF_2 – CCMoid adducts on the surfaces (PABF₂-LSurf), and a significant shift in wavelengths toward NIR.⁵⁰

Detection of BF₃ **in Solution by Immersion of the PA-LSurf**. To determine the viability of the PA-LSurf system and the detection limit using the immersion methodology, several tests were carried out with different concentrations of BF₃, ranging from 2.5×10^{-4} M to 2.3×10^{-3} M of BF₃·O(C₂H₅)₂ in dry DCM as solvent. The BF₃ detection study in the solution was limited to a PA-LSurf immersion time of 1 min, as shown in Figure 8.

Long periods of immersion promoted corrosion of the glass surface, probably due to the attack of HF formed as byproduct.⁵⁸ A blank consisting of immersing PA-LSurf in dry DCM for 1 min was made, verifying that the emission intensity of the PA lines remained constant and that the applied conditions unaffected the stability of the monolayer (Figure S16). All tests were performed on surfaces with micropatterns of 5 and 10 μ m PA lines, correspondingly, to study the relation between the compactness of the patterns in the response of the surfaces. After performing all tests, the changes in the emission of the patterns were quantified by analyzing the increase in fluorescence intensity and the signalnoise rate (SNR) in the red region (detailed in Supporting Information, Figure S17). In both 5 and 10 μ m PA line patterns, changes in intensity were detected analyzing the profiles of the plots from a concentration of 5×10^{-4} M of BF₃, founding an increase in the intensity of 3.20 ± 0.19 a.u. (SNR 4), and 0.41 \pm 0.75 a.u. (SNR = 7), respectively (Figure 8C and Table S3).

The improvement in the SNR value with the 10 μ m lines could be related to a lower initial noise, which implies a better signal, probably due to a greater amount of PA immobilized on the surface and homogeneous distribution along the lines. Indeed, the micropattern of the 5 μ m lines displayed higher variations in the analyzed data, as it can be seen in Figure 8C, while the 10 μ m lines showed an increase in fluorescence with a well-defined linear trend with increasing the BF₃ concentration. Therefore, under the conditions studied, the patterns with 10 μ m lines demonstrated higher stability, presenting a good quality of response and very good reproducibility.

Detection of BF₃ by exposure of PA-LSurf to $BF_3 \cdot O(C_2H_5)_2$ vapors.

Due to the better response of the PA-LSurf with 10 μ m micropatterns, the BF₃ vapor exposition tests were carried out only with these surfaces. For that, the devices used consisted of two pieces of glassware assembled together, with a set of



Figure 7. BF₃ detection methodologies with PA-LSurf by (A) immersion in solution or (B) exposure to BF_3 ·O(C_2H_3)₂ vapors.

Teflon supports, where the surface was installed at a fixed distance of 3 cm to different volumes of BF₃ (in the range 1–15 μ L of BF₃·O(C₂H₅)₂). This system, stabilized with diethyl ether, formed an atmosphere of BF₃ vapors when the functionalized surface was exposed for 1 or 2 min at 25 °C (Figure 9).

The blank was then prepared using only 15 μ L of diethyl ether to determine the stability of the monolayer under these conditions and for comparison reasons. After 2 min of exposure, a decrease in intensity, of approximately 4 a.u., was observed in the PA-LSurf, in the red emission region (Figure S18), but it was considered insignificant, considering that our functionalized substrate was still performing.

The exposition of the PA-LSurf to $BF_3 \cdot O(C_2H_5)_2$ during 1 min, showed that the emission produced for the PABF₂-LSurf lines displayed an increase of 1.7 ± 0.3 a.u in intensity in the red region, by analyzing the plot profile of the lines when 2 μ L were introduced, Figure 9C. However, from 6 μ L onward, it was possible to detect an important change in intensity. Under these conditions, the intensity increased by 2.6 ± 0.3 a.u., and the images were acquired with an SNR of 7, reaching the best SNR of 13 when 15 μ L of BF₃ were employed, with an intensity increase of 3.3 ± 0.2 a.u., Figure 9C and Table S4. In this time frame, the experiments indicated low precision and reproducibility among the tests, concluding that 1 min exposure was not satisfactory; this could relate to the device as well and the lack of a homogeneous atmosphere of BF₃ in all the experiments.

For that, the exposition time was increased to 2 min, where the fluorescence intensity exhibited a linear relationship with the volume used, indicating the robustness of the system and the formation of the adducts on the surfaces, as it is shown in Figure 9C and Table S4. Therefore, it was considered that the optimal time for the test was 2 min. Under these conditions, the increase was detectable from 2 μ L, by analyzing the plot profile, with an increase of 1.9 ± 0.3 a.u, observable with the fluorescence images from 10 μ L with an increase of 5.4 \pm 0.2 a.u., and an SNR ratio of 18.

Similar to the tests at 1 min, the greatest increase in the intensity was observed at the highest volume tested $(15 \ \mu L)$. In this case, after 2 min of exposure, the increase was considerably higher $(6.3 \pm 0.4 \text{ a.u})$. However, the SNR value was low (7), probably because of the increased noise owing to the greater heterogeneity intensity of the lines. This could be explained by the existence of unreacted PA still on the surface producing variations on the pixel values, due to the different intensities of PA-LSurf and PABF₂-LSurf.

The results indicated that the detection of $BF_3 \cdot O(C_2H_5)_2$ vapors is more effective and accurate than the previous detection in solution. Therefore, PA-LSurf surfaces are ideal for the rapid detection of these vapors in industry, providing rapid measurements in 2 min at sort distances of the source (3 cm) without degradation of the surfaces. Moreover, in solution, the response of the surface was also fast (1 min), with a detection limit of 0.5 mM $BF_3 \cdot O(C_2H_5)_2$.

To verify the formation of the PABF₂-LSurf and therefore, the presence of the BF₂-CCMoid adducts, full printed surfaces were further characterized by contact angle measurements and XPS. It is worthy to indicate, that the results agreed well in both approaches, solution and vapor experiments. The contact angle measurements obtained from the PABF₂-LSurf showed a decrease in the surface polarity induced by the terminal -BF₂ groups, with an average contact angle of $68^{\circ} \pm 2$, Figure S10. The ACA and RCA values were $79^{\circ} \pm 1$ and $56^{\circ} \pm 1$, respectively. The hysteresis was similar to that observed for the PA-LSurf (23°), displaying therefore the same surface imperfections with still unreacted PACCMoids on the surface, increasing the chemical variability.

As expected, the coordination of PA-LSurfs with $-BF_2$ groups involved the observation of a new peak in the XPS B1s spectrum, due to the B–F bond, at 195.7 eV and another in the XPS F1s spectrum at 687.8 eV, due to the F–B bond, Figure 10. In addition, the XPS N1s spectrum showed a



Figure 8. Fluorescence microscopy images of PA-LSurf surfaces reacting with BF₃ in solution $(2 \times 10^{-3} \text{ M BF}_3 \text{ in DCM}, 1 \text{ min immersion})$. (A) patterns of 5 μ m, while in (B) patterns of 10 μ m lines. The plot profile of the initial surface is shown in gray (PA-LSurf) and after the reaction with BF₃ in orange (PABF₂-LSurf). (C) Relationship between $(I_f - I_0)/I_0$ and BF₃ concentrations. The intensities of the 5 and 10 μ m lines of PA-LSurf with the standard deviations were compared after being immersed for 1 min in solutions with varying concentrations of BF₃·O(C₂H₅)₂ in dry DCM. The images were acquired using a filter with 510 nm $\leq \lambda ex \leq 550$ nm and $\lambda em \geq 590$ nm, ×20 magnification and aperture 8. Scale bar indicates 30 μ m.

decrease at 401.2 eV, agreeing with the loss of additional imidazole groups in the monolayer (Figure S19). This corroborates the instability of the terminal imidazole groups that remained unreacted in PA-LSurf, as they easily degrade with humidity and moisture from the solvents used during the manipulation of the surfaces.

In conclusion, the shift in the fluorescence emission of $PABF_2$ -LSurf and the observation of the peak assigned to the F–B bond, in the XPS measurements, confirm the reactivity of the PA-functionalized surface to BF_3 . Following these results, studies related to the reversibility of PA coordination with BF_3 and thus the reusability of these responsive surfaces were carried out.

Reversibility and Reusability Studies. The reusability of the PABF₂-LSurf surfaces is an interesting feature, being relevant for their applicability in the design of BF₃ detectors. Several tests were performed to determine the optimal conditions for removal of the BF₂ moiety from the surfaces via hydrolysis. The tests using the PABF₂-LSurf system were based on surface immersion in solutions of different pH values (1, 5, and 12). This way, after 2 min in acidic pH (1–2), the intensity of the lines in the red region decreased but without significant changes; therefore, there was still a high presence of PABF₂ groups, as it was shown by XPS (F1s and B1s) corroborating the presence of F-B bonds at 687 eV and B-F at 197 eV, respectively (Figure S20). Longer immersion times were unreliable due to damage to the surfaces. Increasing the pH to 5, using Milli-Q water, immersion for up to 10 min was required to significantly decrease the intensity of the patterns. However, lower intensities of the patterns in the visible were also obtained from the reused PA-LSurf, Figure 11A. Moreover, some coordinated PABF₂ groups still remained, since traces of F-B and B-F peaks were still identified in the XPS spectra (Figure S20). When this PA-LSurf was re-exposed to BF₃ vapors, the emission was recovered with less intensity and lower contrast between the patterns, suggesting a possible damage of the surface during the process. Nevertheless, when the same process was carried out at pH = 12, upon 4 min of immersion, the intensity of the emission patterns in the NIR decreased significantly and traces of -BF2 were only detected, finding a small band in the F1s XPS spectrum, indicating almost complete recovery of the surface, Figures 11B and S20. The further exposition of this substrate (PA-LSurf) to the BF₃ vapors, showed intensity patterns in the NIR was almost



Figure 9. Fluorescence microscopy images of PA-LSurf surfaces exposed to BF₃ vapors at 25 °C. In (A), an exposure time of 1 min to 15 μ L of BF₃·O(C₂H₅)₂ was used, whereas in (B), 2 min of exposure to 10 μ L of BF₃·O(C₂H₅)₂ was used. The surfaces were kept at a distance of 3 cm from the BF₃ source. (C) Relationship between ($I_f - I_0$)/ I_0 and BF₃·O(C₂H₅)₂ volumes. The intensities of the 10 μ m lines of PA-LSurf were compared after exposure to BF₃·O(C₂H₅)₂ vapors for 1 and 2 min at 25 °C. Standard deviations are also shown. The images were acquired using a filter with 510 nm $\leq \lambda ex \leq 550$ nm and $\lambda em \geq 590$ nm, ×20 magnification and aperture 8. Scale bar indicates 30 μ m.



Figure 10. (A) XPS spectra of B1s and (B) F1s of PA-LSurf and PABF2-LSurf by vapor exposure to 10 μ L of BF₃ for 2 min.

identical to the initial one proving the reversibility and reusability of the PA-LSurf under this conditions, hence, confirming the possibility of performing (ON)-(OFF)-(ON) cycles of the PA-LSurf with BF₃.

CONCLUSIONS

A fluorescent CCMoid (PA) has been designed to be efficiently immobilized on functionalized surfaces (PA-LSurf) by the use of reactive μ CP. First, we show the process of optimizing different parameters, including the printing procedure and the need for humidity control, for the successful generation of fluorescent and active PA-LSurfs. The PA-LSurf proved to be a robust system with high stability that presented PA patterns with emissions in the green region. The shift of the PA emission toward NIR regions upon formation of the $-BF_2$ adduct allowed the development of a methodology for the detection of BF₃ in solution and gas phase. Notably, PA-LSurf provides a fast and easy-to-use system to detect BF₃, 1 min in solution and 2 min with vapors, compared with other similar systems (based on a change in the optical properties of the material) that require longer times. Moreover, PA-LSurf offers a novel tailor-made system for the direct detection of BF₃, instead of degraded byproducts in the environment, that to our knowledge, mainly other systems in the literature use. Reversibility and reuse of the surfaces have been demonstrated by immersion in a basic solution performing on-off-on cycles with BF₃. Finally, PA-LSurf holds promise for further



Figure 11. Fluorescence images of PA-LSurf obtained using a green excitation filter. (A) PA-LSurf emission changes upon contact with BF₃ (ON), after immersion in Milli-Q water for 10 min (OFF), and after reuse for BF₃ detection (ON). (B) PA-LSurf in contact with BF₃ (ON), after immersion in basic water for 4 min (OFF), and upon reuse for BF₃ detection (ON). The images were acquired using a filter with 510 nm $\leq \lambda ex \leq$ 550 nm and $\lambda em \geq$ 590 nm, ×20 magnification and aperture 8. Scale bar indicates 30 μ m.

application in portable chemosensors and its coordination to different metal ions is currently under development using, as it is shown here, the emission capacity of these CCMoid-based responsive surfaces.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.4c19421.

Additional experimental details, materials, and methods. Characterization of the compounds including NMR spectra, MALDI-TOF spectra, FTIR-ATR spectra and crystallographic details of PE CCMoid. Printing optimization experiments. Fluorescent microscopy images of control experiments and details of the fluorescence quantification in digital imaging details (PDF)

Crystallographic data of PE CCMoid (CIF) (CIF) Check CIF (PDF)

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RGM: Investigation, Writing–Original draft, Writing-review and editing; RDT: Investigation; SGC; Data curation; OR: Data Curation; JMDC: Formal Analysis; NAG: Conceptualization, Writing–review and editing, Resources, Project administration, Methodology, Funding acquisition; Supervision; AGC: Conceptualization, Writing–review and editing, Resources, Project administration, Methodology, Funding acquisition; Supervision.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CCMoid, curcuminoid; CCM, curcumin; PDMS, polydimethylsiloxane; μ CP, microcontact printing;; PA, pyrene based CCMoid; PA-LSurf, PA micropatterned surfaces; PABF₂-LSurf, PA-BF₂ adduct-based surfaces; SNR, signal-to-noiseratio; PCA, 1-pyrenecarboxaldehyde; PE CCMoid, PABF₂ pyrene ester based CCMoid; NMR, nuclear magnetic resonance; FTIR-ATR, Fourier transform infrared-attenuated total reflectance spectroscopy; MALDI-TOF, matrix-assisted laser desorption/ionization; XPS, X-ray photoelectron spectroscopy; TPDEA, N-[3-(trimethoxysilyl)propyl] ethylenediamine]; NIR, near-infrared; THF, tetrahydrofuran; DCM, dichloromethane.

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